Determination of Diurnal Cycles of Acrolein and Other Small Carbonyls in Regions Impacted by Vehicle Emissions

FINAL REPORT

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Thomas M. Cahill
Principal Investigator
Arizona State University at the West Campus
Department of Integrated Natural Sciences
P.O. Box 37100
Phoenix, AZ 85069

Nick Spada and Erin Fuji
Undergraduate Research Assistants
DELTA Group
University of California, Davis
Davis, CA, 95616

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Abstract

The objective of this research was to determine the diurnal cycles of acrolein and other carbonyls in both summer and winter. The test site was the Air Resources Board monitoring station at North Sunrise Blvd in Roseville, California since this site is located near several large roadways that were suspected sources of acrolein and it is impacted by high ozone concentrations in the summer that would facilitate the photochemical production of oxidized hydrocarbons. The results showed that different carbonyl chemicals showed different patterns based on their most likely sources. In the summer, acrolein did not correlate with ozone or traffic patterns, which was unexpected based on the common assumptions about the sources of acrolein. In winter, the acrolein showed a clear diurnal cycle with a peak concentration in the evening that correlated very well with a wood smoke tracer. Therefore, it appears that wood smoke was the dominant source of acrolein in winter. Most of the chemicals that were routinely detected could be ascribed to a specific source such as photochemical generation (glyoxal, glycolaldehyde), wood smoke (2-furaldehyde), transport from the Sierra Nevada Mountains (pinonaldehyde) or direct vehicle emissions (tolualdehydes). Surprisingly, primary vehicle emissions seemed to contribute few carbonyls at this site that was located to detect vehicle emissions.

Executive Summary

Introduction:

Acrolein is a highly reactive unsaturated carbonyl that often ranks as one of the highest non-cancer health hazards among organic pollutants in hazard assessments. Acrolein has many different sources such as vehicle emissions, secondary oxidation in the atmosphere, biomass burning, etc. These numerous sources of acrolein makes it more difficult to identify which source is the most important for determining ambient acrolein concentrations. The US EPA as given acrolein a reference dose (RfD) of $0.02\mu g/m^3$, which is the maximum exposure that would not result in any long-term effects. This low RfD combined with the ubiquitous nature of acrolein has resulted in considerable concern about the possible impacts of ambient acrolein on health effects.

Despite the relatively high level of concern about acrolein, there are relatively few time-resolved data available. Most of the data are 24 hour averages or longer from DNPH, DNSH or canister sampling. However, these long sampling times may mask diurnal cycles of acrolein and other chemicals that might be used to identify or suggest which sources may be the most important at given site. The ability to identify the sources of acrolein would help to focus mitigation efforts on the dominant sources.

Methods:

The objective of this research project was to determine the diurnal and seasonal cycles of acrolein and other volatile carbonyls at a site impacted by vehicle traffic. The sampling consisted of four intensive sampling episodes, two in summer and two in winter, at the Air Resources Board monitoring site on North Sunrise Blvd. Each of these intensive sampling efforts collected ambient air samples every two hours around the clock starting on Sunday morning at 06:00 and ending on Wednesday at 06:00. This sampling regiment was designed to test for differences between weekend days and work days as well as the diurnal cycles of acrolein. A fifth sampling episode was conducted at a control site along Putah Creek in Solano County on the west side of the Sacramento Valley to test for the background concentrations of the carbonyls.

The sample collection method uses a mist chamber to collect carbonyls by forming water-soluble carbonyl-bisulfite adducts that effectively trap the carbonyls in the solution. After the sample collection, the carbonyls are then liberated from the bisulfite through the addition of hydrogen peroxide that converts the bisulfite to sulfate, which reverses the bisulfite addition reaction. The free carbonyls are then derivatized by pentafluorohydroxlyamine, which stabilizes the analytes and makes them easier to detect by electron-capture negative ionization mass spectrometry (ECNI-MS). The derivatives are then extracted and analyzed by gas chromatography mass spectrometry.

Results:

The results showed that there was considerable variation in the gaseous carbonyl concentrations on a daily and seasonal basis which was the result of different carbonyl sources at different times. Most of the carbonyls that were regularly detected in this research were could have been ascribed to one of four major potential sources based on the temporal trends observed and the correlation of a chemical with a known tracer of a given source, although these field

observations cannot prove the chemical source. The major sources of the carbonyls appeared to be: 1) photochemical oxidation in the atmosphere, 2) wood smoke, 3) transport from the Sierra Nevada Mountains and 4) direct vehicle emissions.

The ambient concentrations of acrolein showed some unexpected trends. The concentrations in the summer were much lower than expected, and were below the limit of quantification for the entire second sampling episode. The acrolein concentrations did not correlate with ozone concentrations or traffic patterns. The highest summertime concentrations were detected on the nighttime down-slope flow from the Sierra Nevada Mountains. The winter time samples showed a very different trend with a spike in concentration every evening that correlated very well with a tracer of wood smoke, thus it appeared that the winter time concentrations of acrolein were likely the result of wood burning. In neither the summer or the winter sampling episodes were primary vehicle a significant contribution to acrolein concentrations. This result was unexpected since the air monitoring site at North Sunrise Blvd was deliberately located to observe vehicle emissions from Interstate 80 and two busy surface streets, namely Douglas Blvd and Sunrise Ave.

Although acrolein was the focus of this research, the analytical method was able to detect a number of other carbonyls. For the most part, these chemicals were assigned to their most probable source as:

1) Photochemically derived chemicals: glyoxal, glycolaldehyde methyl glyoxal
2) Wood smoke (winter): 2-furaldehyde, acrolein, methacrolein, benzaldehyde, 1,4-benzoquinone, 2,3-butanedione, 2,4-pentanedione, 3,4-hexanedione, *m,o,p*-tolualdehyde
3) Transport from the Sierra Nevada Mountains (summer): pinonaldehyde, acrolein, methacrolein, 2-furaldehyde, 2,3-butanedione, 3-methyl-2-butenal, methylglyoxal, methyl vinyl ketone
4) Primary vehicle emissions: *m,o,p*-tolualdehyde

A comparison between the observed acrolein concentrations and those routine reported by the Monitoring and Laboratory Division (MLD) of ARB using canister samplers showed that the concentrations reported by the mist chamber method were considerably lower than the MLD concentrations. Side-by-side sampling (n=2 for each sampler type) also illustrated the difference between the methods despite extensive quality control procedures for the mist chamber samplers. Currently, the reason for this difference is not known.

The overall conclusion of this research is that wintertime concentrations of the carbonyls are dominated by emissions from wood smoke rather than vehicle emission as was expected. This suggests that mitigation efforts, if they are deemed necessary, should be focused on reducing emissions from wood burning during the winter.

Introduction:

Acrolein, also called 2-propenal, is a highly reactive unsaturated aldehyde that is a common constituent of both indoor and outdoor air (1, 2). Acrolein is produced by the incomplete combustion of organic material as well as the atmospheric oxidation of chemicals such as 1,3-butadiene, which is a primary component of motor vehicle exhaust. Sources of acrolein include vehicle emissions (3-5), cooking fats/oil (6-8), cigarette smoke(9), incense, candles and wood-burning fireplaces (10-14). Although considered by regulatory agencies to be one of the most dangerous components of toxic air mixtures (15-18), acrolein is often omitted from studies of carbonyls in the atmosphere (19-29) or is reported as "below the limit of detection" (30). A review of the literature reveals that the acrolein concentrations that are reported vary widely, which results in no consensus about what the concentrations of acrolein are in the ambient atmosphere.

One of the major reasons for the relative scarcity of reliable data is the lack of sensitive and accurate analytical methods to detect acrolein concentrations in the ambient atmosphere. Most of the methods that are available are based on cartridge samplers that use a derivatization agent such as dinitrophenylhydrazine (DNPH) (31-33), 2-(hydroxymethyl)piperidine (34), dansylhydrazine (DNSH) (20, 21, 35). These cartridge samplers tend to have low sensitivity and long sampling times due to the low flow rate of air through the cartridges. There are also serious questions about the stability of the acrolein derivatives in the cartridges (36-40). Even the canister sampling method utilized by the Monitoring and Laboratory Division of the California Air Resources Board meters in the air over a 24 hour period. As a result, very little time-resolved acrolein data is available.

However, highly time resolved acrolein data would be valuable to assess the potential sources of acrolein. Acrolein is a known motor vehicle emission as well as a secondary photochemical product, but it is unclear which of these sources is the most important in determining the ambient acrolein concentrations. Determining the diurnal cycles of acrolein over the course of a day would allow the acrolein concentrations to be correlated with other parameters, such as ozone concentrations or traffic patterns, to assess which is the most important source of acrolein. Seasonal variation in acrolein concentrations would also support these conclusions since photochemical oxidation of chemicals is limited in winter while the traffic patterns are assumed to be relatively constant.

The objective of this research project was to determine the diurnal and seasonal cycles of acrolein and other volatile carbonyls in both the summer and winter in Roseville, California. The primary study site was the ARB monitoring station on North Sunrise Blvd, which is located near Interstate 80 and two busy surface streets. This site is impacted by primary vehicle emissions and it experiences high ozone concentrations in the summertime. There were a series of 4 sampling episodes, two in the summer and two in the winter, where acrolein concentrations were determined every two hours around the clock starting on a Sunday at 06:00 and continuing until the next Wednesday at 06:00. In addition, one sampling episode was conducted at a control site along Putah Creek on the western side of the Sacramento Valley. These data were then correlated with traffic conditions, ozone or known tracers of species types of emissions to try to identify the source of the acrolein.

Materials and Methods:

Sampling Site Locations:

Ambient samples were collected at two sites during this study. The primary site was the Air Resources Board site at North Sunrise Boulevard in Roseville, California. This site was chosen for a number of reasons. The first reason is that MLD division of ARB conducts regular acrolein analyses at the site, thus there will be a large amount of background data from the MDL canister sampling method for air toxics. This will give an indication about the consistency of the two methods since they will have been collected at the same site. In addition, ARB had considerable instrumentation at the site to monitor meteorology and ozone concentrations. This will provide information on the direction of the wind and hence where the air mass has come from.

The second reason for selecting the ARB North Sunrise site for intensive sampling is that this site is located near several large vehicle emissions (Figure 1 and 2). Interstate 80 (I-80) is just to the west of the site by approximately 300 meters. This section of the freeway frequently slows down during the evening rush hour. The freeway could be observed from the site, so traffic counts were conducted during sample collection. In addition to I-80, the site was near both Sunrise Blvd and Douglas Blvd, both of which are heavily traveled surface streets. There are a few large stop lights on Douglas Blvd that tend to have cars backing up at the stop lights.

Figure 1. A close-up view of the location of the ambient sample collection site at the ARB sampling site on North Sunrise Blvd in Roseville, California. Sunrise Blvd is just to the west of

the sampling site. The shopping center south of the site had many restaurants that used fry-cooking. The map was taken from Google Earth.

Figure 2. A wide view of the location of the ambient sample collection site at the ARB sampling site on North Sunrise Blvd in Roseville, California. Interstate-80 is visible to the west of the site. Douglas Blvd is the large east-west road that is south of the site. The intersection of I-80 and Douglas Blvd typically has traffic congestion during rush hour. The map was taken from Google Earth.

The third consideration is that Roseville is often down-wind of Sacramento, hence the air quality at this site can be representative of an urban area. This site often has high ozone concentrations in the summer, thus photochemical effects should be observed for chemicals that have a photochemical origin. This is important considering that 1,3-butadiene oxidation has been hypothesized to be a major contributor to ambient acrolein concentrations. The 1,3-butadiene is emitted from vehicles combined with ozone could produce acrolein, hence this site was selected to have both of these conditions.

The last consideration in selecting the site at North Sunrise was that this site has facilities (line power for pumps and night lights, refrigerator, office, etc.) that allows for relatively easy sample collection compared to remote areas.

The second site was located near Putah Creek upstream of Lake Solano in Solano County, California (Figure 3). The approximate location of the sampler was Lat 38°30’54.31” N

by Long 122°03’29.31” west. This site was chosen as a control site since it was located in the Sacramento Valley, but it is not near any urban sources of air pollution. The site was located in a blue oak savannah at the base of the coast range foothills. Therefore, it was designed to determine the rural background concentration of acrolein and other carbonyls. In particular, carbonyls from biogenic sources should be identified by this remote site.

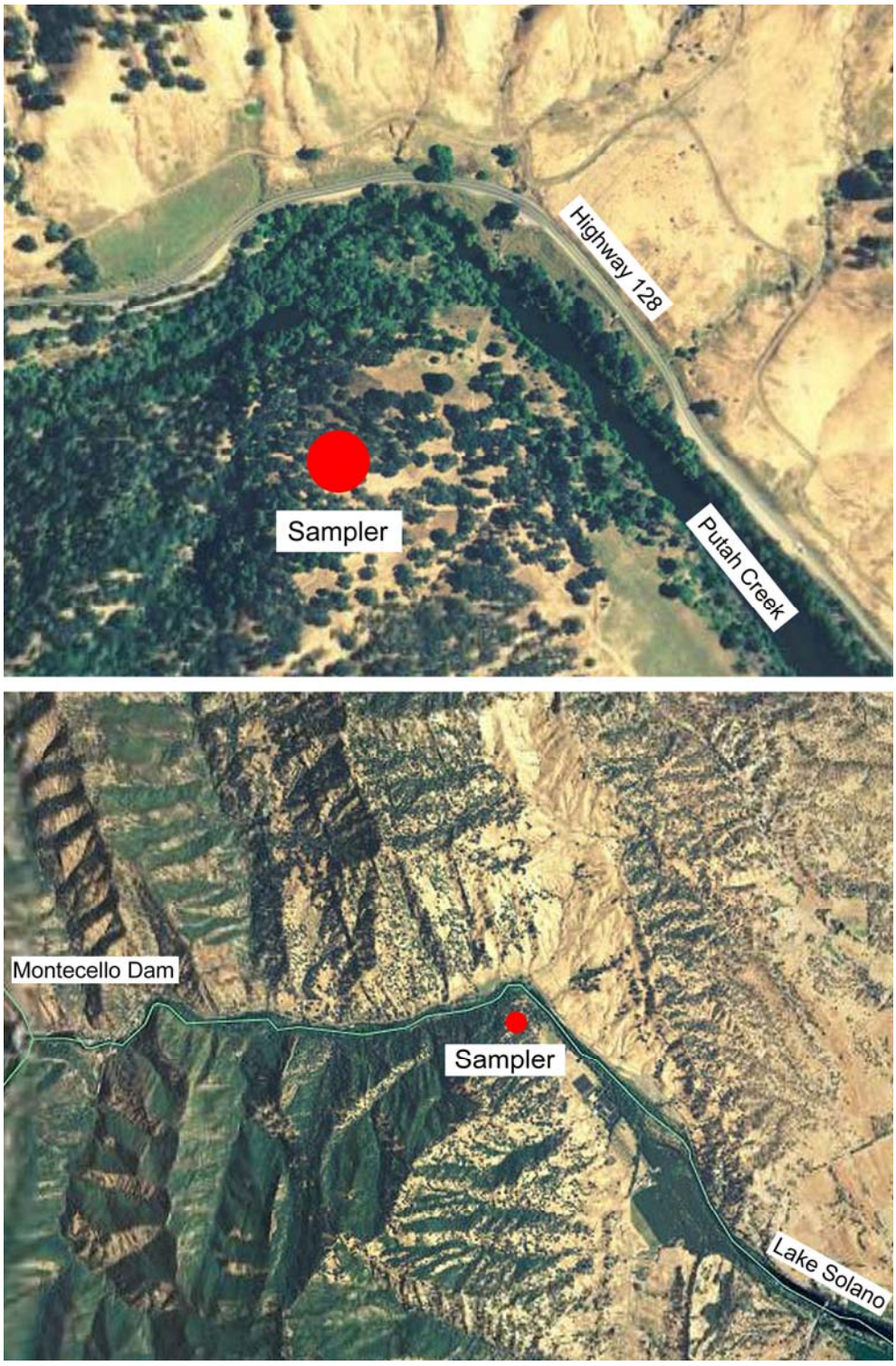


Figure 3. Location of the control site at Putah Creek. The site is located in rural Solano County. The pictures were taken from Google Earth.

Unlike the ARB North Sunrise site, this site did not have any line power, so all the sample collection was conducted using 12V batteries and power inverters. Basic battery-powered meteorological instrumentation (temperature, relative humidity, wind speed) was taken

to the site to collect meteorological information. The site was located at the mouth of the Putah creek canyon, so the local winds at the site were characterized by "up-valley" and "down-valley" air flows. The up-valley air flows represented air movement from the Sacramento Valley up the Putah Creek canyon, so the wind would be blowing to the west. The down valley flows are just the opposite with the air coming from the coast range and going into the Sacramento Valley.

Since this site did not have any line power, the samples and standards were placed in a cooler with ice to keep them refrigerated during the sample collection episode as a precaution against chemical degradation. Furthermore, the samples were returned to the laboratory on a daily basis so they could derivatize under the standard condition called for in the sample collection and analysis standard operating procedure.

Sample Collection Times:

The primary objective of this project was to determine the diurnal and seasonal fluctuations of acrolein concentrations. Two sampling episodes were conducted in Roseville in the summer of 2006 and two more sampling episodes were conducted in the winter of 2006/2007 to determine the seasonal effect of acrolein concentrations. A third sampling episode was conducted at Putah Creek in the summer of 2006 as a control site. The first Roseville sampling episode was conducted from June 25th to June 28th while the second sampling episode was conducted between July 16th and July 19th, 2006. There were actually two Putah creek sampling episodes. The first was from June 18th to June 21st, but this episode had analytical problems that prevented the data from being reliable. Therefore, the Putah creek sampling was repeated from July 9th to July 12th to collect quality data for a control site.

The last two sampling episodes were conducted in winter at the Roseville site to test for summer-winter differences in acrolein and other carbonyls. The dates of these sample collection episodes were December 17th to the 20th in 2006 and January 7th to the 10th in 2007.

Each sampling episode consisted of 72 hours of sampling where duplicate samples were collected every two hours around the clock. The intensive sampling intervals were designed to determine the diurnal fluctuations in acrolein concentrations within a day. In particular, we expected to see vehicle contributions to acrolein during the rush hours and lower concentrations at night. The sampling times were also designed to test for photochemical generation of acrolein since the sampling will encompass high ozone periods during the late afternoon and low ozone periods at night.

Lastly, all sampling episodes started at 06:00 on a Sunday morning such that one weekend day and two work days were sampled during each sampling episodes. Therefore, comparisons can be made between weekend traffic that lacks a rush hour and the workday traffic that has a very predictable rush hour. Samples were collected every two hours on the even hours until 06:00 on the following Wednesday. The complete field collection log is presented in Appendix 5 that details the exact times of each sample, the meteorological conditions and any comments or missed samples.

Sample Collection Procedure:

Duplicate samples were collected at every time interval according to the Standard Operating Procedure (SOP) detailed in Appendix 1. A complete description of the method development and optimization is published in Analytical Chemistry (41). Briefly, two mist chambers are used in series to trap ambient carbonyls in a 0.1 M bisulfite solution (Figure 4).

Vacuum pumps pull air at a rate of 13 to 20 L/min through the mist chambers. The air passes through a nebulizer the pulls up the 0.1 M bisulfite solution and creates a fine mist. The gas-phase carbonyls partition into the mist droplets where they are attacked by the bisulfate to will form sulfonate adducts. The sulfonates are not volatile since they are both water soluble and ionic, thus they remain in the solution. Two mist chambers are used in series to achieve a good collection of the gas-phase carbonyls. After the sample collection is complete, the bisulfite solution is removed from the mist chambers, along with two rinses of the mist chambers, and transferred to a "reaction tube". The reaction tubes contain hydrogen peroxide, hexane, acidified water, and pentafluorobenzylhydroxyamine (PFBHA). The bisulfite is oxidized to sulfate by the hydrogen peroxide, thus releasing the carbonyls. The free carbonyls are then derivatized by PFBHA for form stable, non-polar derivatives that partition into the hexane. The samples are allowed to react for 4 days after which the PFBHA-carbonyls are extracted in hexane, concentrated by nitrogen evaporation and spiked with the injection standard mixture.

The samples are analyzed by gas chromatography negative chemical ionization mass spectrometry (GC-NCI-MS). The pentafluorobenyl functional group is easily detected by the negative chemical ionization analysis mode, thus providing a highly sensitive analysis procedure. The chemicals are separated on an Agilent DB-5 ms column. The details of the instrumental conditions are detailed in Appendix 1.

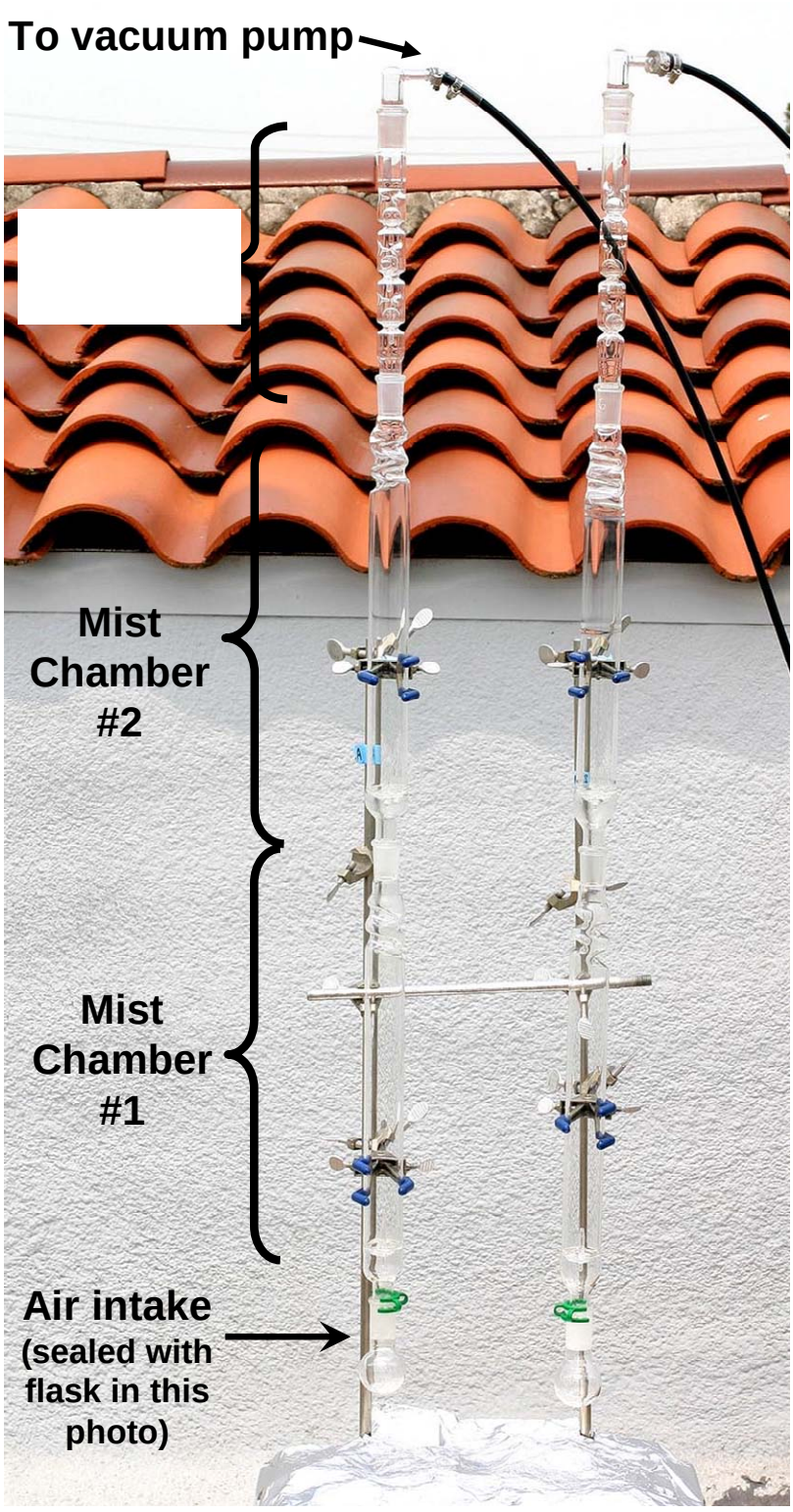


Figure 4. Photograph of the mist chamber system used to collect ambient air samples on the roof of the ARB North Sunrise monitoring station.

Spike-recovery Experiments:

Before conducting the field sampling episodes, a series of spike-recovery experiments were conducted to validate the analytical methodology on a wide range of chemicals other than just acrolein. The method was tested on a set of 57 common aldehydes and ketones (Table 2).

The experimental procedure was to connect two mist chambers in series and operate them at a flow rate of 19.7 L/min. The mist chambers were loaded with 10 ml of 0.1 M bisulfite that had been enriched with acrolein-d_4, benzaldehyde-d_6 and acetaldehyde-d_4 according to the SOP presented in Appendix 1. A glass elbow tube (hereafter "spiking tube") was placed upstream of the first mist chamber where the analytes will be added to the system. The spiking tube was connected to a cylinder of 99.997% pure nitrogen that was further purified by passing the nitrogen through a charcoal trap. Therefore, the entire system is closed from the nitrogen cylinder to the vacuum pump. The analyte spiking solution, prepared in acetonitrile, was added to the spiking tube where the analytes would volatilize into the stream of nitrogen and enter the mist chambers in the gas phase in a similar fashion as chemicals in ambient air samples. The experiments were conducted at room temperature, so heat was not added to help the analytes volatilize into the gas phase. The analyte spiking solution had a target concentration of approximately 100 ng/μL for each of the 57 analytes and 10 μL of the solution was used for each analysis run. Therefore, the mass of each analyte added to the system was approximately 1 μg. This mass loading is higher than expected field sample values to ensure detectable concentrations of the analytes in the second mist chamber.

Two series of experiments were conducted in triplicate. The first was the standard 10 minute sample utilized in the analysis of ambient samples in this report. In this case, the spike was added to the experimental apparatus after 5 minutes, which is half-way through the sample collection. The second set of experiments utilized a 30 minute sample collection time. The spike was also added 5 minutes into the sample collection to be consistent with the first set of experiments. The longer sampling time would allow for greater loss of the chemical by volatilization, thus there experiments were designed to demonstrate chemical loss as a function of sample collection time as well as determining if a longer sampling time is feasible as a mechanism for improving sensitivity.

After the sample collection was complete, the efficacy of the method was evaluated in two fashions, namely:

1) Collection efficiency determination
2) Spike-recovery determination
3) Retention of internal standards

Each of these approaches has advantages and disadvantages.

The first approach was the "collection efficiency" approach that was utilized earlier in this report and in previous research (e.g.(42)). This approach uses the chemical concentrations determined in the two chambers to calculate the chemical collection efficiency (%) as:

$$\text{Collection efficiency (\%)} = [1 - (C_2/C_1)]\times 100 \qquad (X)$$

where C_1 and C_2 are the concentrations of the chemicals in the first and second mist chambers. It is important to note that the collection efficiency calculation is a relative measure between the two mist chambers and is not related to the initial mass of chemical added to the spiking tube. One advantage of this approach is that air concentration of the chemicals does not need to be known since the collection efficiency is a relative difference between the mass of chemical

collected in the two chambers. This relative concentration approach can be applied to any sample where the two mist chamber concentrations are determined separately, so the collection efficiency can be determined during field sampling under "real" sampling conditions. The disadvantage of this approach is that it is vulnerable to systematic biases. For example, if half the chemical mass in each mist chamber is lost to wall adhesion, then the collection efficiency calculation will still give a high collection efficiency since it is a relative measure between the two chambers even though half the mass is lost.

The second approach was the spike-recovery approach, which is also called mass balance or mass recovery. In this case, the mass of the analytes was determined in each mist chamber separately as well as in a bisulfite rinse of the spiking tube, which was conducted to determine the mass of chemical that never volatilized into the air stream. The total mass recovered from the mist chambers and spiking tube after the sample collection was then compared to the initial mass of chemical added to the spiking tube. Therefore, the spike-recovery (%) was calculated as:

$$\text{Spike-recovery (\%)} = [(m_{\text{chamber \#1}} + m_{\text{chamber \#2}} + m_{\text{spiking tube}})/m_{\text{inital}}]\times 100 \qquad \text{(X)}$$

where $m_{\text{chamber \#1}}$ and $m_{\text{chamber \#2}}$ were the mass recovered from mist chambers #1 and #2, respectively, m_{spiking} tube is the mass recovered from the spiking tube (chemical that did not volatilize) and m_{initial} is the mass of chemical initially added to the spiking tube. It should be noted that there are glass surfaces in the bottom of the first mist chamber where chemical could adsorb and be lost from the mass balance calculation. We anticipate this to be minor except for the less volatile chemicals. It is also important to note that, unlike the collection efficiency calculation, the spike-recovery calculation is an absolute calculation that directly related to the initial amount of chemical present. This is a more rigorous approach to determining the effectiveness of the sampler in collection carbonyls from the gas-phase because it relates the collected mass to the known initial mass of chemical added to the system. The spike-recovery approach is a common method to assess the accuracy of analytical methods since chemical lost by any mechanism (volatilization, degradation, adsorption, incomplete derivatization, sample spillage, etc.) will appear as a low recovery by the spike-recovery approach. The disadvantage of this approach is that it cannot be applied during field sample collection since you must have a known amount of chemical to start with.

The last approach to determine the efficiency of the methods is to determine the retention of internal standards added to each sample before sample collection starts. The internal standards used were acrolein-d_4, benzaldehyde-d_6, and acetaldehyde-d_4. Unlike the two previous approaches, the chemicals are directly added to the collection solution, so this does not evaluate the ability of the mist chambers to remove chemicals from the air stream. The retention of the internal standards provides an effective measurement of any loss processes resulting from re-volatilization, degradation or sample handling. The advantage of this approach is that it can be applied to every field sample with no increase in sample analysis. The inherent assumption is that the deuterated internal standards will behave in the same fashion as the target analytes, therefore any losses that affect the internal standard will also affect the analytes. If the majority of the internal standard is recovered, then it suggests that the majority of the analyte that enters the bisulfite solution should also be retained and that the method appears to be working well under field conditions. Conversely, if a large fraction of the internal standard is lost in a sample, then the analyte will likely be lost as well. This would indicate that there is a problem with the

sample collection and analysis for a particular sample. It should be noted that the analytes are quantified relative to these internal standards, thus the concentration data reported are "normalized" to these standards. Therefore, the magnitude of the analyte concentration corrections due to using a relative response factor based on the internal standards is related to the retention of the internal standards. The greater the internal standard retention, the smaller the correction due to using a relative response factor based on the internal standards. To determine the retention of the internal standards, the peak areas of the internal standards are normalized to an injection standard, generally octafluoronaphthalene, to account for instrument drift. This is the only application of the injection standards for quantification of chemicals.

Quality Control Program:

Acrolein is a notoriously difficult chemical to quantify due to its high reactivity. Therefore, this project had several quality control mechanisms to ensure the accuracy of the results.

Enrichment of all samples with deuterated acrolein, acetalydehyde and benzaldehyde:

All sample solutions were enriched with isotopically labeled acrolein-d_4, acetaldehyde-d_4 and benzaldehyde-d_6 prior to sample collection. These deuterated compounds were designed to account for chemical loss due to volatilization, degradation or incomplete derivatization. These spiking solutions were allowed to react with the bisulfite solutions for 10 minutes before the bisulfite solutions were added to the mist chamber. The spiking procedure is more conservative than most analytical procedures where the labeled standards are added after sample collection. By adding the spiking chemicals before the sample collection, the chemical loss by volatilization and possible degradation during sample collection can be determined. These three internal standards were also added to all blanks and calibration standards at the same concentrations as the samples.

Duplicated Samples:

Duplicate samples were collected at every sampling time. This provides a measure of method consistency for the field samples. It also helps to identify potential errors in the quantification and integration steps of the analysis procedure. If the two replicates at a given sampling time gave different results, then the results can be double-checked. Lastly, it provided greater confidence in temporally-short spikes in concentrations. A single high value could have been an analytical error or contamination but if both replicates gave similar high values, then the results are far more likely to be real.

The duplicate samples also provide insurance against sample loss. Samples can be broken during storage, transport and handling in the laboratory. Therefore, having duplicate samples collected at each time it is unlikely that both samples will be lost in sample handling.

Calibration Curves Prepared in the Field:

Calibration curves were prepared from stock solutions in the field for each field sampling episode. The derivatization procedure is sensitive to the duration of the derivatization, thus it was decided that is would be the most accurate to prepare the calibration curve in the field and store it with the samples. The calibration curve was prepared by adding a small amount of the standard mix (0, 1, 3, 10, 30 and 100μL) to a randomly-selected set of bisulfite solutions. One of

the "standards" had no chemicals added, other than the internal standard mixture, and thus it provided a reagent blank. The bisulfite solutions were allowed to react with the standards for 10 minutes before they were poured into the reaction tubes, which neutralized the bisulfite and derivatized the analytes. The calibration curve was generally prepared on the middle day of sampling and single 10μL standards were prepared on all sampling days to ensure consistency.

In retrospect, the calibration curves between the different sampling episodes were very consistent, so the excessive duplication of standards may not have been needed. However, it was safer to err on the side of redundancy rather than insufficient standards. Having standards prepared from sample vials in the field and stored with the samples also provides insurance against delays in getting the samples back to the laboratory.

Replication of Standard Analysis during Instrumental Analysis:

Mass spectrometers are sensitive instruments that are subject to drift from sample contamination. In particular, the ionization source in the mass spectrometer may become dirty over a long sample analysis run. To identify possible instrumental drift, all sample analyses were bracketed by a calibration curve at the beginning of the sample run and at the end of the sample run. Consistency between these two calibration curves proves the lack of instrumental drift during the sample analysis run. Furthermore, calibration standards were analyzed every 6 to 8 field samples to monitor for drift. The results showed that no significant instrument drift occurred during the sample analyses in this study. Quantification of the analytes was conducted by combining all the standards analyzed during a sample run to create a single calibration curve.

Dual Quantification of Acrolein:

The derivatization agent, namely pentafluorohydroxylamine (PFBHA), contains a double bond at the site of attachment. Therefore, most of the carbonyls give two peaks in the chromatogram corresponding to the *cis*- and *trans*- isomers. For most of the carbonyls, the base ion in the larger of the two peaks was used for quantification.

The quantification of acrolein was conducted slightly differently. The main quantification was conducted using the base ion (*m*/*z* 231) in the larger of the two isomer peaks as with the other carbonyls, but this quantification was "double-checked" by quantifying a different ion (*m*/*z* 251) in the smaller isomer peak. If the two quantification measures provided similar results, then we had a great deal of confidence that peaks observed were due to acrolein and not an interfering compound. Therefore, acrolein was quantified using the larger peak and confirmed using a different quantification ion in the smaller peak. Qualifying ions were also used in both peaks to ensure the identity of the peaks.

Preparation of Standards:

During previous research it was observed that carbonyl standards prepared in methanol and stored in a refrigerator degraded over relatively short time periods. It was also discovered that acetonitrile was the best solvent for storing the carbonyl standards, but even it could have carbonyl losses over time. Therefore, just prior to the summer field sampling episodes, all the chemical standards were prepared from primary standards into acetonitrile and frozen at -20^{o}C in glass-sealed ampules. Fresh calibration standards were prepared from these stock solutions the day before the commencement of a field sampling episode. The standards were then refrigerated in the field at Roseville or placed in a cooler with ice in the Putah Creek sampling times. After

each sampling episode, the left-over standards were discarded and new ones were prepared for the next episode.

The internal standard mixtures (acrolein-d_4, benzaldehyde-d_6 and acetaldehyde-d_4) had additional quality controls associated with their use. Since this mixture was opened and handled 12 times a day, evaporative loses could have occurred over long sampling episodes. Therefore, a separate vial of internal standards was prepared for each day of sampling to prevent drift of the internal standard concentration over the three day sampling episodes. At the end of each sampling day, the left-over internal standard mix was discarded and a new vial was opened for the next day's sampling efforts. The internal standard mixtures were also refrigerated or put in a cooler with ice in the same fashion as the calibration standards.

Consistency of Acrolein and Acrolein-d_4 Standards:

Two acrolein standards from different sources were utilized during this research. The first was unlabeled acrolein obtained from Sigma-Aldrich chemical company. This liquid standard was diluted into acetonitrile and was included in the calibration standard solutions that contained all the calibration chemicals.

The second source of acrolein was acrolein-d_4 that was custom synthesized by Cambridge Isotope laboratories. This standard was delivered as a 10% solution in nitrobenzene. The standard was diluted into acetonitrile and mixed with the labeled benzaldehyde-d_6 and acetaldehyde-d_4. This standard became part of the internal standard solution that was added to each sample and standard.

Therefore, the two separate acrolein standards came from different sources and were mixed into different solutions. The two standards were never mixed until a calibration curve sample was being prepared. One of the calibration solutions deliberately had almost identical concentrations of acrolein and acrolein-d_4. If the instrumental response is assumed to be similar for the two compounds, then the ratio of these instrument responses for these provides a measure of the consistence of the two standards from different sources and different solutions. The acrolein to acrolein-d_4 ratio for the two winter sampling episodes was 1.16 ± 0.067 (n = 21 standards) and the ratio was 1.22 ± 0.065 (n= 26) for the three summer sampling episodes. The results showed that the two standards from different sources were very consistent in the 5 different field sampling episodes. There is a slight bias towards the unlabeled acrolein giving results that are about 20% higher than the labeled acrolein. This bias may be real, namely the result of errors in standard creation, or it may be an instrumental artifact such that the instrumental response to acrolein-d_4 may be lower than acrolein.

Field Blanks:

Two field blanks were prepared on each day of sampling. The field blanks were prepared and handled in the exact same fashion as the samples except that the vacuum pumps were not turned on. Therefore, the field blanks were spiked with the internal standard mix, allowed to react for 10 minutes, then poured into the mist chambers, sat in the mist chambers for 10 minutes with the vacuum pumps off, and then poured into the reaction tubes along with two rinses of the mist chambers. These field blanks are the best representation of the contamination resulting from both the reagents themselves and sampling handling/storage in the field. The field blanks were generally prepared around noon after the samplers had been in use for awhile.

The minimum detectable limit (MDL) was calculated using the field blanks rather than the reagent blanks or instrument signal-to-noise ratios. The limit of detection was the mean field

blank from the sampling episode (n = 6) plus three standard deviations of the blank. Values below the MDL are reported as "Not detected". The minimum quantification limit (MQL) was defined as the mean field blank plus six standard deviations of the blank. Values below the MQL but above the MDL were positively detected, but the absolute quantification of the analytes in rather uncertain. Numerical values are reported, but they are flagged to indicate that they represent the "best estimate" of the value but they are not as reliable as values above the MQL.

Retention of Internal Standards:

The addition of internal standards was designed for the isotope-dilution method of quantification where the analyte is quantified against the internal standard so that any chemical losses, such as spillage, incomplete derivatization, etc, can be accounted for during quantification. The second use of the internal standards is to determine the amount of internal standard lost during the sample collection, derivatization and extraction process. In this case, the instrument response for the internal standards is divided by the instrument response for the injection standard, which normalizes instrument response and sample volume between analyses. The degree of internal standard loss is then calculated as the average internal standard relative response factors for the samples divided by the average internal standard relative response factor for the standards. This gives the result as a ratio, so it is typically multiplied by 100 to turn the value into a percent. Typically, values of 80% to 120% are considered good and values between 60% and 130% are considered acceptable. In this project, any sample that had an internal standard retention value less than 50% was not reported due to failing to pass quality control. While the internal standard would account for this loss during the quantification processes, a low recovery of an internal standard results in poorer quantification since the uncertainty about the internal standard concentration becomes larger.

The average retention of the three internal standards utilized in this project are given in Table 1. These results showed very low retention of acetaldehyde-d_4 for all episodes, which is why acetaldehyde concentrations are not reported since the method is ineffective at retaining this analyte. The winter-time episodes had considerably better retention, which implies that the loss of the internal standard was dependent on the ambient temperature. The hot summer time temperatures probably helped to volatilize this very volatile compound while the cooler winter temperatures help retain the labeled standard. The retention of both acrolein-d_4 and benzaldehyde-d_6 was generally good, thus providing strong evidence for the efficacy of the analytical methodology.

Table 1. The average internal standard retention during the 5 field sampling episodes.

Internal standard	Roseville Summer 1 (n=68)	Roseville Summer 2 (n=88)	Roseville Winter 1 (n=73)	Roseville Winter 2 (n=74)	Putah Creek (Summer) (n=81)
Acetaldehyde-d_4	4.0%	3.3 %	16.5%	29.0%	4.0%
Acrolein-d_4	79.1%	113.3%	117.1%	107.2%	102.9%
Benzaldehyde-d_6	95.3%	81.7%	76.1%	83.5%	79.0%

Results

Spike-Recovery Experiment:

The results (Table 2) provided significant insight to mechanisms and limitations of the mist chamber methodology. The first observation is that the calculated collection efficiency is a rather poor measure of the methods efficacy since many compounds have good collection efficiency values but very poor spike-recovery values. It is possible that the collection efficiency calculation is systematically flawed for the mist chamber methods. The second mist chamber experiences a higher vacuum compared that may result in greater volatilization of chemicals or less partitioning into the chemicals in the aqueous phase in the second chamber. This would result in systematically lower concentrations in the second chamber relative to the first chamber, thus artificially inflating the collection efficiency values. Therefore, the two chambers are not treated in the same fashion as was assumed in the collection efficiency calculation. Therefore, we believe that the spike-recovery calculation is probably a more accurate measure of the mist chamber effectiveness to trap chemicals from an air stream.

The results of the spike-recovery calculations showed the method generally "acceptable" (>70% recovery) or marginal (50% to 69% recovery) for 1) saturated aldehydes with less than 8 carbons, 2) mono-unsaturated aldehydes with less than six carbons, 3) aromatic aldehydes, 4) diones with less than 6 carbons, and 5) miscellaneous small polar compounds such as glyoxal, methyl glyoxal, 2-furaldehyde, nopinone, and pinonaldehyde. The notable exceptions were methacrolein, 2-methyl-2-butenal, 3-hydroxybenzaldehyde and 2,4-pentanedione. In general, the spike-recovery values tended to decline with increasing molecular mass within a homolog group (e.g. saturated aliphatic aldehydes). This is presumably due to the lower aqueous solubility of the larger, less polar hydrocarbons. The larger and less water soluble chemicals are less likely to partition into the 0.1M bisulfite solution and be trapped. The recovery of methacrolein was surprising low (31% for 10 minute sample) considering the good recoveries of acrolein (97%) and crotonaldehyde (86%). These three chemicals would be expected to have similar behavior since the all have an aldehyde functional group and a double bond. The reason for the low recovery of methacrolein is not known. Some chemical had recoveries greater than 100%, which indicates that some background contamination is present. The data was "blank subtracted" based on a single set of blanks, thus this estimate of the blank may not be perfect for chemicals that tend to have high and somewhat variable blanks (e.g. acetaldehyde and glyoxal).

The method performed very poorly for the ketones, including methyl vinyl ketone. The ketones could be derivatized and produce linear calibration curves, so the problem appears to be with the retention of these compounds in the mist chambers. Many of the diones gave reasonable results. Considering that the diones are more water soluble and less volatile, they would be expected to be retained by the mist chamber collection solutions. Thus it appears that the poor retention of the mono-ketones was due to their volatility or relative lack of water solubility compared to the aldehydes. We suspect that the bisulfite may not bind to the ketones in the same fashion as the aldehydes, and thus it may not trap then like the aldehydes. The lack of a bisulfite adduct would result in greater re-volatilization from the mist chambers.

Two other groups of chemicals that the method does not produce accurate results for are the doubly unsaturated aldehydes ("dienals") and the quinones. The dienals did not produce very good calibration curves probably due to reactions with the bisulfite at two unsaturation functions groups other than the aldehydes functional group. The quionones, as exemplified by

benzoquinone, were easily derivatized by PFBHA in pure water, but they could not be derivatized in the 0.1 M bisulfite / hydrogen peroxide / PFBHA solution and hence calibrations curves could not be created. We suspect that the peroxide was oxidizing the quinone to the hydroquinone which is then not available for derivatization. Other quinones would likely suffer from the same problem.

The longer, 30 minute sampling time had greater volatilization of the lighter compounds and thus poorer spike-recovery values. Conversely, some of the heavier compounds had better recoveries with the long sampling times. This is likely an artifact of the spiking methodology where the spike was applied to a glass tube before the mist chamber. Therefore, the chemical must volatilize into the gas phase and enter the mist chamber. The quick rinse of the spiking tube may not have dissolved all of the analyte that remained in the spiking tube, particularly if it is fairly insoluble in water. Also, there are sites for adsorption to occur in the bottom parts of the mist chambers and in the nebulizer, thus the chemical may stick on the glassware entering the MCs. Therefore, the longer sampling time gives more time for the chemical to volatilize into the air stream and enter the chamber to be trapped. For field sampling campaigns, the higher recovery for the less volatile compounds is probably more representative of their actual collection rate.

The retention of acrolein-d_4 and benzaldehyde-d_6 internal standards agrees well with the spike-recovery data presented above (Table 3). All the mist chambers were spiked with acetaldehyde-d_4, acrolein-d_4 and benzaldehyde-d_6 in 10 μL of acetonitrile before sample collection. The fraction of the labeled standard at the end of the sample collection could then be compared to the initial mass of chemical added directly to the collection solution. Benzaldehyde-d_6 was unaffected by the longer sampling time while acrolein-d_4 retention decreased by about 14%. Acetaldehyde-d_4, however, is an enigma. The labeled standard showed extensive loss, probably due to volatilization, while the spike-recovery values were pretty good despite some background contamination. It is possible that the background contamination in the spike recovery tests is obscuring a poor sampler collection rate, but this is not likely. It is also possible that the labeled acetaldehyde in acetonitrile associated with the solvent in some fashion that allowed it to be more volatile. The experiment needed to solve this question is simple, namely added the labeled acetaldehyde to the spiking tube and allow it to volatilize into the mist chambers in the gas phase like the "normal" acetaldehyde spike conducted above. However, until this issue is clarified, the acetaldehyde values should only be used for qualitative trends.

The investigation of the "spiking-tube" rinse showed that they spike was completely volatilized for the 10 minute sample with less than 10% of the spiking mass being recovered for all compounds except for pinonaldehyde, naphthaldehyde, hydroxybenzaldehyde, glyoxal, methyl glyoxal, and 2-hexanone. Acetaldehyde, propanal, butanal, and 2-butanone also formally showed more than 10% mass recovered in the spiking tube, but these compounds had high blank values so the mass recovered from the spiking tube for these compounds may have been due to an imperfect blank subtraction. These chemicals are also volatile, so they would not be expected to be retained in the spiking tube. The 30 minute sample time test showed even better volatization with only propanal, 2-butanone, pinonaldehyde, glyoxal, and methyl glyoxal having greater than 10% of the spike recovered from the spiking tube rinse.

Table 2. The collection efficiency (%) and spike-recovery (%) of the mist chamber methodology for a wide range of carbonyls.

	10 minute sampling time (*n*=3)		30 minute sampling time (*n*=3)	
Compound	Collection efficiency (%)	Spike-recovery (%)	Collection efficiency (%)	Spike recovery (%)
Saturated aldehydes				
acetaldehyde	81 ± 2	151 ± 8	66 ± 1	118 ± 4
propanal	74 ± 3	179 ± 24	62 ± 7	112 ± 7
butanal	65 ± 10	109 ± 3	49 ± 13	73 ± 13
pentanal	71 ± 4	87 ± 4	48 ± 7	77 ± 3
hexanal	68 ± 6	101 ± 4	52 ± 4	91 ± 7
heptanal	73 ± 21	53 ± 6	47 ± 20	55 ± 17
octanal	59 ± 10	53 ± 2	27 ± 4	42 ± 5
nonanal	59 ± 8	44 ± 2	36 ± 8	35 ± 4
decanal	57 ± 12	41 ± 2	31 ± 7	32 ± 4
2-methylpropanal	61 ± 13	57 ± 1	43 ± 8	52 ± 2
3-methylbutanal	63 ± 12	72 ± 2	35 ± 11	61 ± 6
Unsaturated aldehydes				
acrolein	80 ± 3	97 ± 1	71 ± 2	73 ± 5
methacrolein	65 ± 10	31 ± 3	77 ± 2	6 ± 2
crotonaldehyde	84 ± 4	86 ± 4	74 ± 4	54 ± 8
2-methyl-2-butenal	62 ± 21	9 ± 3	73 ± 10	<1
3-methyl-2-butenal	89 ± 1	83 ± 4	79 ± 2	73 ± 7
2-hexenal	77 ± 6	62 ± 3	68 ± 5	38 ± 7
2-heptenal	78 ± 15	47 ± 8	66 ± 5	28 ± 5
4-decenal	84 ± 23	17 ± 3	80 ± 6	9 ± 6
2,4-hexadienal	99 ± 1	7 ± 2	95 ± 3	8 ± 5
2,4-heptadienal	99 ± 1	11 ± 3	97 ± 3	10 ± 6
Aromatic aldehydes				
benzaldehyde	88 ± 2	83 ± 2	82 ± 2	89 ± 7
o,m-tolualdehyde	88 ± 1	67 ± 1	81 ± 1	70 ± 5
p-tolualdehyde	90 ± 1	66 ± 2	82 ± 2	68 ± 6
2-ethylbenzaldehyde	84 ± 2	58 ± 4	73 ± 3	63 ± 4
3,4-dimethylbenzaldehyde	90 ± 1	58 ± 3	83 ± 1	67 ± 5
4-methoxybenzaldehyde	93 ± 1	53 ± 2	92 ± 1	68 ± 5
3-hydroxybenzaldehyde	75 ± 4	39 ± 7	76 ± 3	34 ± 4
1-naphthaldehyde	87 ± 3	138 ± 17	85 ± 2	124 ± 5
Ketones				
acetone	[a]	[a]	[a]	[a]
2-butanone	[a]	[a]	[a]	[a]
methyl vinyl ketone	77 ± 5	4 ± 2	0	0

3-pentanone	0	4 ± 1	0	1 ± 1
2-pentanone	35 ± 19	11 ± 1	0	1 ± 2
2-hexanone	[a]	[a]	[a]	[a]
2-heptanone	67 ± 31	6 ± 3	82 ± 35	0
2-octanone	57 ± 36	5 ± 1	0	0
3-nonanone	0	0	0	0
2-decanone	48 ± 46	4 ± 1	53 ± 44	1 ± 0.1
Diones				
2,3-butanedione	88 ± 1	72 ± 10	87 ± 2	91 ± 3
2,3-pentanedione	88 ± 1	68 ± 5	83 ± 2	84 ± 7
3,4-hexanedione	83 ± 1	65 ± 2	78 ± 1	76 ± 3
2,4-pentanedione	75 ± 6	41 ± 5	71 ± 4	32 ± 2
2,3-hexanedione	86 ± 1	65 ± 1	80 ± 2	71 ± 4
3,5-heptanedione	59 ± 8	27 ± 4	79 ± 4	12 ± 1
Other compounds				
glyoxal	42 ± 31	139 ± 15	61 ± 5	154 ± 11
methyl glyoxal	69 ± 2	60 ± 4	75 ± 2	69 ± 4
3-phenyl-2-propenal	95 ± 1	49 ± 1	93 ± 1	58 ± 7
glycolaldehyde	[b]	[b]	[b]	[b]
hydroxyacetone	89 ± 5	52 ± 14	99 ± 5	36 ± 7
5-hexen-2-one	52 ± 25	31 ± 4	81 ± 18	5 ± 3
4-hexen-2-one	58 ± 15	3 ± 1	73 ± 100	<1
2-furaldehyde	96 ± 3	63 ± 4	94 ± 1	49 ± 15
glutaraldehyde	[b]	[b]	[b]	[b]
nopinone	5 ± 22	61 ± 11	50 ± 5	23 ± 7
pinonaldehyde	69 ± 17	83 ± 11	67 ± 15	88 ± 4
1,4-benzoquinone	[c]	[c]	[c]	[c]

[a] Quantification not reliable due to high background contamination in the blanks.
[b] Calibration standards inconsistent, presumably due to poor derivatization.
[c] Benzoquinone can be derivatized by PFBHA in water, but not in the hydrogen peroxide and bisulfite mixture. This compound is likely oxidized by the peroxide to form hydroquionone, which no longer has any carbonyl functional groups for derivatization.

Table 3. Retention (%) of isotopically-labeled standards directly added to collection solutions before spike-recovery sample collection. The retention was calculated for only one (the first) mist chamber.

Compound	Retention (%) 10 minute sampling time (n=3)	Retention (%) 30 minute sampling time (n=3)
acetaldehyde-d_4	7.2 ± 1.4	3.8 ± 0.4
acrolein-d_4	92.9 ± 3.9	78.7 ± 4.1
benzaldehyde-d_6	87.8 ± 4.7	87.4 ± 7.0

Meteorology and Sampling Conditions:

The meteorology was monitored by the ARB instrumentation on the 10 m met tower at the site, so these are ambient temperature. However, the temperatures at the surface of the roof were a little hotter in the summer and cooler (by radiant cooling) in the winter, so the recorded temperatures were slightly different than the temperatures at the sampler.

The meteorology was fairly typical for the time of year the samples were collected. Both of the summer sampling episodes occurred during heat waves where the temperatures reached the high 30s to low 40s Celsius (Figure 5). The temperature peaked in the late afternoon on each day. The winter sampling events were just the opposite and were collected during some of the coolest times of the year. The temperatures neared or went below 0°C. The first night of winter sampling was cool enough to start causing freezing problems with the sampler. These problems were easily addressed by using heat lamps to keep the sampler warm between sampling times. The daytime maximum temperatures during the winter sampling times were between 10 and 15 °C. The relative humidity followed the inverse trend of the temperature. The relative humidity was typically highest when the temperatures were the lowest and vice-verses (Figure 6).

Ozone concentrations, which is an index for the photochemical processes, was highest during the heat of the summer. The highest daily ozone concentrations during the summer episodes were in the 80 to 110 ppb range while the wintertime daily maximum concentrations were 30 to 35 ppb range (Figure 7). The average ozone concentration during the summer sampling episodes was 52.1 ppb while the winter time average ozone concentrations were 10.6 ppb. Therefore, there were considerable seasonal differences in ozone concentrations, which is important for chemicals that are expected to be derived from photochemical oxidation.

The last location "condition" monitored was the traffic on Interstate-80 during the sampling times. This was monitored by conducting 30 second long vehicle counts in the eastbound traffic lanes each time a set of ambient samples were collected. During the summer, vehicle counts of the west-bound lanes were also conducted, but a new building was constructed before the winter sampling that blocked the view of the west-bound traffic lanes. Therefore, the vehicles counts presented are only for the east-bound lanes that could be seen during all sampling episodes. The traffic patterns did not show any seasonal differences, which is not surprising (Figure 8). The traffic showed a strong diurnal cycle with fairly uniform traffic loading during the middle of the day, from about 06:00 to 20:00, and almost no traffic after midnight. The Sunday traffic had similar peak traffic load in the middle of the day, but the traffic levels typically increased after 08:00 whereas the traffic typically increased at 06:00 during the work week. The Sunday traffic also seemed to drop off a little earlier in the evening. Overall, the traffic counts indicate that vehicle emissions should be more uniform during the day than we had anticipated.

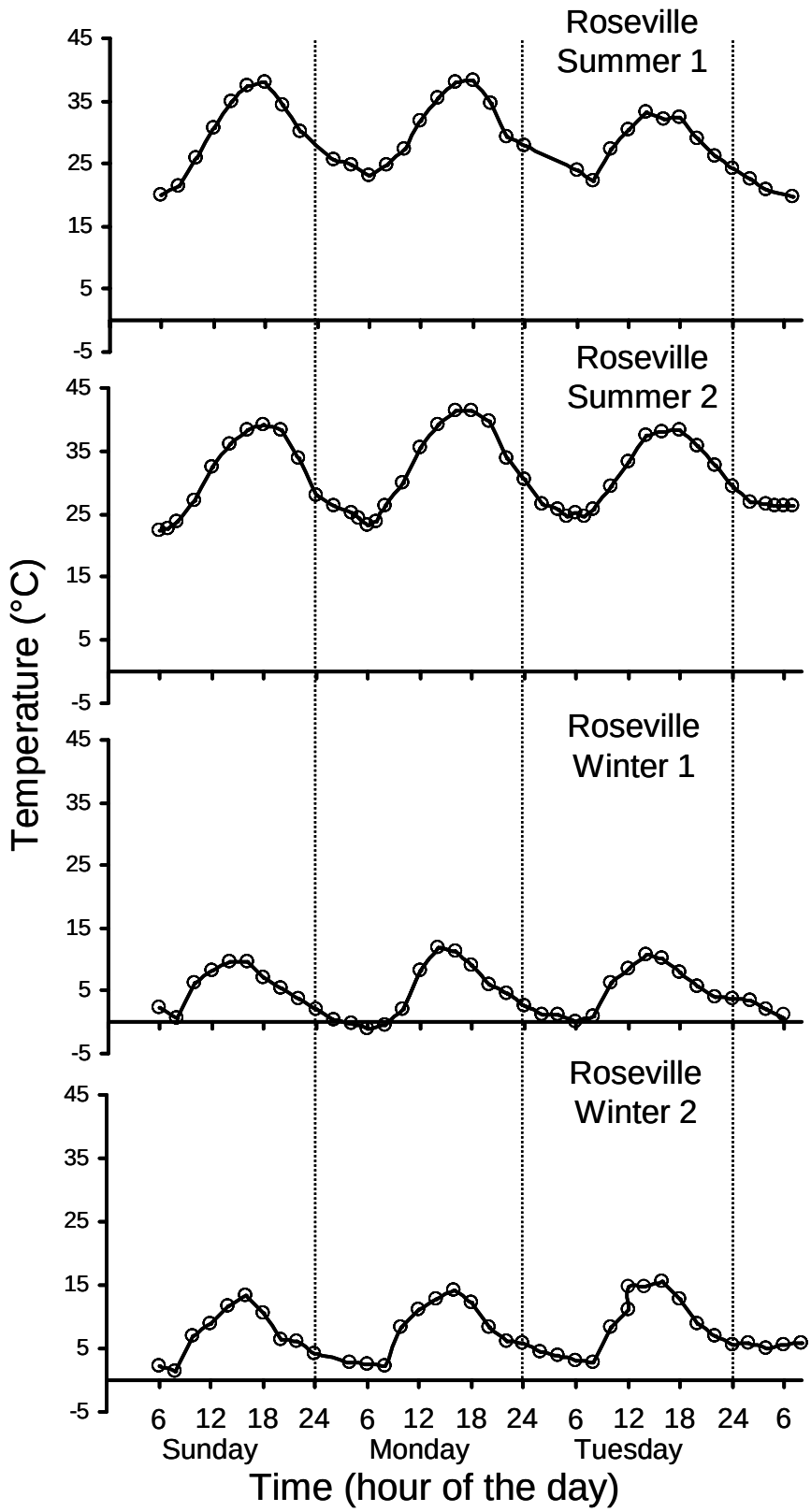


Figure 5. Ambient temperatures (°C) during Roseville sampling episodes.

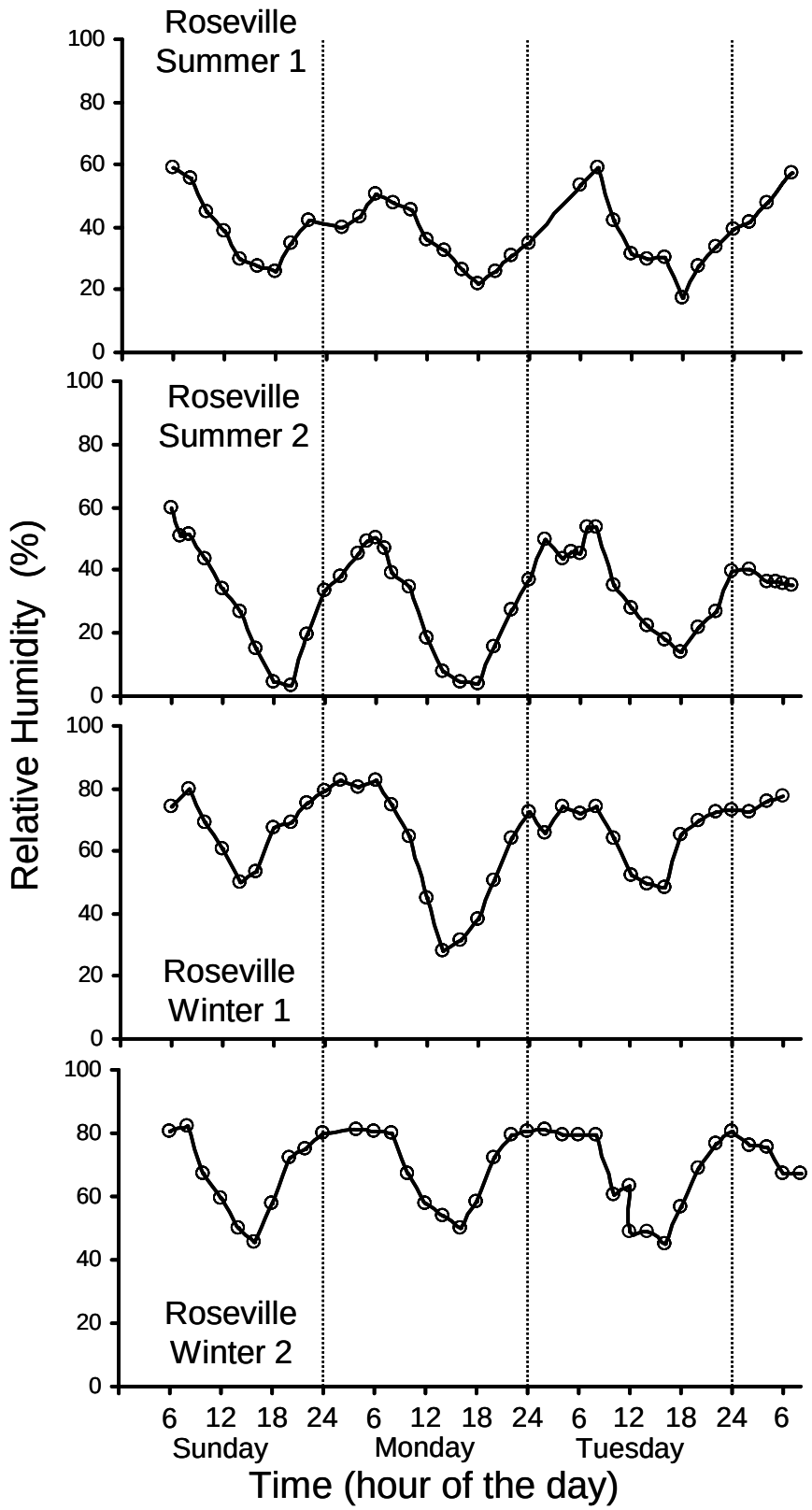


Figure 6. Relative humidity (%) during Roseville sampling episodes.

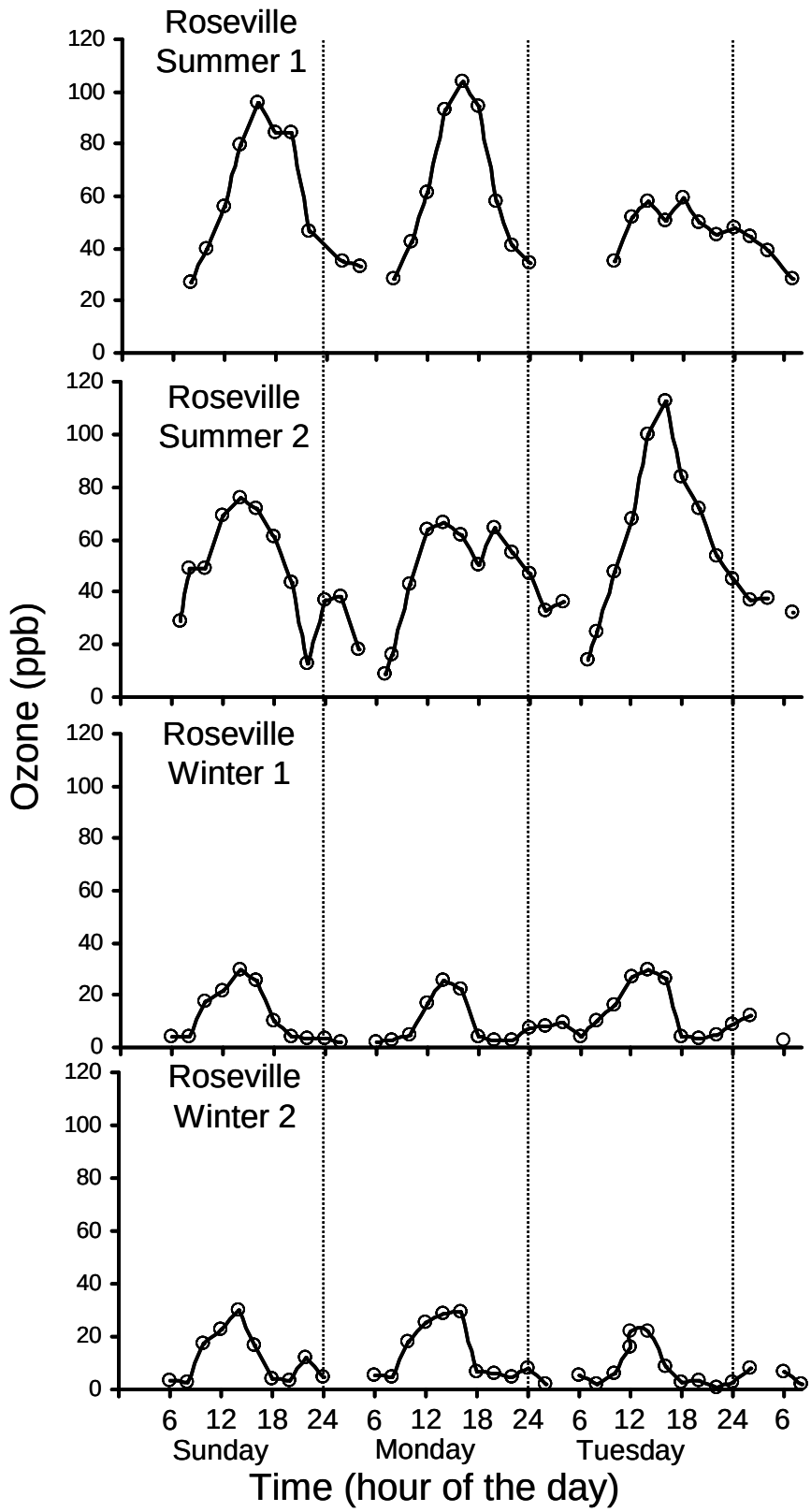


Figure 7. Ozone concentrations (ppbv) during Roseville sampling episodes.

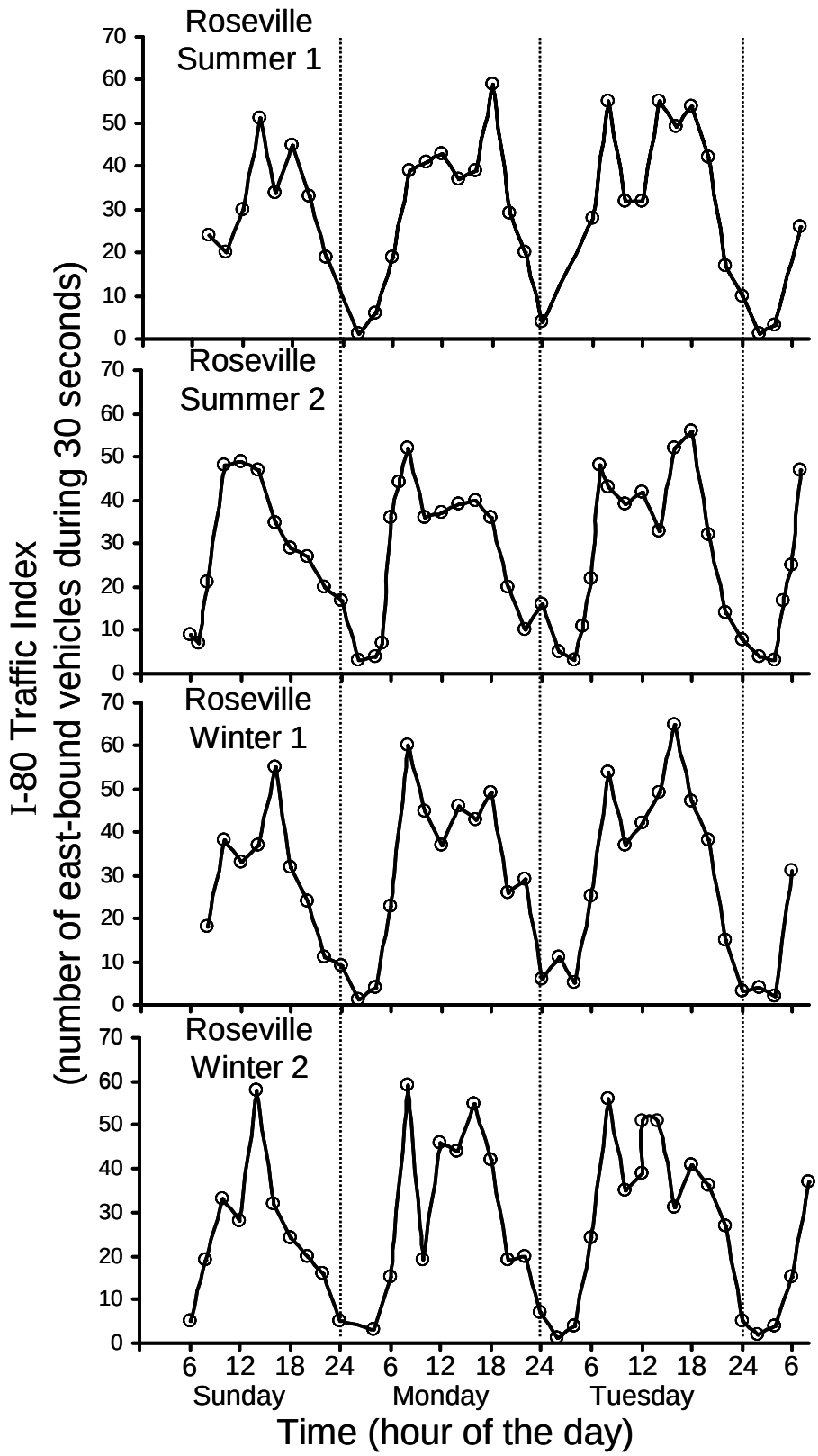


Figure 8. Relative traffic density on I-80 as determined by a 30 second vehicle counts of the east-bound traffic.

Ambient Roseville Results:

The ambient sampling at Roseville results showed a high degree of diurnal and seasonal variability in carbonyl concentrations. The variability of the carbonyls can be qualitatively explained by the potential sources of the carbonyls and how these sources changed other time. The carbonyls will be grouped into their suspected sources, although it should be noted that we cannot conclusively prove that these carbonyls came from the suspected source. During this study, it appeared that carbonyls came from four different sources, namely photochemical formation, wood smoke, transport from the Sierra Nevada, and vehicle emissions.

The results from all four Roseville sampling episodes will be graphically portrayed in the following discussion. The concentration of the chemicals will be plotted as a function of time. The time will be indicated by the day and the hour of the day (24:00 hour scale). The sample collection always commenced at 06:00 on a Sunday morning and concluded at 06:00 on a Wednesday morning. In all cases, both field replicates at each time will be plotted on the graph and the line will represent the average of the field replicates. This presents a measure of method consistency for side-by-side samples collected at the same time. The average MDL for the four sample collection episodes will be given in the caption of each graph. These graphs are created for all chemicals that were regularly detected in at least half the samples of at least one sampling episode. Chemicals that were not regularly detected in one of the sub-graphs are labeled as such.

Acrolein:

Acrolein was the focus of this study, so its results will be presented first, but the discussion about the suspected sources of the acrolein will wait for the results from the other chemical groups that identified specific sources.

One of the quality control measures for acrolein was the dual quantification using both isomer peaks of the derivatized acrolein. Therefore, acrolein concentrations were determined using two different peaks and a different ion was selected as the quantification in each of the peaks. This was designed to prevent a co-eluting compound from interfering with the acrolein quantification. The correlation between the primary acrolein quantification peak and the secondary quantification peak for all samples in this study was very good (R^2 = 0.988, slope = 1.088, n = 178) (Figure 9). These results combined all acrolein samples where acrolein was detected by at least one of the peaks. If acrolein was only detected by one of the peaks, then the "best estimate" of the second value was used even though it was less than the MDL. These results clearly demonstrate that acrolein was not subject to interferences during the chromatographic and mass spectrometric analyses for any of the field samples. Furthermore, the chromatograms showed very few other chemicals that had the same quantification ions as acrolein, thus the probability of and interfering compound was low even in the absence of this dual quantification (Figure 10). The quantification used hereafter utilized the primary acrolein quantification peak since it was larger and provided a better limit of detection.

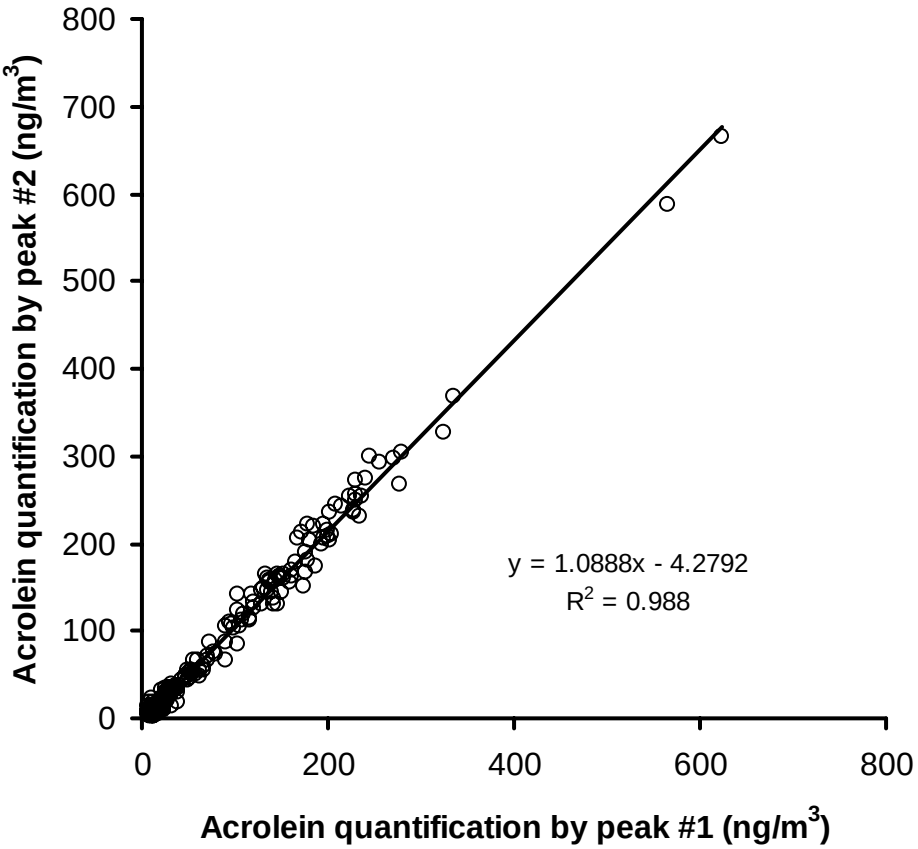


Figure 9. Comparison between the acrolein quantification from the primary peak (#1) and the secondary peak (#2). The comparison utilized all field samples for which acrolein was detected by at least one of the peaks (n = 178). The excellent correlation between the different isomer peaks demonstrates that neither peak was impacted by chromatographic or mass-spectral interferences, which helps to verify the identity of the chemicals in all of the samples collected in this study.

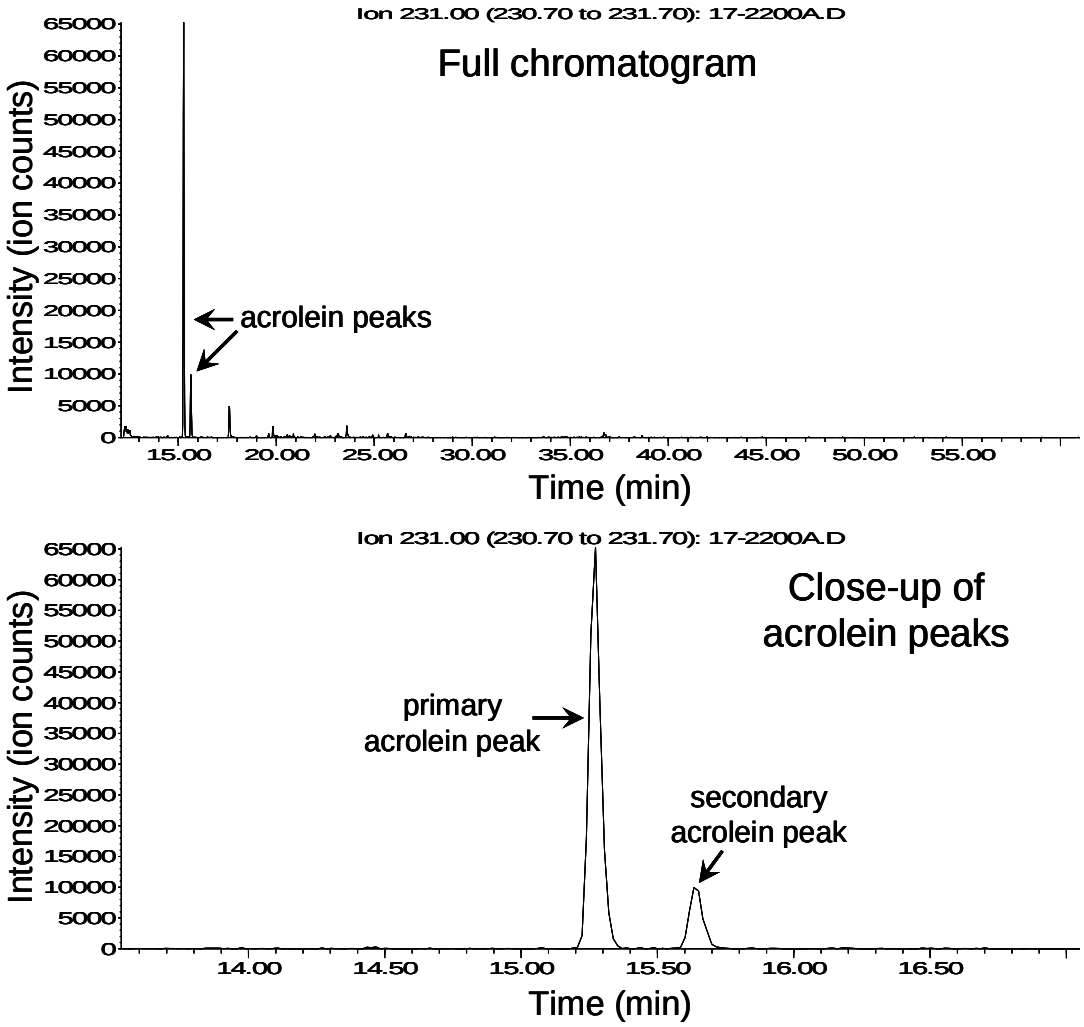


Figure 10. Single ion chromatograms (*m/z* 231) for acrolein from the 22:00 December 17, 2006 field sample A. The top chromatogram shows the whole chromatogram while the lower chromatogram is a close-up designed to show the two isomer peaks of the derivatized acrolein. Quantification was conducted using the primary peak because it was more intense and gave a lower detection limit.

The acrolein concentrations (Figure 11) showed that there was no regular discernable diurnal cycle in the summer months. This result was unexpected since acrolein was predicted to be formed from the photochemical oxidation of 1,3-butadiene. The ambient acrolein concentrations showed no correlation (R^2 = 0.025) with ozone (Figure 12). There was also no observable relationship between the traffic load on I-80 and the acrolein concentrations, which argues against direct emission from vehicles as being a dominant source of acrolein. Furthermore, the highest concentration of acrolein occurred in the middle of the night. The winter time samples showed a very different trend. There was a spike in acrolein concentrations each evening between 6:00 pm and 10:00 pm. The timing of this spike in concentrations clearly rules out vehicles and photochemistry as potential sources. These acrolein spikes in the evening are believed to arise from wood smoke based on other characteristic tracer chemicals that

showed an identical pattern of concentrations (see "wood smoke derived chemicals" below). It is important to note that these samples were collected during the coldest time of the year to date, so may people may have been using fireplaces or wood stoves for heat. There was a slight increase in acrolein concentrations in the mornings from around 6:00 to 10:00 am which may be the result of vehicle emissions, but the increase is very slight relative to the wood smoke derived acrolein.

Two small intercomparison projects were conducted to identify the source of this difference. The first of which was side-by-side sampling between the canister method and the mist chamber method conducted at 06:00 on July 17, 2006. Mike Poore from the MLD division collected three canister samples at the same time that two mist chamber samples were collected. The two mist chamber samples did not have detectable concentrations of acrolein, thus the concentration is below the minimum detectable limit of 54 ng/m^3 in this sampling episode. The concentrations reported from the canister samples were reported as 950 and 1300 ng/m^3. This showed that there are real differences between the two sampling method.

The second test was a gas-phase spike of mist chamber from a pressurized canister with a known amount of acrolein in the gas phase. This spike-recovery experiment was conducted twice with one spike being conducted on January 8, 2007 at 10:00 and the second spike being conducted on January 9, 2007 at 14:00. The samples were analyzed and the data reported to William Vance of the ARB before the amount of the chemical spike was revealed. Therefore, the experiment was a blind experiment. The mass of acrolein added to the mist chamber was calculated to be 44.9 ng for the first sample and 24.6 ng for the second sample. The mass of acrolein reported to have been added to the mist chambers was 551 ng and 525 ng. Once again, the measured value significantly deviated from the reported mass added. This is puzzling since gas-phase spikes of the mist chamber method (see mass balance experiments) have performed well. The source of the discrepancy is still unknown after these tests, but it is clear that there are significant differences between sampling methods.

Comparisons with acrolein concentrations in the literature are complicated by the fact that there are very few reliable measurements of acrolein in ambient air samples. Many of the common carbonyl methods, such as DNPH (31-33), have been proven unreliable for acrolein (37) or they lack the sensitivity for the quantification of ambient concentrations (43). A review of the literature shows that the concentrations observed in this research are comparable or lower than previous research projects. The outdoor acrolein concentrations determined in Seaman et al (44) in Placer County averaged 200 ng/m^3 in the morning and 350 ng/m^3 in the evening. These concentrations are fairly comparable, albeit a little higher, than the concentrations observed in this study. That research showed a very significant geographic difference in acrolein concentrations with ambient concentrations in the LA basin being 4 to 6 times higher than in Placer County. The Seaman et al research utilized the exact same analytical methods as employed in this research project. Concentrations reported in Roseville, Salt Point, CA and Lassen National Park, CA were reported to be 290 ng/m^3, 56 ng/m^3 and 89 ng/m^3 respectively, which are comparable to the range of values observed here (41). In particular, the low concentrations observed on the coast were comparable to the Putah Creek control site when there was rapid transport from the ocean based on HYSPLIT trajectories. Destaillats et al (45) quantified acrolein at toll booths in the San Francisco Bay Area and reported concentrations ranging from 31 to 140 ng/m^3 which are fairly comparable to the observed concentrations in this study. A modeling study by Morello-Frosch et al (18) predicted median ambient acrolein concentrations in California to be 360 ng/m^3 based on toxic emission inventories and a model

derived from the EPA's Human Exposure Model. While there are great uncertainties ins this type pf modeling, from the accuracy of the emissions inventory to the average climatic conditions, it does provide an estimate that is within a factor of 10 as the concentrations observed in this study. This study also predicted that acrolein was the greatest non-cancer health risk from organic pollutants in California.

The California Air Resources Board's Monitoring and Laboratory Division routinely determines acrolein concentrations at the same site using the EPA TO-15 method, which collects the sample air in a stainless steel canister followed by analysis by GC/MS. The mean concentrations recorded at the site were 985 ng/m^3 in 2005 and 1,240 ng/m^3 in 2006 with a detection limit of 0.3 ppbv (690 ng/m^3)(46). Most of the reported values are within a factor of 2 of the reported minimum detection limit where quantification is often difficult. The other interesting observation is that the reported acrolein concentrations from around the state had an average of 0.55 ppbv (1,260 ng/m^3) and a range from 0.45 ppb to 0.75 ppb, which seems rather consistent despite varied sample locations.

Another recent study showed a median outdoor concentration of 0.46 μg/m^3 (47), but the median value is close to the reported limit of detection of 0.14 μg/m^3 (40) and only 68% of the outdoor samples were above the detection limit (47). This method, which employs DNSH derivatization, was shown to give inconsistent results for ambient acrolein determination during a recent comparison between the DNSH passive samplers, OSHA method 52 and the mist chamber method in Buffalo, NY. (48). Also, the DNSH improves the sensitivity of the analysis by attaching a more readily detectable functional group to the molecule, but the derivatization functional group is the same as DNPH so the same instability problems observed for DNPH may also occur for DNSH.

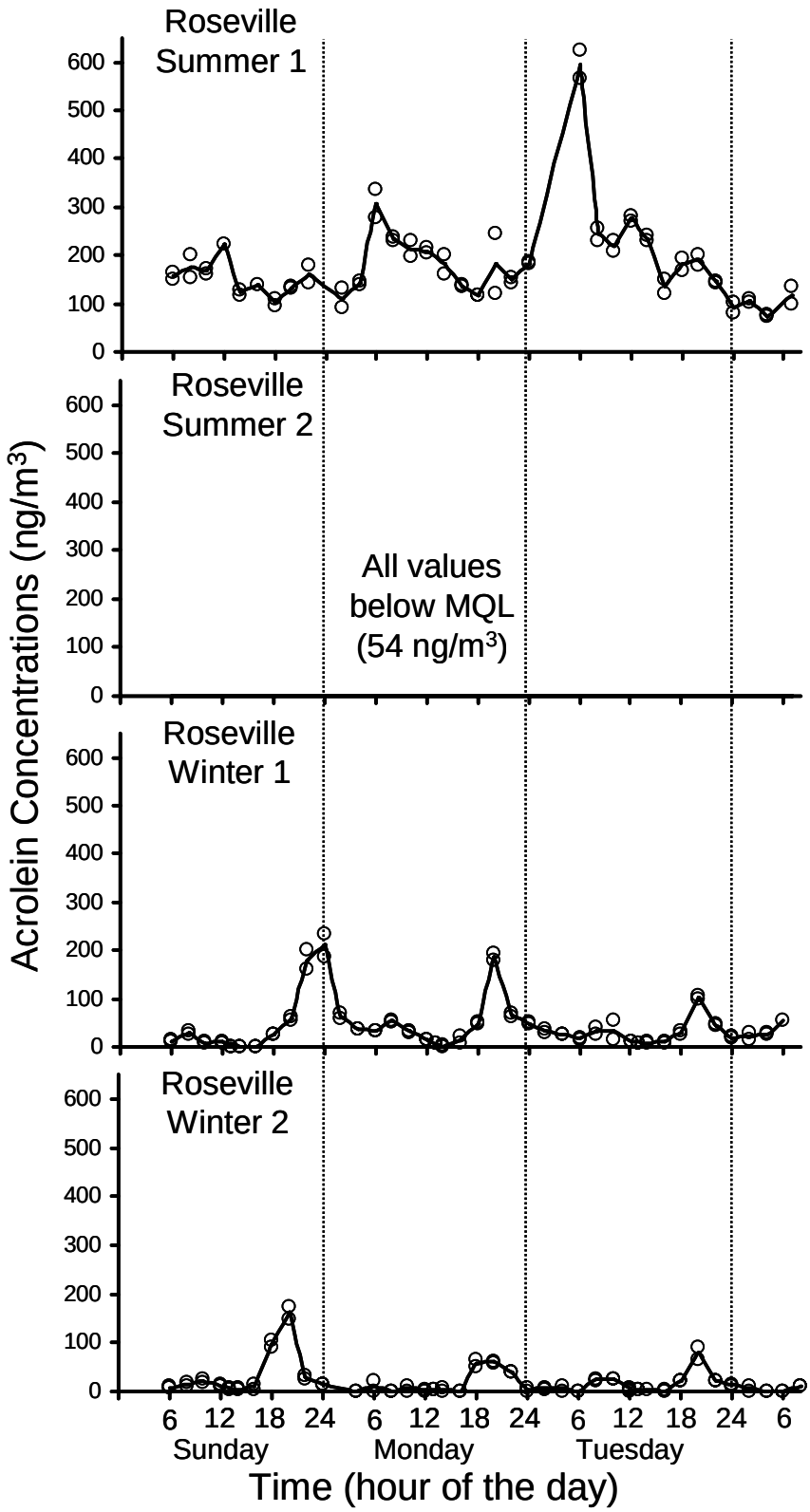


Figure 11. Concentrations of acrolein during the four Roseville sampling episodes. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 11.6, 26.4, 6.3 and 6.6 ng/m^3 respectively.

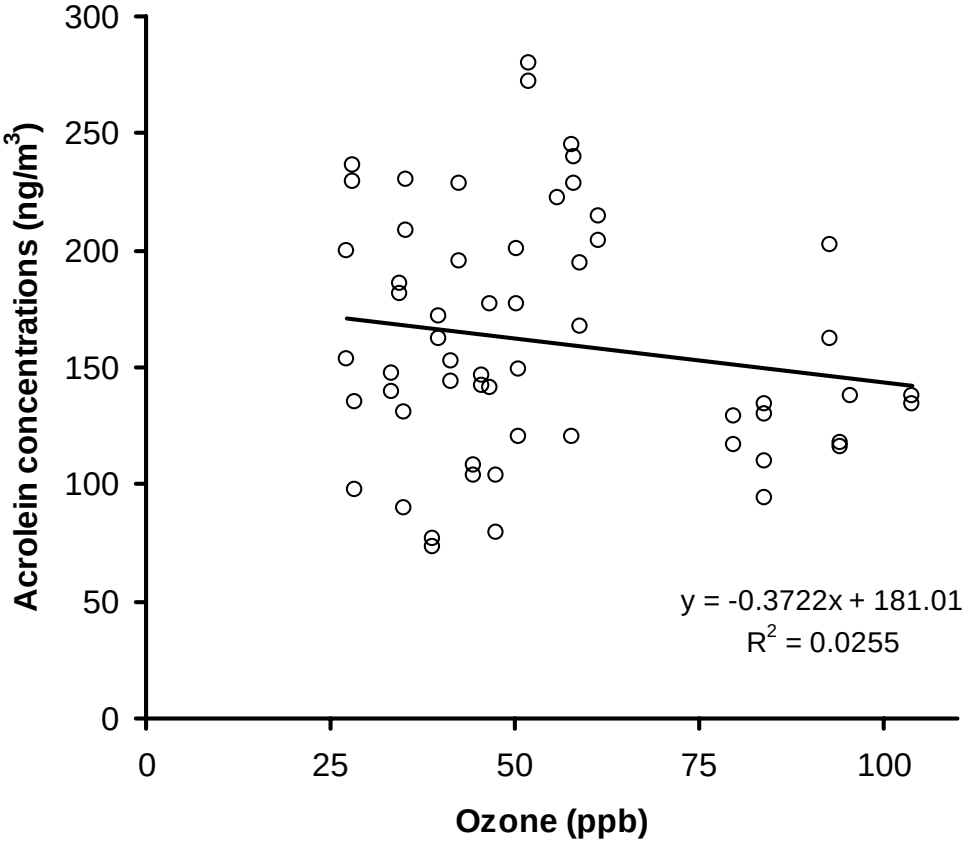


Figure 12. Correlation between ambient ozone concentrations and acrolein for the summer sampling episode with detectable acrolein concentrations. The results show no correlation between these two chemicals. The slope of the regression is negative, which suggest a negative relationship if a statistical relationship did exist.

Photochemically-derived chemicals:

Higher concentrations of photochemically derived compounds were expected in the summer due to the high ozone concentrations at the site. However, most of the chemicals did not have temporal or seasonal changes in concentrations that correlated with ozone concentrations. The chemical that best exemplifies a photochemically-derived origin group is glyoxal ($C_2H_2O_2$) which showed a very regular diurnal cycle in summer (Figure 13) that matches the diurnal cycle in ozone. Furthermore, the concentrations of glyoxal were considerably lower in winter when temperatures and ozone concentrations were lower. The glyoxal concentrations correlated reasonably well (R^2 = 0.61) with ambient ozone concentrations (Figure 14). Although the presence of a correlation does not prove a causal relationship, it does suggest that atmospheric oxidation can generate glyoxal. The lack of significant concentrations of glyoxal in winter eliminates vehicle emissions as a major source since the vehicle traffic did not change between the seasons. However, vehicles are known to produce glyoxal.

Another chemical that follows a similar diurnal cycle in the summer is glycolaldehyde (Figure 15). Glycolaldehyde is a difficult chemical to quantify due to its sometimes erratic calibration curves. Only two of the sampling episode had field-prepared calibration curves that were acceptable and allowed for quantification during those sampling episodes. Like glyoxal, the concentrations of glycolaldehyde were much higher in the summer than the winter and there was a clear diurnal cycle with a peak in day near noon. Unlike glyoxal, the glycolaldehyde had a much narrower time interval over which the high concentrations were observed, which was typically between 10:00 to 12:00. While glycolaldehyde probably came from photochemical sources, there was another potential source worth mentioning. There were many Asian restaurants in the shopping plaza to the south and cooking oil could be smelled during some of the sample collections, so fry cooking may contribute to the narrow glycolaldehyde peak. However, the fry cooking hypothesis is refuted by the low concentrations of glycolaldehyde in winter when fry cooking could be smelled during sample collection (see field log in Appendix 5). Therefore, fry cooking cannot be the causal mechanism by itself and thus it appears that photochemistry is the source of this compound as well.

Acrolein, unlike glyoxal and glycolaldehyde, showed no diurnal cycle with a peak concentration in the middle of the day. Therefore, it would appear that photochemical processes were not a major contributor to ambient acrolein concentrations during this study. The lack of acrolein correlation with ambient ozone concentrations likewise argues against a photochemical source of acrolein being the dominant source.

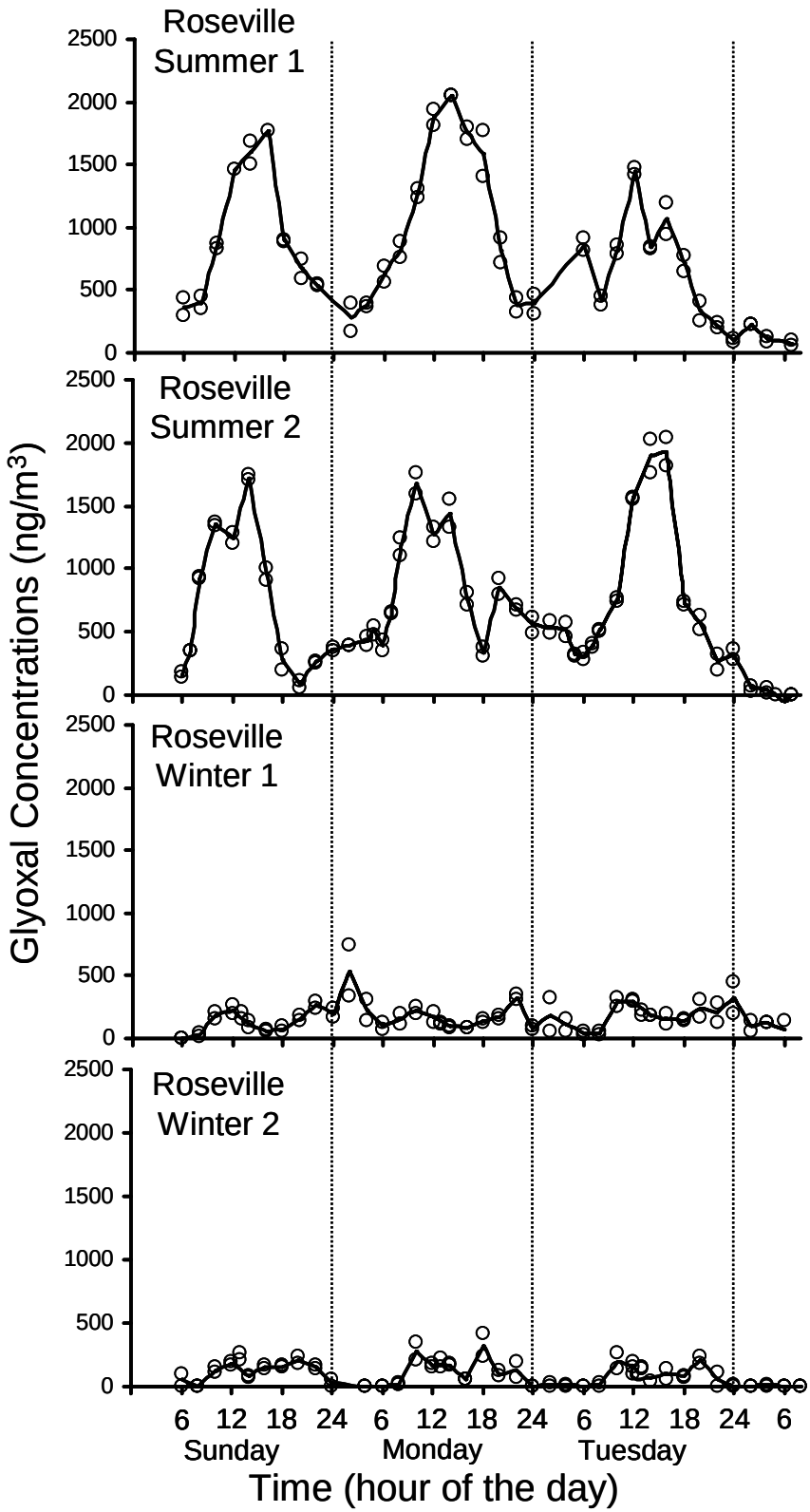


Figure 13. Concentration of glyoxal (ng/m^3) in Roseville, CA. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 133, 95, 110 and 80 ng/m^3, respectively.

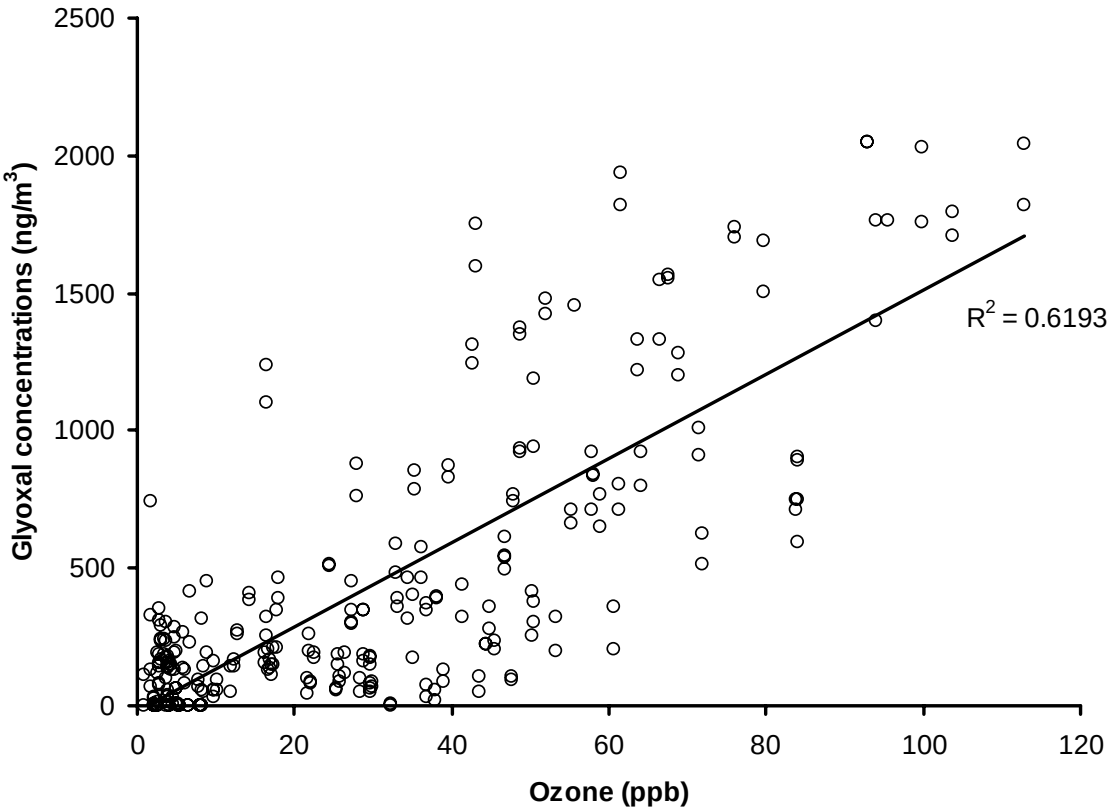


Figure 14. Correlation between ozone concentrations and ambient glyoxal concentrations for the summer and winter sampling episodes. Glyoxal was the chemical that showed the strongest correlation with ozone of all the chemicals quantified in this study.

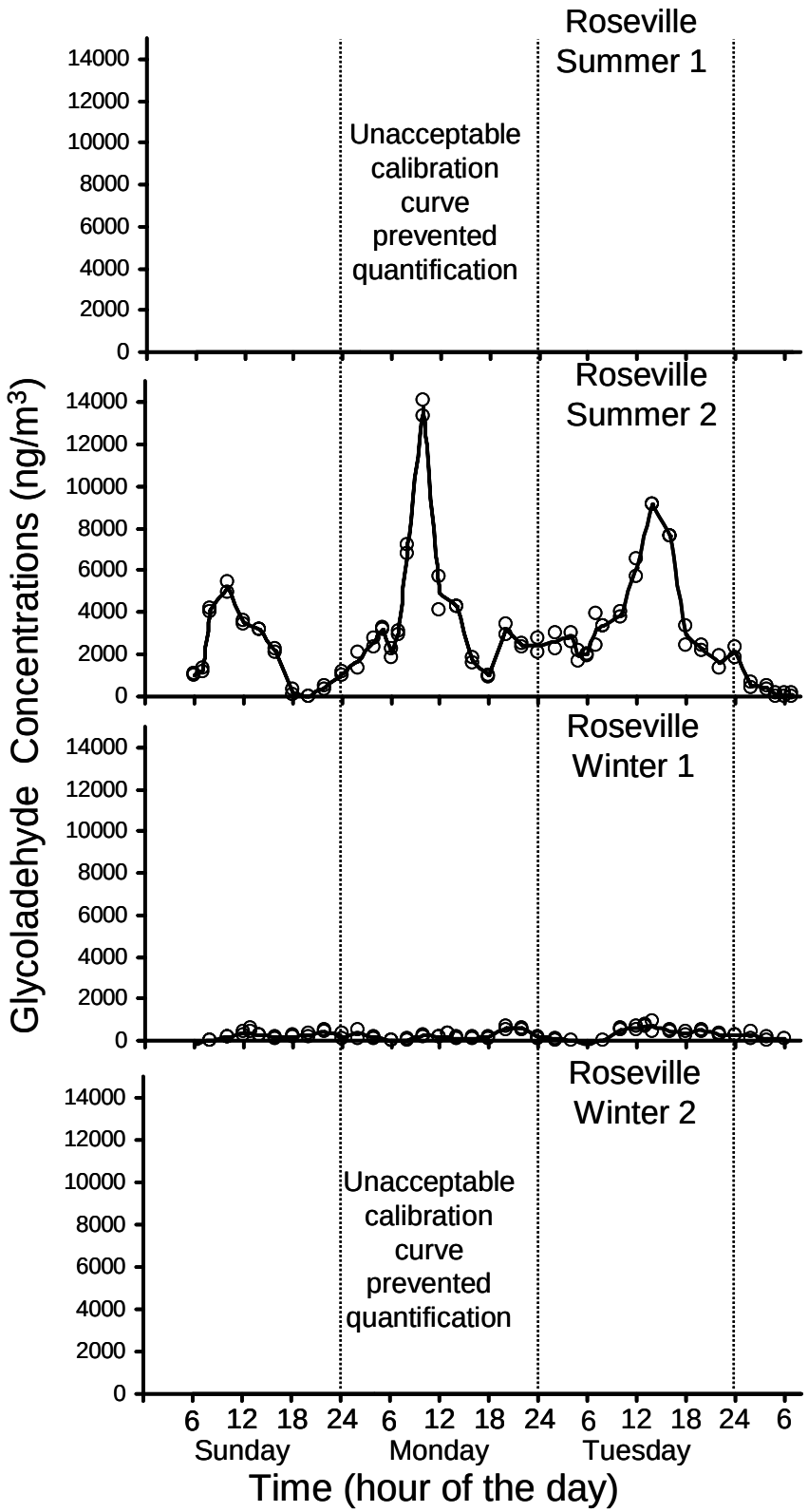


Figure 15. Concentrations of glycolaldehyde during the two sampling episodes with acceptable calibration curves that allowed for analyte quantification. The MDLs for the summer 2 and winter 1 sampling episodes were 698 and 60 ng/m^3, respectively.

Wood Smoke Derived Chemicals:

The next group of chemicals that had an easily identified source were the chemicals that were the result of wood smoke. The winter sampling episodes were conducted during the coldest weather of the year to date and the ambient temperature fell below zero. As a result, people may have been using fireplaces and wood stoves for heat during the cold period.

The best carbonyl tracer that we quantified for the presence of wood smoke is 2–furaldehyde. The diurnal and seasonal variation in this chemical is striking; there was very little furaldehyde during the summer and the winter sampling episodes showed a very high spike in furaldehyde concentrations every evening from about 8:00 pm to 12:00 pm (Figure 16). This time period matches the time in the evening people may be using their fireplaces. This pattern clearly does not correlate with traffic patterns or ozone concentrations. Furaldehyde was regularly detected in the summer, but the concentrations were insignificant compared to the winter concentrations.

The presence of a strong tracer of wood smoke combined with a regular spike in concentrations in the evening each day in winter allows other chemicals that follow the same winter time pattern to be grouped into the "suspected wood smoke source" category. The number of these chemicals is quite large since wood smoke emits a lot of different compounds. However, many of these chemicals were not regularly detected enough times to make for reasonable graphs, but the full data is presented in the attached raw data file accompanying this report (see attached Microsoft Excel file). The chemicals that followed the same temporal pattern in winter were methylglyoxal (Figure 17), 2,3–butanedione (Figure 18) and 1,4–benzoquinone (Figure 19). Both methylglyoxal and 2,3–butanedione have additional summertime sources that will be discusses in the "Sierra Transported Chemicals" section below. All of these sources "suspected wood smoke" chemicals showed strong correlations with 2–furaldehyde (Figure 20) which is good evidence that they came from the same source. The tolualdehydes showed increased concentrations in the evening that temporally matched the 2-furaldehyde, but they also had increased concentrations during the day that suggest they may arise from more than one source.

The strong wood smoke tracer also allowed the identification of the winter time acrolein source. These acrolein temporal trends in winter match the 2-furaldehyde temporal trends with a spike in concentration every evening at the same time. The correlation between 2-furaldehyde and acrolein showed a very strong correlation between the two chemicals with an R^2 of 0.88 (Figure 21). This provides very strong evidence that the source of the acrolein is the same source as the 2–furaldehyde, namely biomass burning. Given the location of the sampling station in an urban area and the diurnal pattern in the chemical concentration, it appears that the source of these chemicals is wood smoke from residential fireplaces and wood stoves in particular.

Biomass combustion is a well documented source of acrolein (9-14), so this result is hardly unexpected that wood smoke would contribute to ambient acrolein concentrations. However, the magnitude of the wood smoke contribution is particularly important since this site was deliberately located near Interstate 80 and two very busy surface streets in an effort to track vehicle emissions. The winter time acrolein concentrations do not correlate with traffic or ozone, which basically eliminates vehicles as being the dominant acrolein source during the winter at a site designed to assess vehicle emissions. The spike in concentrations occurred in the evening after sunset, so that further eliminates photochemistry or oxidation of 1,3-butadiene as a possible

source. Therefore, we must conclude that biomass combustion is the most likely source of the winter time acrolein and that biomass combustion was the dominant source at this site.

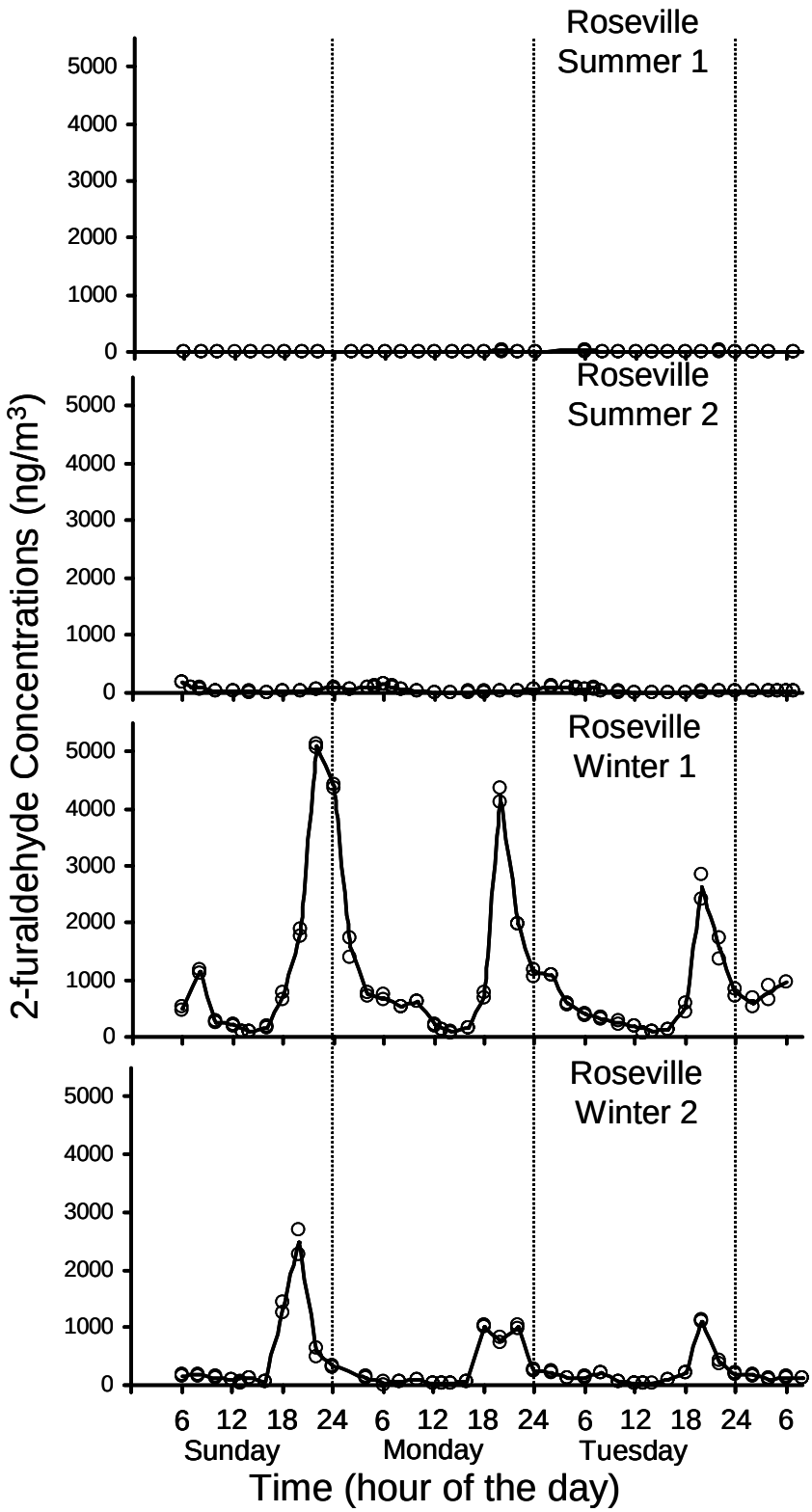


Figure 16. Concentrations of 2−furaldehyde in all four Roseville sampling episodes. 2−furaldehyde is a good tracer of biomass combustion. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 3.5, 6.2, 12.3 and 5.1 ng/m^3, respectively.

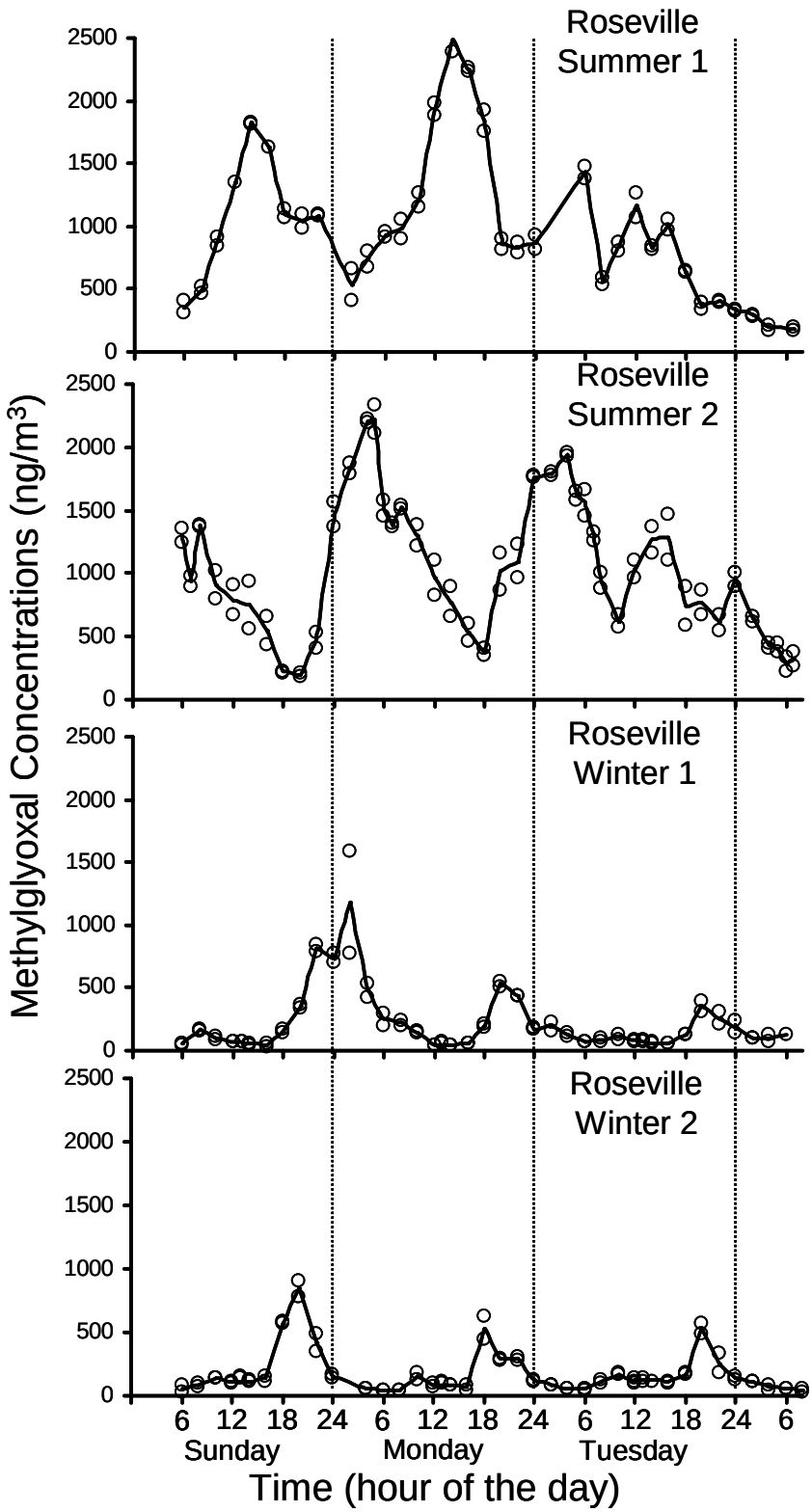


Figure 17. Concentrations of methylglyoxal in summer and winter in Roseville. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 34, 23, 16 and 22 ng/m^3, respectively.

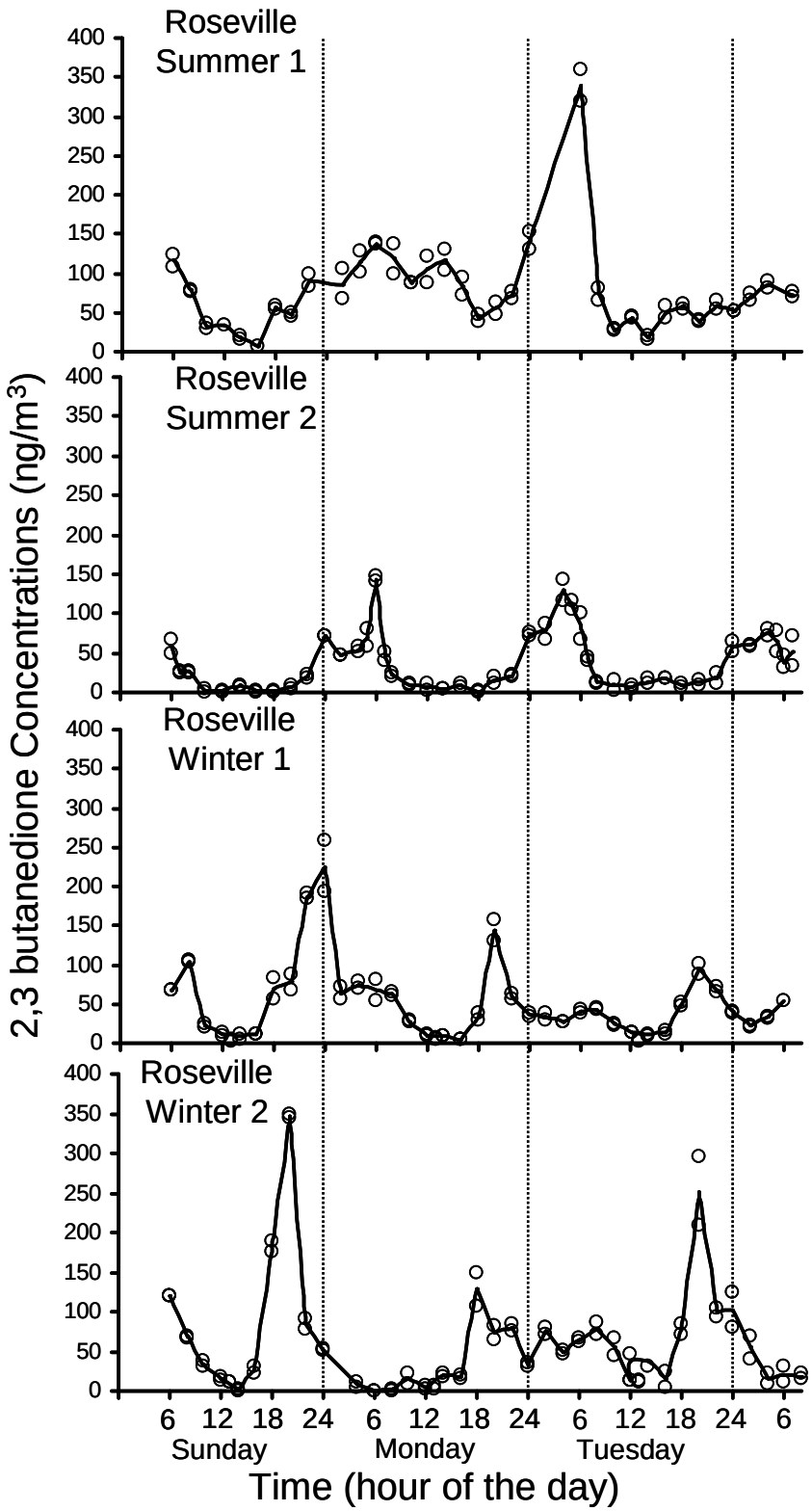


Figure 18. Concentrations of 2,3−butanedione in summer and winter in Roseville. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 12.2, 16.9, 6.0 and 24.2 ng/m^3, respectively.

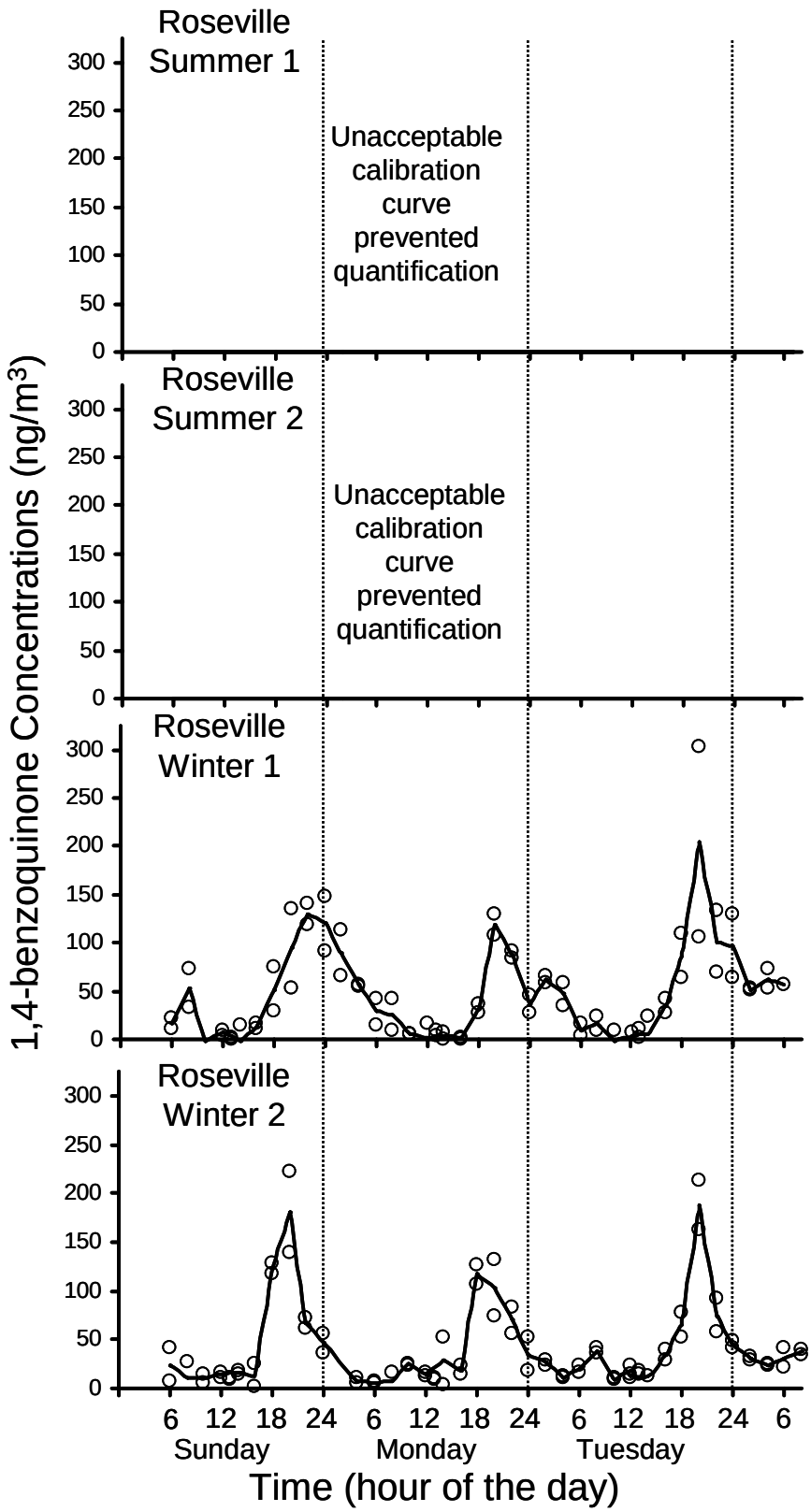


Figure 19. Concentrations of 1,4–benzoquinone in winter in Roseville. The MDLs for the winter 1 and winter 2 sampling episodes were 19.2 and 24.1 ng/m^3, respectively.

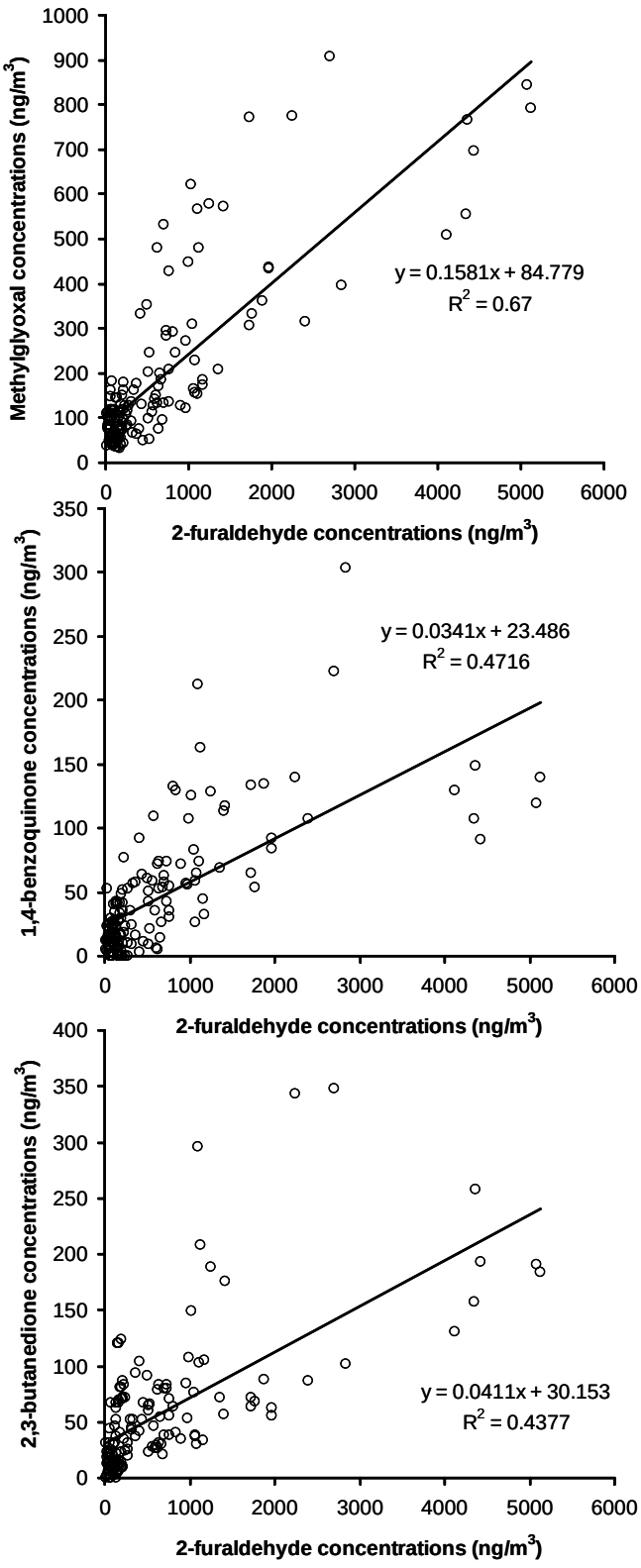


Figure 20. Correlation between the wood smoke tracer of 2-furaldehyde and three suspected wood smoke chemicals for the two winter sampling episodes.

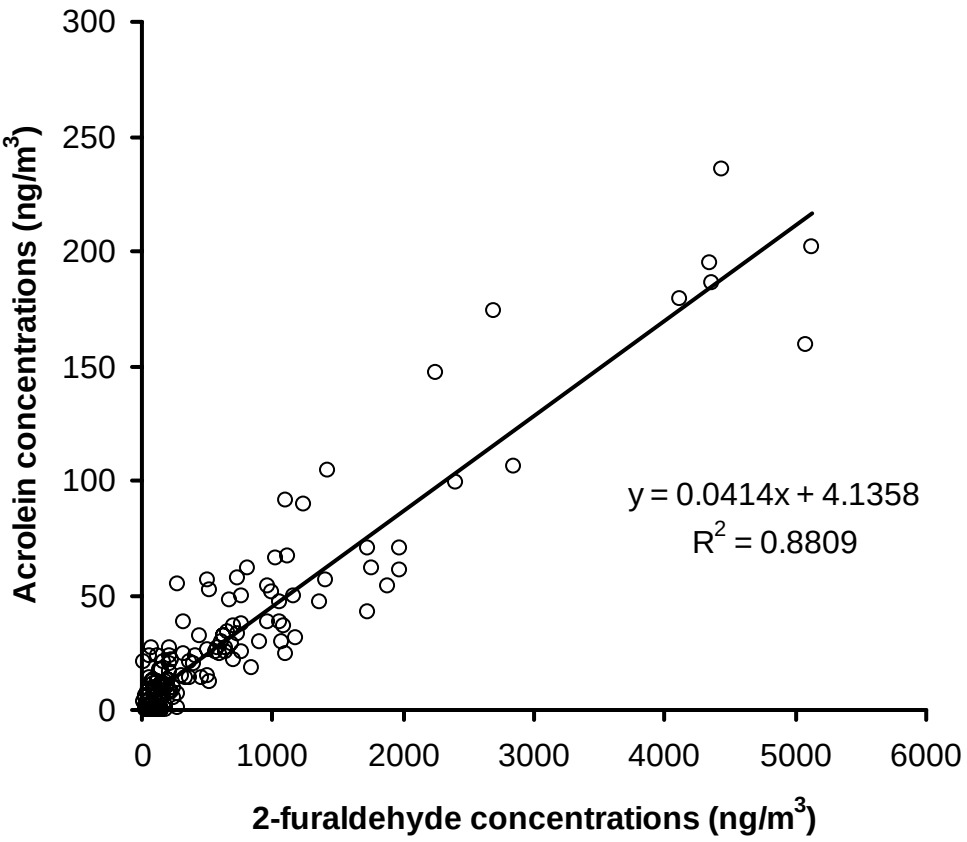


Figure 21. The correlation between the wood smoke tracer of 2−furaldehyde and acrolein for the winter sampling episodes. The very strong correlation provides good evidence that the acrolein source is the same as the 2-furaldehyde source, namely biomass burning and probably residential wood burning.

Chemicals Transported from the Sierra Nevada:

The next class of chemicals observed represent chemicals that are transported from the Sierra Nevada Mountains by a night-time down-slope air flow. The best tracer of these chemicals is pinonaldehyde (Figure 22), which is an oxidation product of α-pinene and other biogenic gases released from pine trees (49). Therefore, this chemical comes from the pine forest of the Sierra Nevada (50). This chemical has couple important attributes. The pinene precursors are only released when the trees are active, thus the emission of pinene dramatically decrease in winter when the trees are dormant. Therefore, we did not expect to observe this chemical in winter and it was not observed. The second attribute of pinonaldehyde is that it is the oxidation product of pinenes(49), so it is a marker of past oxidation that has occurred in the air mass.

The down-slope air flow from the Sierra Nevada Mountains was also readily confirmed by the meteorology at the site. The night-time wind directions between about midnight and 6:00 am were often from the east of the south east (see field notes). The downslope flow is a common occurrence at the site according to Kent Bretwiser, who is the technical administrator of the site.

Given both the rather unique source of pinonaldehyde and supporting meteorology, we can safely assume that chemicals that follow the same temporal pattern as pinonaldehyde probably came from the same source region. This does not mean that all of these chemicals come from biogenic sources, but rather the same source region. There were a large number of chemicals in the "Sierra Transported" group and they showed the strongest diurnal cycles in the summertime chemicals with the exception of glyoxal.

The chemicals that showed the best temporal agreement with pinonaldehyde were 3-methyl-2-butenal (Figure 23) and 2,3–butanedione. 2,3-butanedione was also tracked the wood smoke tracer in the winter, so it has been discussed above. However, during the summer, it follows pinonaldehyde pattern and therefore its suspected source is the Sierra Nevada Mountains. Little is known about 3-methyl-2-butenal, but is appears to be an oxidized biogenic compound.

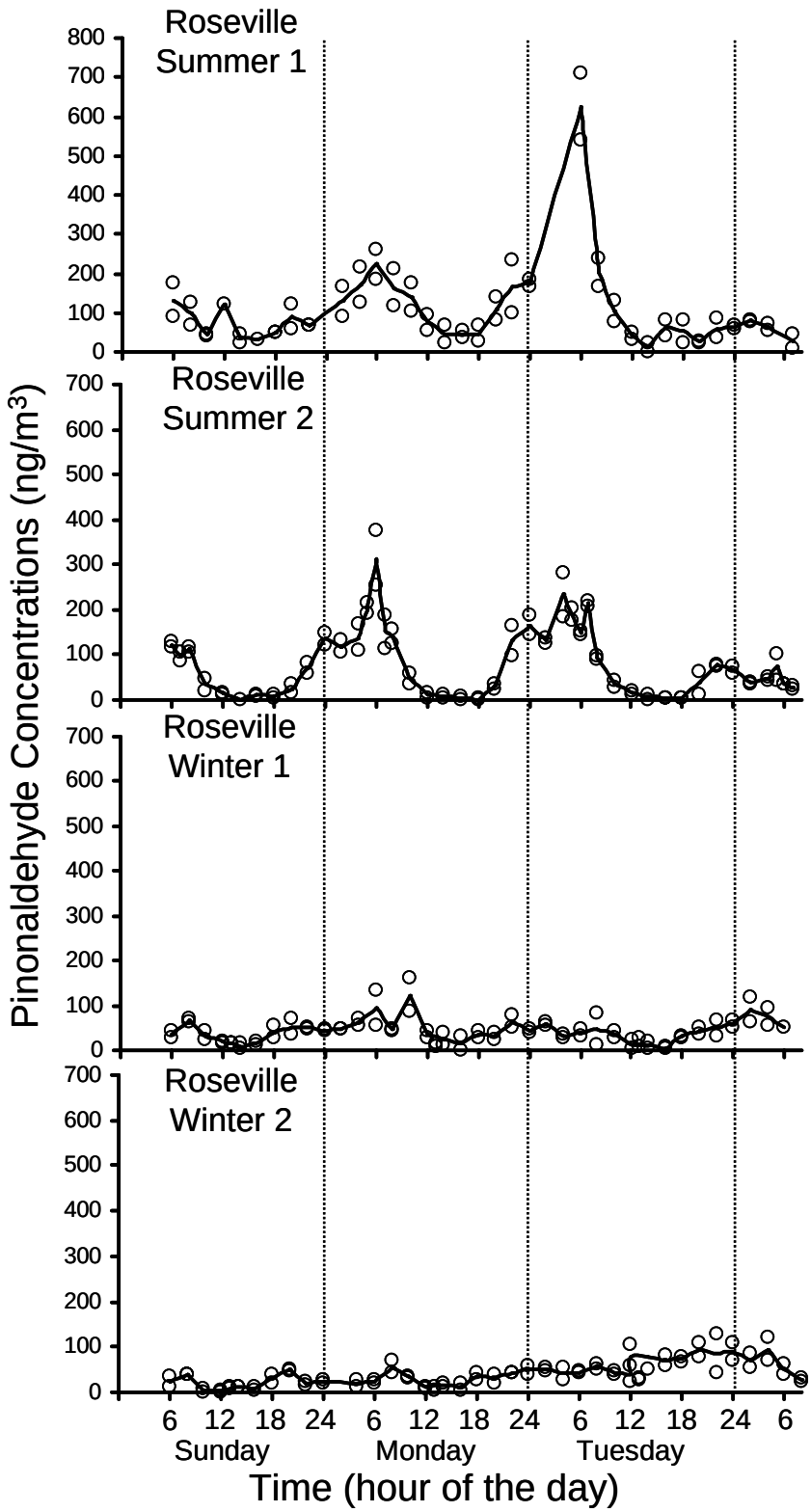


Figure 22. Concentrations of pinonaldehyde, which is a good tracer for pine forest sources, in Roseville. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 9.3, 7.1, 8.1 and 15.8 ng/m^3, respectively.

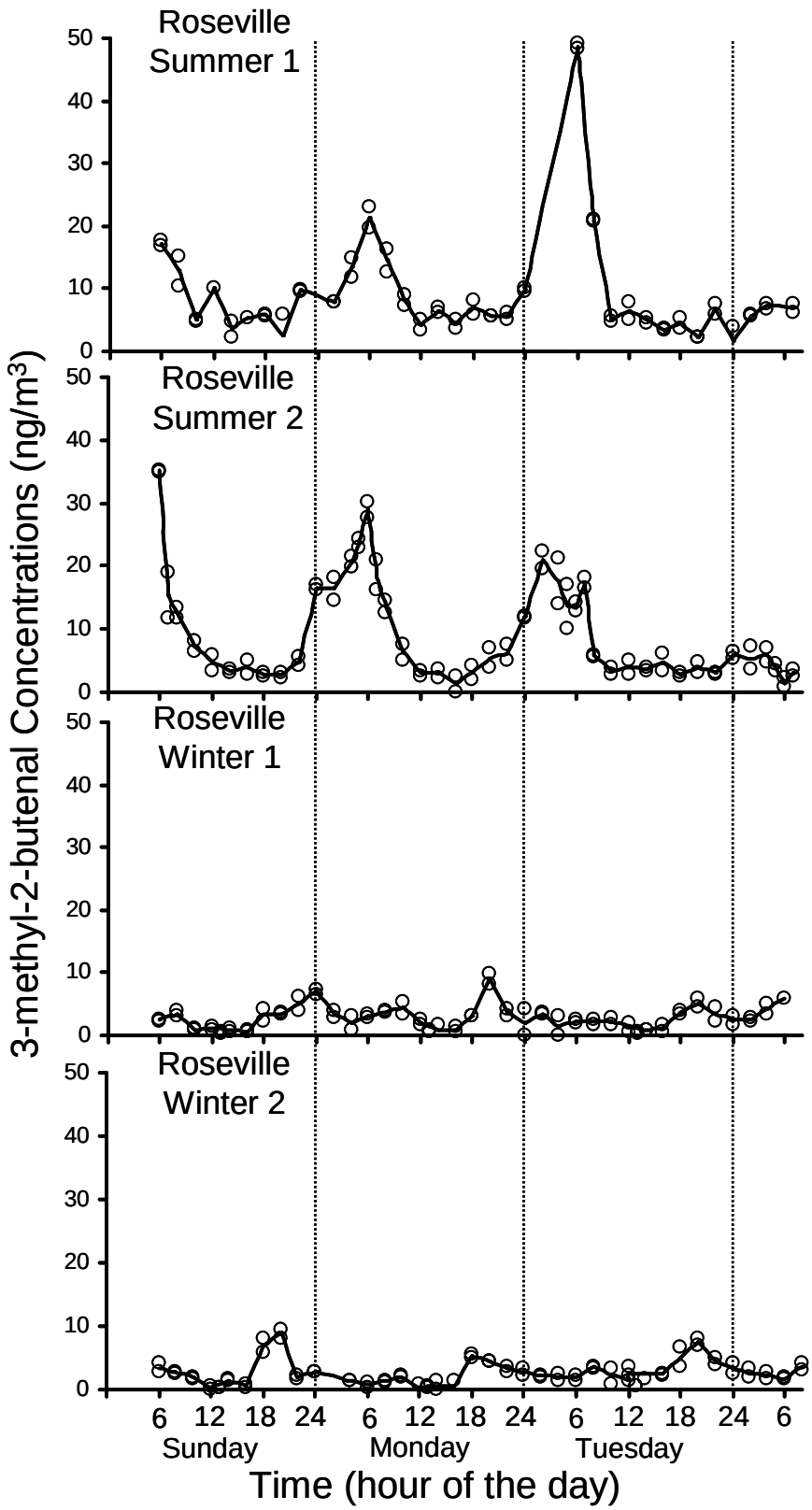


Figure 23. Concentrations of 3-methyl-2-butenal. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 1.8, 3.4, 1.0 and 0.6 ng/m^3, respectively.

Chemicals from Direct Vehicle Emissions:

The last class of chemicals are compounds that are suspected to be directly emitted from vehicles. The ARB site at North Sunrise Blvd was selected to specifically look for emissions from vehicle traffic, so it was a little surprising that relatively few compounds appeared to follow vehicle traffic. Unlike the last two classes of compounds, there is no highly selective tracer for vehicle emissions. Therefore, the chemical was suspected to be a primary vehicle emission if: 1) the compound appeared to have an increase in concentrations between 06:00 and 10:00 on weekdays and 2) the compound is known to be produced by vehicles. The only chemicals that fit these two criteria were the tolualdehydes. There are three isomers of the tolualdehydes, but in our analysis the *meta*- and *ortho*- substituted isomers co-elute on the gas chromatograph column and they could not be separated. These two isomers were then summed and reported as "*m*,*o*-tolualdehyde" (Figure 24). The *para*- substituted isomer was chromatographically separated from the other two isomers, so it is reported separately as "*p*-tolualdehyde" (Figure 25). Benzaldehyde would also be a good tracer of vehicle traffic (4), but the results between the field replicates were not always consistent, so that chemical is considered suspect and the values, while presented in the full data set, are not presented here.

The emission of the aromatic aldehydes (benzaldehyde, *m,o,p*-tolualdehydes, dimethylbenzaldehyde, etc.) from vehicles was confirmed by two small side projects. The first side project collected samples on roadways from a moving vehicle in traffic (See Appendix 3). Most of the chemicals showed similar concentrations compared to the stationary site with the exceptions of the tolualdehydes which showed higher concentrations in the "on-road" samples. The second side project was to collect emission samples from idling cars (See Appendix 4). These samples showed that the aromatic aldehydes were the most abundant carbonyls emitted. The aromatic aldehydes represented approximately 58 to 72% of the carbonyl mass that was collected and quantified. It should be noted that no attempt was made to quantify formaldehyde, acetaldehyde and acetone, all of which are frequently reported at the most abundant carbonyls emitted from vehicles. Given the large fraction of aromatic hydrocarbons in gasoline, it would appear that these compounds arose from unburned fuel.

Therefore, the emission data, the "on-road" data and the ambient data are all in agreement that the vehicles seem to be emitting largely aromatic aldehydes. These results are consistent with literature emission estimations that show aromatic aldehydes are emitted by vehicles (3-5). This is not surprising since gasoline contains a considerable fraction of aromatic compounds (51) and vehicle emissions contain aromatic compounds (52, 53).

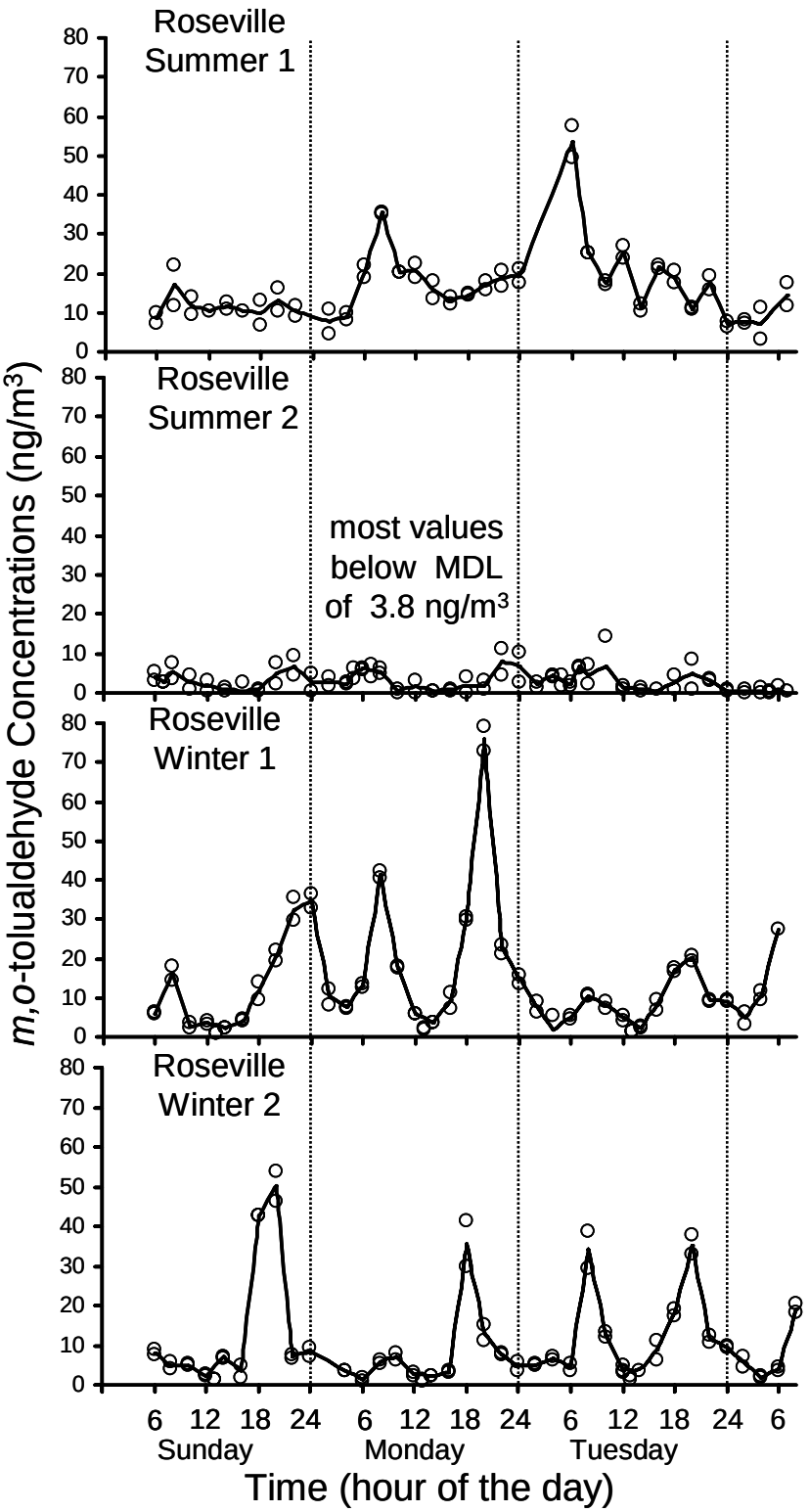


Figure 24. Concentrations of *meta+ortho*-tolualdehyde. These two isomers co-elute on the gas chromatograph and thus could not be separated. The MDLs for *meta+ortho*-tolualdehyde during the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 4.7, 3.8, 1.1 and 2.2 ng/m^3, respectively.

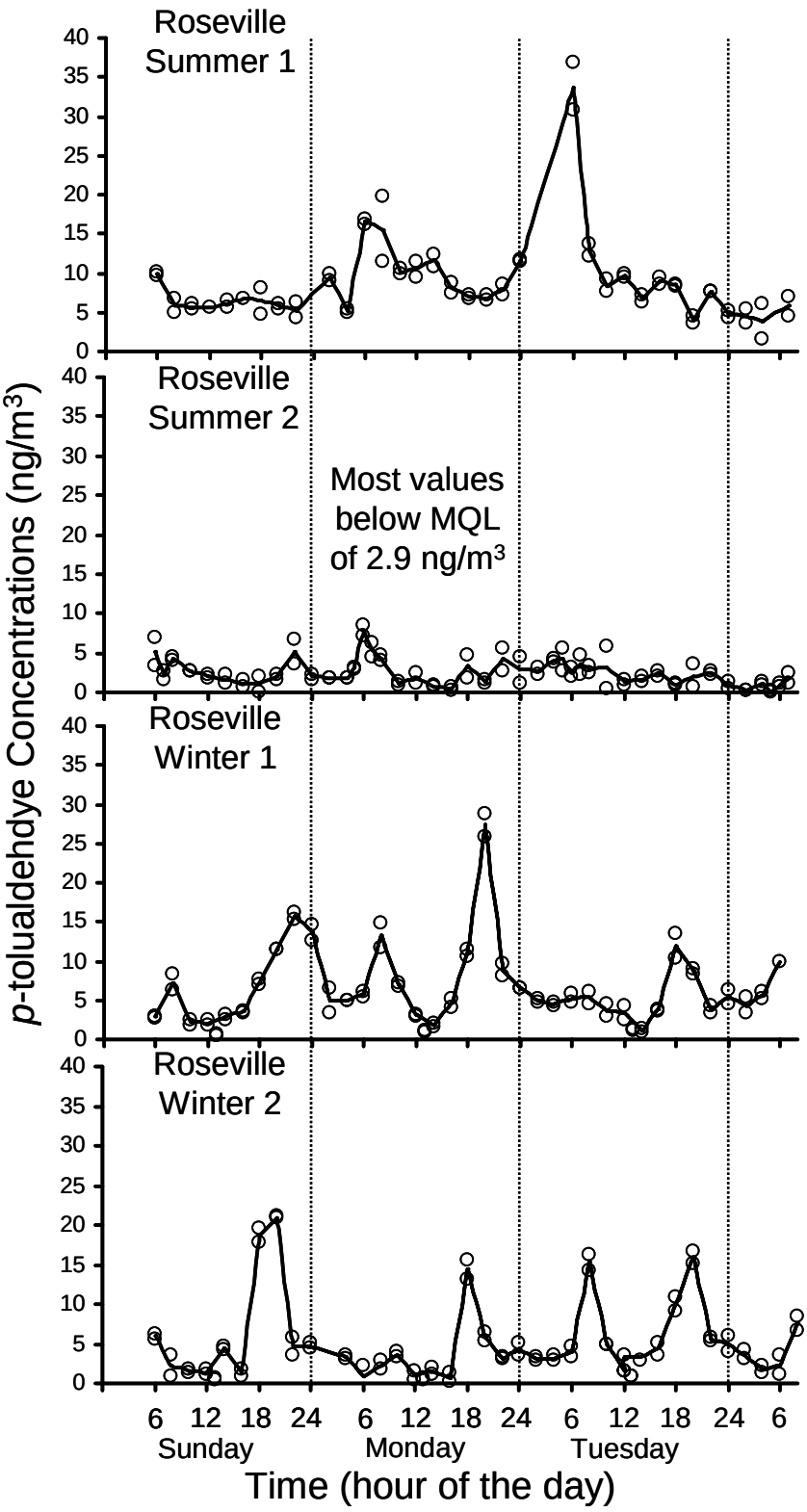


Figure 25. Concentrations of *para*-tolualdehyde. The MDLs for the summer 1, summer 2, winter 1 and winter 2 sampling episodes were 1.7, 1.5, 0.8 and 0.6 ng/m^3, respectively.

Regression Comparisons Between Major Chemical Species:

The preceding interpretation was based on the investigation of linear regressions between the major chemical species and the time series of chemical concentrations. However, space limitations prevented all possible regression comparisons from being presented. Therefore, William Vance prepared condensed graphics that were able to show all the regression comparisons for each of the Roseville sampling episodes (Figures 26 to 29). The second summer sampling in Roseville had a considerable number of non-detected analytes that made correlations more difficult. These figures reinforce the observations in the preceding analysis in that:

1) m+o-tolualdehydes correlated well with p-tolualdehyde. No other chemicals showed a strong correlation with the tolualdehydes.
2) Glyoxal and methylglyoxal correlated well in the summer sampling episodes when their concentration were fairly high.
3) In the second summer sampling, the concentrations of pinonaldehyde and 2-furaldehyde had the best correlation of any chemical against pinonaldehyde, which is a tracer of secondary oxidation from biogenic emissions in conifer forests. This implies some air transport from the Sierra Nevada mountains. There were no good correlations with pinonaldehyde in the winter where the concentrations were lower.
4) In the winter sampling events, acrolein correlated well with furaldehyde, which is known to arise from biomass burning. There are many co-correlations in the winter samples, which implies that many chemicals have the same source. This source appears to be wood smoke based on the high concentrations of 2-furaldehyde (which was much higher than in the summer) and the time series that shows the high concentrations in the early evening when fireplaces were probably being used for home heating on the cold winter nights.

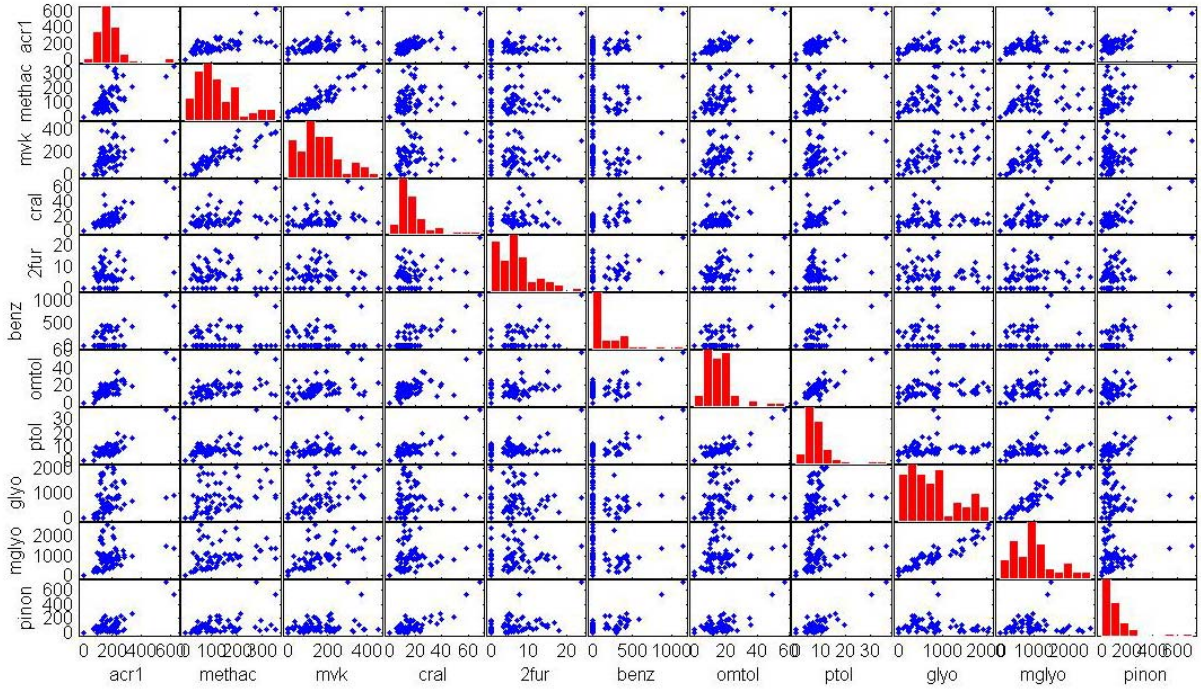


Figure 26. Regression comparisons of the major chemical species during the first summer time Roseville sampling. The chemicals presented are acrolein (acr1), methacrolein (methac), methyl vinyl ketone (mvk), crotonaldehyde (cral), 2-furaldehyde (2fur), benzaldehyde (benz), *o*+*m*-tolualdehyde (omtol), *p*-tolualdehyde (ptol), glyoxal (glyo), methylglyoxal (mglyo) and pinonaldehyde (pinon).

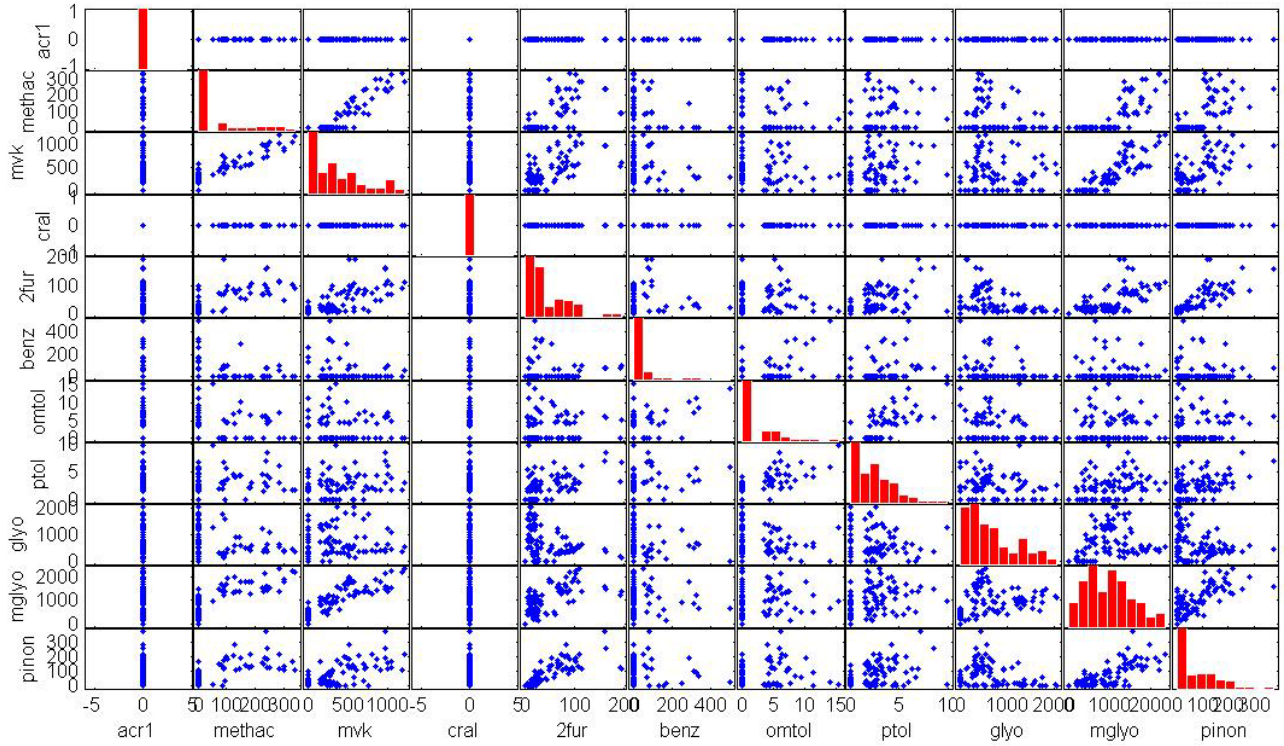


Figure 27. Regression comparisons of the major chemical species during the second summer time Roseville sampling. The chemicals presented are acrolein (acr1), methacrolein (methac), methyl vinyl ketone (mvk), crotonaldehyde (cral), 2-furaldehyde (2fur), benzaldehyde (benz), *o*+*m*-tolualdehyde (omtol), *p*-tolualdehyde (ptol), glyoxal (glyo), methylglyoxal (mglyo) and pinonaldehyde (pinon).

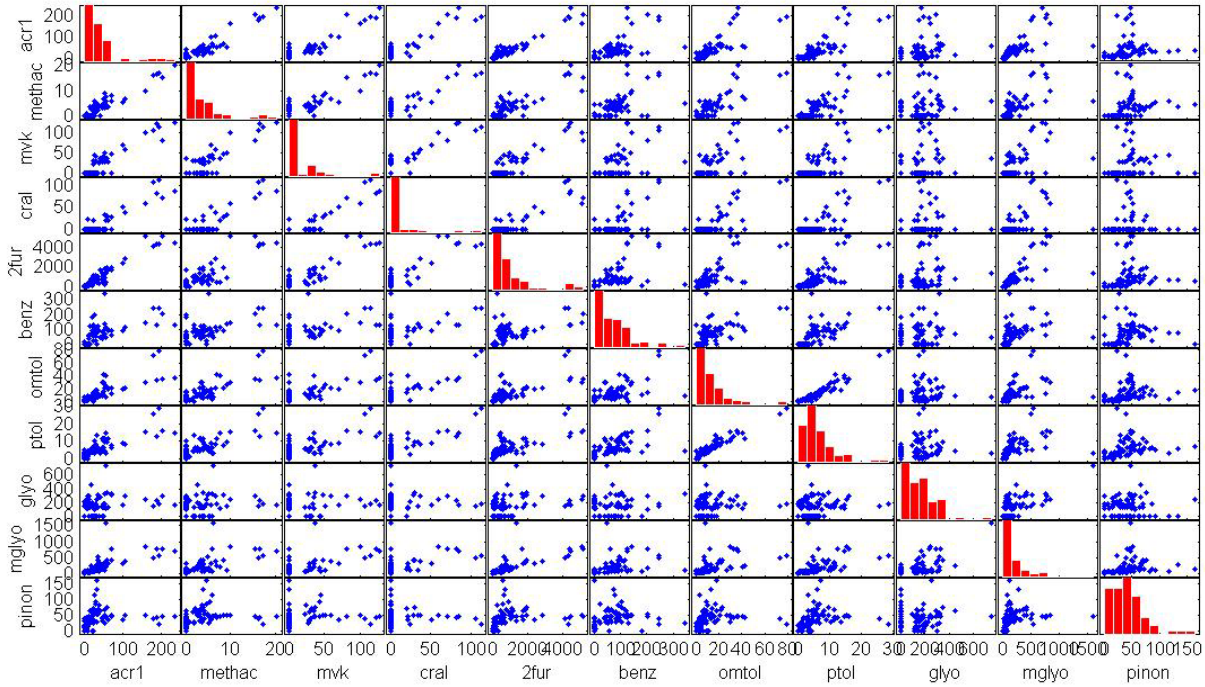


Figure 28. Regression comparisons of the major chemical species during the first winter time Roseville sampling. The chemicals presented are acrolein (acr1), methacrolein (methac), methyl

vinyl ketone (mvk), crotonaldehyde (cral), 2-furaldehyde (2fur), benzaldehyde (benz), *o*+*m*-tolualdehyde (omtol), *p*-tolualdehyde (ptol), glyoxal (glyo), methylglyoxal (mglyo) and pinonaldehyde (pinon).

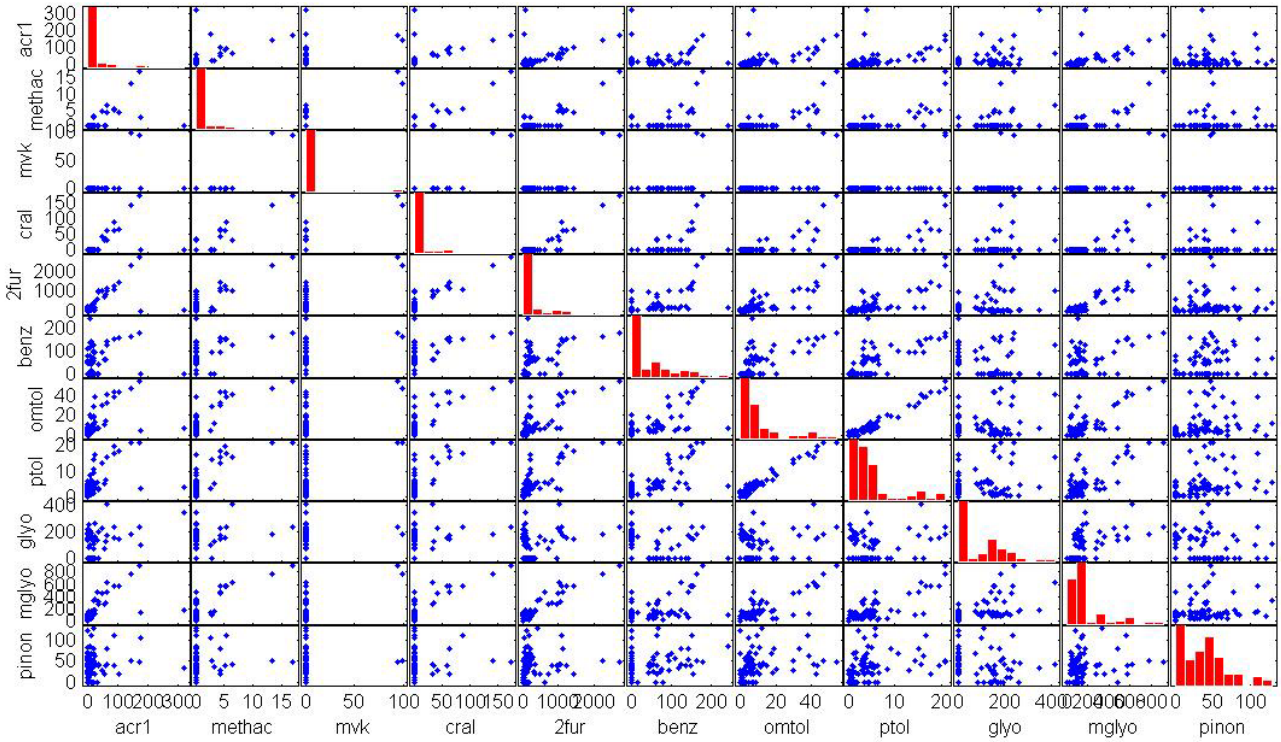


Figure 29. Regression comparisons of the major chemical species during the second winter time Roseville sampling. The chemicals presented are acrolein (acr1), methacrolein (methac), methyl vinyl ketone (mvk), crotonaldehyde (cral), 2-furaldehyde (2fur), benzaldehyde (benz), *o*+*m*-tolualdehyde (omtol), *p*-tolualdehyde (ptol), glyoxal (glyo), methylglyoxal (mglyo) and pinonaldehyde (pinon).

Results from the Summer Putah Creek Control Site:

In addition to the routine sampling at the ARB site on North Sunrise Blvd, there was a single valid sampling episode conducted at Putah Creek, which is a rural area on the west side of the Sacramento Valley. The objective of this site was to determine the regional background of the carbonyls in the absence of local urban emissions. The sampling followed the exact same temporal protocol. The only differences between this sampling episode and the Roseville episodes were: 1) the meteorology was determined at ground level with battery powered instruments; 2) the vacuum pumps were run using a 12V battery and a power inverter; and 3) the standards and samples were stored in an ice chest and returned to the lab on a daily basis.

The meteorology during this sampling episode changed significantly over the three sampling days. The first day started with stable hot summertime pattern where there was and up-stream air flow from the Sacramento Valley during the heat of the day and then a down-creek flow during the cool evening. Over the next two sampling days, the winds became stronger from

the west (from the coast) and there was less Sacramento Valley influence. On the last day, the wind was exclusively from the west and the temperature was much lower.

The acrolein concentrations were largely below the limit of detection except for the first day of sampling that had considerable valley influence at the sampling site (Figure 30). The concentrations on the first day were slightly lower than the first Roseville summer episode. As the sampling time progressed and the meteorology shifted towards a more coastal air mass, the concentrations fell below the limit of detection. The raw peak areas, which are the best estimate of the trends below the MDL, continued to decline over the time period.

Methacrolein was demonstrated to be poorly collected by the mist chamber sampling system, so it is only reported as relative amounts to investigate the fluctuations of the chemical concentrations over time (Figure 30). Methacrolein, like most chemicals at Putah Creek, showed the highest concentrations on the day that had the greatest Sacramento Valley influence. The methacrolein concentrations tended to show an increase in concentrations in the late afternoon, which probably corresponds to photochemical formation of methacrolein from other compounds. This peak was even observed on the cleanest air day that had no valley influence, thus this methacrolein probably arises from the oxidation of biogenic compounds.

The photochemical production of oxidized chemicals at the site was clearly visible in the glyoxal and glycolaldehyde concentrations (Figure 31). Glyoxal showed a very regular diurnal cycle of concentrations were the concentrations peak at approximately 14:00 to 16:00 hours each day. This cycle exactly replicates the glyoxal cycle in Roseville in the summer with both same maximum concentration time and similar absolute concentrations. However, even the glyoxal concentrations declined on the last day of sampling where there was a rapid air flow from the coast. Glycolaldehyde showed a similar pattern with a peak in concentrations also around 14:00 to 16:00 hours each day. The duplicated measurements of glycolaldehyde were sometimes less consistent than glyoxal, and one high outlier was removed from the data set, but the trends are very solid. Therefore, we were clearly able to observe photochemical formation of some aldehydes at our control site in the absence of any local emissions. Furthermore, these chemicals also showed the lowest amount of change was the meteorology shifted, which implies that they come from oxidation of biogenic compounds.

The last two chemicals that showed diurnal cycles worth mentioning are 2-furaldehyde and methylglyoxal (Figure 32). The concentrations of furaldehyde were low during the period, but there was a slight increase in the concentration in the early morning. In contrast, the concentrations of furaldehyde in the second summer sampling episode at Roseville were much higher and showed a definite diurnal cycle that matched with the tracers of Sierra transport. The first Roseville sampling episode had similar concentrations and very little variation. Methylglyoxal, which can arise from primary emissions or secondary atmospheric transformations, showed peak concentrations in the late afternoon like glyoxal and glycolaldehyde. Therefore, these peaks appear to be the result of photochemical production of methylglyoxal. However, like most other chemicals, the concentrations steadily fell during the sampling episode as the winds shifted towards a coastal air mass and away from Sacramento Valley influence. Therefore, there seems to be a background of methylglyoxal in the Sacramento Valley air that is then augmented with photochemical formation in the late afternoon.

One group of chemicals that are notable in their absence were the aromatic aldehydes and the three tolualdehydes in particular. The tolualdehydes were some of the only chemicals that could reasonably be inferred to arise from direct vehicle emissions in the Roseville sampling episode (see “Chemicals from Direct Vehicle Emissions” on page 45) and the source emission

samples (Appendix 4). While they were consistently detected at Roseville, they were never detected at the Putah Creek control site. This result helps to confirm that 1) the Putah Creek site was not impacted by primary vehicle emissions and 2) the tolualdehydes detected in Roseville are not the result of natural background, and thus are more likely to result from an anthropogenic source.

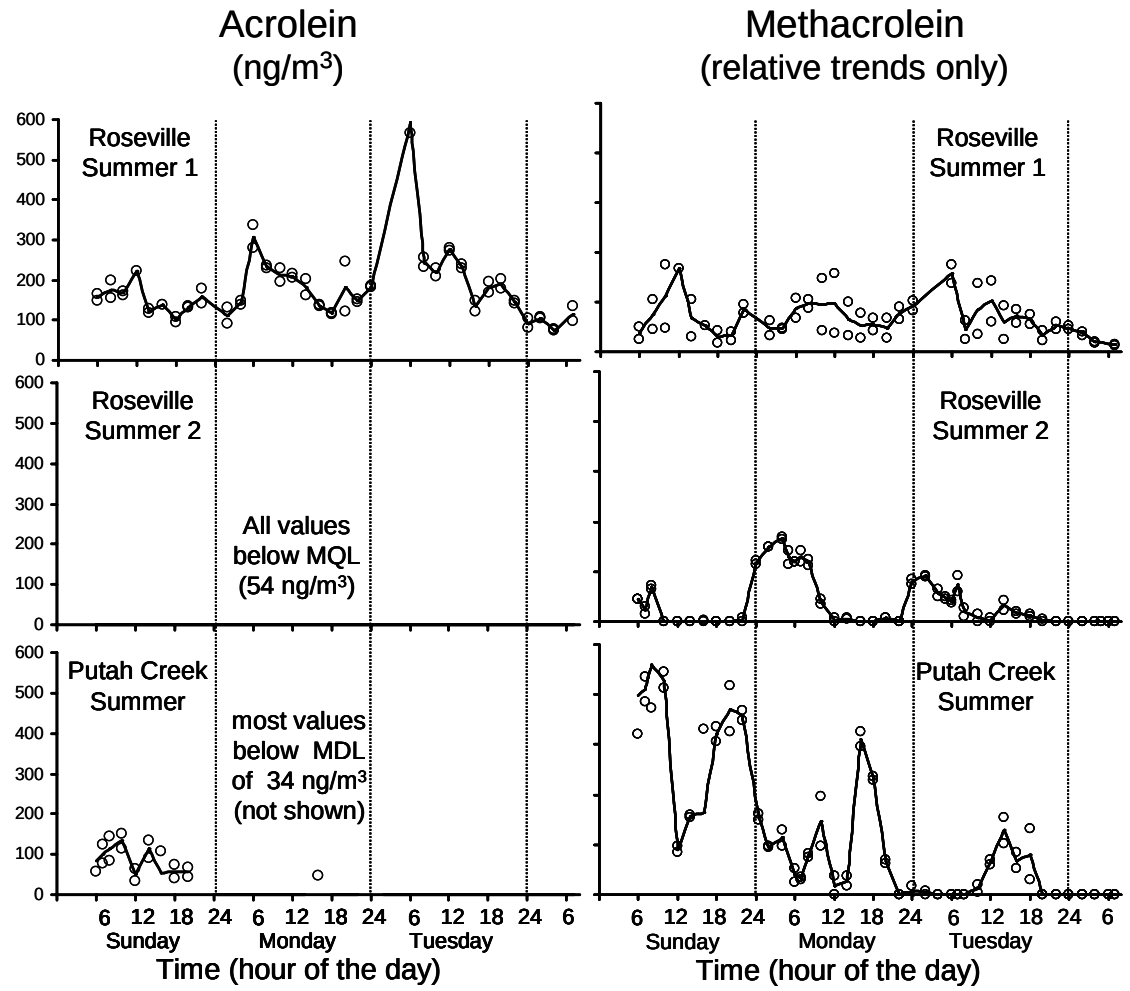


Figure 30. Concentrations of acrolein and methacrolein at the control site at Putah Creek compared to the primary study site in Roseville. Note that the spike-recovery trials for methacrolein showed a poor recovery for methacrolein and thus no quantification was attempted. The methacrolein graph should only be used to show the relative temporal variation of methacrolein.

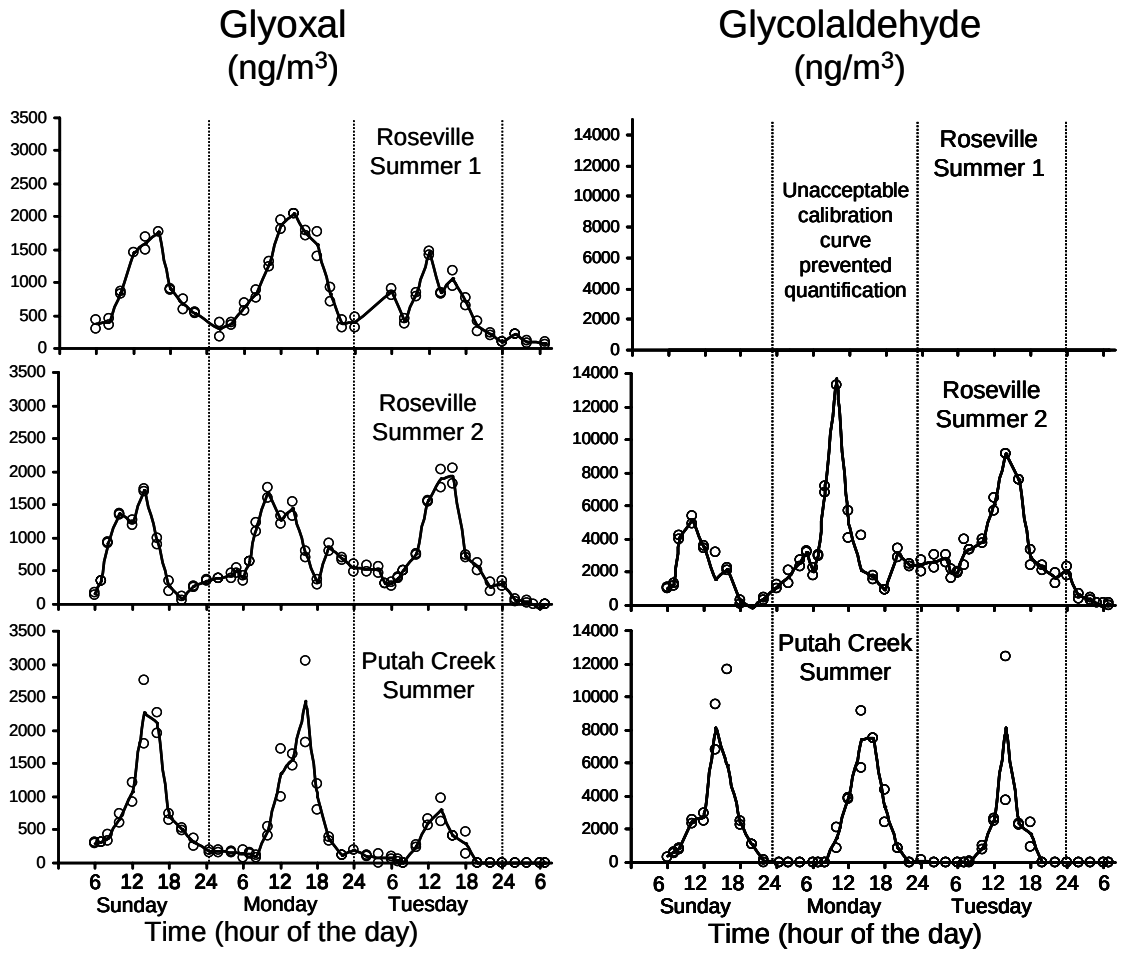


Figure 31. Concentrations of glyoxal and glycolaldehyde at the control site at Putah Creek compared to the primary study site in Roseville. Note that one high outlier was eliminated from both the Putah Creek and Roseville summer 2 graphs.

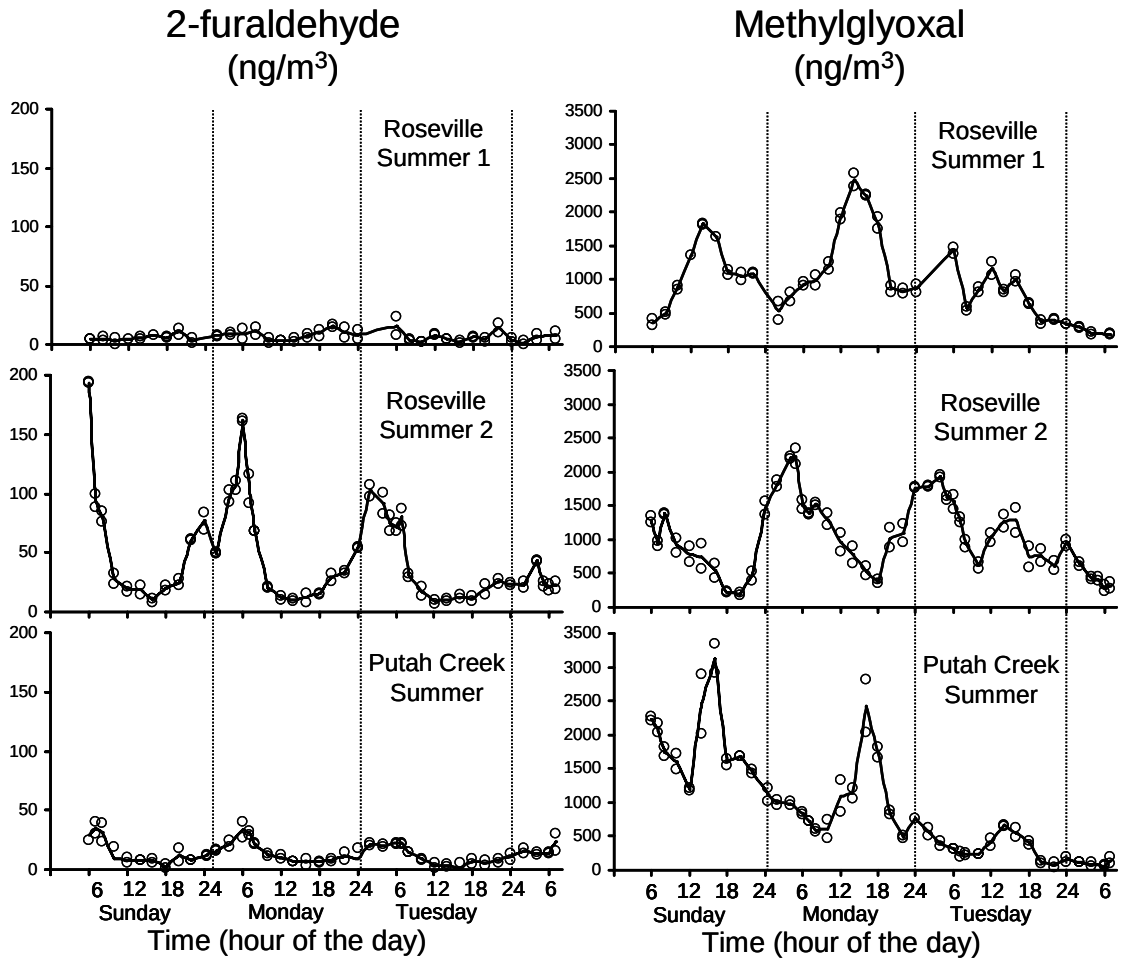


Figure 32. Concentrations of 2-furaldehyde and methylglyoxal at the control site at Putah Creek compared to the primary study site in Roseville.

Discussion:

The objective of this research was to determine the ambient acrolein concentrations at a site that was expected to be impacted by vehicles. The underlying expectation was the acrolein concentrations would be related to traffic patterns over the course of a day and between weekend days and week days. The results did not agree with these expectations and they show that acrolein concentrations at Roseville are dominated by wood smoke in the winter and by transport from the Sierra Nevada Mountains in the summer.

The research identified four different potential sources of carbonyls at Roseville. These potential sources and the criteria used to assign them to a potential source group were:

1) Photochemically-derived chemicals. These were chemicals that showed a diurnal cycle in the summer with the highest concentrations in the afternoon when ozone concentrations are the highest. The lack of a strong diurnal cycle in winter also helps to identify these chemicals as dependent on atmospheric transformation rather than direct emission.
2) Wood smoke derived chemicals: These are chemicals that show a strong correlation with a biomass-burning tracer of 2-furaldehyde. A strong agreement in temporal trends was also required to list a chemical as a potential wood smoke source. Since there was no appreciable use of fireplaces/wood stoves in the summer, the lack of these chemicals in the summertime samples helps to confirm wood smoke as the most probable source. Emission source samples confirmed 2-furaldehyde as the best tracer of wood smoke.
3) Transport from the Sierra Nevada: This is a group of chemicals that follow the pinene oxidation product of pinonaldehyde. This is a highly selective tracer for biogenic emissions from pine forests, which indicated that the air mass was over the Sierra Nevada Mountains. Correlation with pinonaldehyde does not mean that all the chemicals were of biogenic origin, but rather their source (biogenic or anthropogenic) was in the Sierra Nevada Mountains. Unfortunately, most of the pine trees are dormant in winter and therefore not emitting pinene, thus this tracer was only useable for the summer sampling episodes. The presence of pinonaldehyde also indicates that chemicals in the air mass have been oxidized since ozone is needed to convert pinene to pinonaldehyde.
4) Direct vehicle emissions: These are compounds that appear to be relatively independent of the season in which they were collected and they also seem to have an increase in concentrations in the weekday mornings around 06:00 and 10:00. These compounds were also classified as probable vehicle emissions if they are known to arise from vehicles. The absence of these chemicals at the control site further supports the chemicals classification as probably direct vehicle emission.

Here is a summary of which chemicals fell into the most probable potential emission source based on the data collected (Table 4):

Table 4. The most probable source of each of the major chemicals quantified in this study. Since some chemicals arise from multiple sources, so some chemicals are assigned to multiple categories. Compounds marked with a question mark are the best fit with the patterns, but they were not expected to fall into that class.

Season	Photochemical Derived	Wood smoke	Sierra Transport	Direct Vehicle Emission
Summer	glyoxal glycolaldehyde methylglyoxal	---	pinonaldehyde acrolein methacrolein[1] 2-furaldehyde 2,3-butanedione 3-methyl-2-butenal *p*-tolualdehyde(?) *m*,*o*-tolualdehyde(?) 4-methoxybenz-aldehyde(?) methyl vinyl ketone[1] methylglyoxal	*p*-tolualdehyde[2] *m*,*o*-tolualdehyde[2]
Winter	---	2-furaldehyde[2] acrolein[2] methylglyoxal[2] benzaldehyde 1,4-benzoquinone 2,3-butanedione 2,4-pentanedione 3,4-hexanedione 3-hydroxybenzaldehyde *p*-tolualdehyde *m*,*o*-tolualdehyde	---	*p*-tolualdehyde[2] *m*,*o*-tolualdehyde[2]

[1] Due to poor mist chamber retention of these analytes, absolute quantification was not attempted, so the assignment to a source class is based on the relative changes in concentration.
[2] Emission of this chemical from this source was confirmed with the source samples presented in Appendix 4.

Conclusions:

The main objective of this research was to determine the diurnal and seasonal variation in acrolein concentrations at an ARB monitoring station impacted by local vehicle emissions and by high ozone concentrations in the summer. The results showed both diurnal and variation in acrolein and other carbonyls, but the temporal patterns did not follow the expected pattern. Acrolein concentrations did not correlate with ozone or traffic patterns but the acrolein concentrations did correlate well with a wood smoke tracer in the winter and down-slope transport from the Sierra Nevada Mountains in summer. Thus, it appears that vehicle emissions were not the dominant source of acrolein in either the summer or winter.

In addition to acrolein, many other volatile carbonyls were also quantified. For most of the chemicals that were routinely detected, the source appeared to be wood smoke (winter) or transport from the Sierra Nevada Mountains (mostly summer). Only a few compounds, such as glyoxal, methylglyoxal and glycolaldehyde, showed a considerable contribution from photochemical formation. The most surprising result was that relatively few compounds, mainly the tolualdehydes, appeared to originate from direct vehicle emissions. Considering the large local sources of vehicle emissions, we had expected higher concentrations of carbonyls from vehicles.

Directions for Future Research:

This research project has contributed to our understanding of the sources of ambient acrolein concentrations in an urbanized area. However, this project also highlights research areas that need more attention in the future. The following is a list of projects that would further our understanding of acrolein in the environment:

1) Expanded source identification. The results from the three vehicles we tested for source samples showed a tremendous variation between the three vehicles. One of the vehicles had no detectable concentrations of acrolein in non-diluted exhaust samples while one vehicle, which was the newest, had very high concentrations. Therefore, vehicle emissions for a wide variety need to be tested. In addition, the emission tests should be conducted both under idling and under load conditions. These characterization tests should be conducted in such a fashion as to be able to calculate the vehicle emission rates rather than simple tail pipe concentrations as was done in this experiment. Diesel vehicles also need to be tested and characterized.
2) Resolve the differences between the mist chamber method and the canister method utilized by MDL. Currently, it is very clear that there is a discrepancy between the two methods, but both research groups are confident in their methodology. One of the mostly likely causes for the differences would be a calibration error given the magnitude of the differences in acrolein concentrations observed. A calibration error could arise from diverse problems such as a standard that had degraded or condensation of acrolein during transfer from a compressed gas cylinder to the sample container.

   The tests that are needed to resolve this difference is to create a uniform air mixture containing the analytes (at room temperature at standard pressure) and then have both research groups sample the exact same air. This can be accomplished by filling a Tedlar bag (~200 L in volume) with a known amount of acrolein and other analytes. The advantage of a Tedlar bag is that the pressure of the gas remains at atmospheric pressure, so there are no condensation or evaporation issues arising from changes in pressure or temperature. The bag could first be filled by a NIST certified gas cylinder that MLD typically uses for canister calibration. After a few minutes (which allows for equilibration and mixing of the gas) a canister sample can be taken and then the mist chamber would collect a sample. This process should be repeated three times so that statistics can be used to evaluate the data. To ensure that the problem is not associated with the NIST gas cylinder, a second set of experiments should be conducted where the source of the acrolein is a brand-new liquid standard purchased from Aldrich. The acrolein would then be introduced into the Tedlar bag by evaporating it into a nitrogen air stream that is used to fill the bag. In addition acrolein-d_4 can also be introduced to the air at the same concentration. Once again, both groups would sample the same air mass in the bag and three replicates should be conducted. The presence of acrolein-d_4 helps to verify that the quantified acrolein is subject to an interference that shares a common ion with acrolein. The experiments should also used a concentration of acrolein that is comparable to field concentrations. Lastly, a series of both pre- and post- blanks should be prepared to determine any contamination from sample handling.

3) Assessing regional differences in ambient carbonyl concentration. The results from the summer sampling episodes showed that acrolein appeared to be transported from the Sierra Nevada Mountains. This raises the question if the observed acrolein was due to biogenic oxidation or from wood smoke from the Sierras. It also raises questions about what the natural background of acrolein is, which is a key aspect of any risk assessment. Therefore, there should be a systematic assessment of acrolein concentrations is a variety of both remote and urban areas to determine the background concentrations of acrolein. The results from the MLD toxics monitoring show rather consistent acrolein concentrations around the State of California, which is counter-intuitive. Thus it would be useful to confirm these results by a second analytical method.

References:

1. CICAD, Concise International Chemical Assessment Document *World Health Organization* **2002,** 43, (Acrolein).
2. Agency for Toxic Substances and Disease Registry, A. *Toxicological Profile for Acrolein*; U.S. Public Health Service, USPHS: 1990.
3. Grosjean, D.; Grosjean, E.; Gertler, A. W., On-road emissions of carbonyls from light-duty and heavy-duty vehicles. *Environ. Sci. Technol.* **2001,** 35, (1), 45-53.
4. Zervas, E.; Montagne, X.; Lahaye, J., Emission of Alcohols and Carbonyl Compounds from a Spark Ignition Engine. Influence of Fuel and Air/Fuel Equivalence Ratio. *Environ. Sci. Technol.* **2002,** 36, (11), 2414-2421.
5. Ho, K. F.; Ho, S. S. H.; Cheng, Y.; Lee, S. C.; Yu, J. Z., Real-world emission factors of fifteen carbonyl compounds measured in a Hong Kong tunnel. *Atmos. Environ.* **2007,** 41, (8), 1747-1758.
6. Casella, I. G.; Contursi, M., Quantitative analysis of acrolein in heated vegetable oils by liquid chromatography with pulsed electrochemical detection. *J. Agr. Food Chem.* **2004,** 52, (19), 5816-5821.
7. Umano, K.; Shibamoto, T., Analysis of Acrolein from Heated Cooking Oils and Beef Fat. *J. Agr. Food Chem.* **1987,** 35, (6), 909-912.
8. Svendsen, K.; Jensen, H. N.; Sivertsen, I.; Sjaastad, K., Exposure to cooking fumes in restaurant kitchens in Norway. *Ann. Occup. Hyg.* **2002,** 46, (4), 395-400.
9. Singer, B. C.; Hodgson, A. T.; Guevarra, K. S.; Hawley, E. L.; Nazaroff, W. W., Gas-phase organics in environmental tobacco smoke. 1. Effects of smoking rate, ventilation, and furnishing level on emission factors. *Environ. Sci. Technol.* **2002,** 36, (5), 846-853.
10. Zhang, J. F.; Smith, K. R., Emissions of carbonyl compounds from various cookstoves in China. *Environ. Sci. Technol.* **1999,** 33, (14), 2311-2320.
11. Ghilarducci, D. P.; Tjeerdema, R. S., Fate and effects of acrolein. In *Reviews of Environmental Contamination and Toxicology, Vol 144*, 1995; Vol. 144, pp 95-146.
12. OEHHA *Chronic Toxicity Summary, Acrolein*; December 2000, 2000; p Batch 2A.
13. Lipari, F.; Dasch, J. M.; Scruggs, W. F., Aldehyde Emissions from Wood-Burning Fireplaces. *Environ. Sci. Technol.* **1984,** 18, (5), 326-330.
14. Highsmith, V. R.; Zweidinger, R. B.; Merrill, R. G., Characterization of Indoor and Outdoor Air Associated with Residences Using Woodstoves - a Pilot-Study. *Environ. Int.* **1988,** 14, (3), 213-219.
15. U.S. Environmental Protection Agency *Integrated Risk Information System, Acrolein (CASRN 107-02-8)*; U.S. Environmental Protection Agency: June 2003, 2003.
16. Tam, B. N.; Neumann, C. M., A human health assessment of hazardous air pollutants in Portland, OR. *J. Environ. Manage.* **2004,** 73, (2), 131-145.
17. State of California, A. R. B. *Toxic Air Contaminant Identification List Summaries, Acrolein*; California Air Resources Board: Sacramento, September 1997, 1997; pp 1997-11-12.
18. Morello-Frosch, R. A.; Woodruff, T. J.; Axelrad, D. A.; Caldwell, J. C., Air toxics and health risks in California: The public health implications of outdoor concentrations. *Risk Anal.* **2000,** 20, (2), 273-291.

19. van Leeuwen, S. M.; Hendriksen, L.; Karst, U., Determination of aldehydes and ketones using derivatization with 2,4-dinitrophenylhydrazine and liquid chromatography-atmospheric pressure photoionization-mass spectrometry. *J. Chromatogr. A* **2004,** 1058, (1-2), 107-112.
20. Pereira, E. A.; Carrilho, E.; Tavares, M. F. M., Laser-induced fluorescence and UV detection of derivatized aldehydes in air samples using capillary electrophoresis. *J. Chromatogr. A* **2002,** 979, (1-2), 409-416.
21. Pereira, E. A.; Rezende, M. O. O.; Tavares, M. F. M., Analysis of low molecular weight aldehydes in air samples by capillary electrophoresis after derivatization with 4-hydrazinobenzoic acid. *J. Sep. Sci.* **2004,** 27, (1-2), 28-32.
22. Pires, M.; Carvalho, L. R. F., An artifact in air carbonyls sampling using C-18 DNPH-coated cartridge. *Anal. Chim. Acta.* **1998,** 367, (1-3), 223-231.
23. Brombacher, S.; Oehme, M.; Dye, C., Qualitative and quantitative analysis of carbonyl compounds in ambient air samples by use of an HPLC-MSn method. *Anal. Bioanal. Chem.* **2002,** 372, (5-6), 622-629.
24. Grosjean, E.; Grosjean, D., Performance of DNPH-coated C-18 cartridges for sampling C-1-C-9 carbonyls in air. *Int. J. Environ. An. Ch.* **1995,** 61, (4), 343-360.
25. Shibamoto, Y. A. a. T., Gas chromatographic determination of trace amounts of aldehydes in automobile exhaust by a cysteamine derivatization method. *J. Chromatogr. A* **1994,** 672, 261-266.
26. Coutrim, M. X.; Nakamura, L. A.; Collins, C. H., Quantification of 2,4-Dinitrophenyl-Hydrazones of Low-Molecular-Mass Aldehydes and Ketones Using Hplc. *Chromatographia* **1993,** 37, (3-4), 185-190.
27. Bakeas, E. B.; Argyris, D. I.; Siskos, P. A., Carbonyl compounds in the urban environment of Athens, Greece. *Chemosphere* **2003,** 52, (5), 805-813.
28. Zhang, J. F.; He, Q. C.; Lioy, P. J., Characteristics of Aldehydes - Concentrations, Sources, and Exposures for Indoor and Outdoor Residential Microenvironments. *Environ. Sci. Technol.* **1994,** 28, (1), 146-152.
29. Sax, S. N.; Bennett, D. H.; Chillrud, S. N.; Kinney, P. L.; Spengler, J. D., Differences in source emission rates of volatile organic compounds in inner-city residences of New York City and Los Angeles. *J. Expo. Anal. Env. Epid.* **2004,** 14, S95-S109.
30. Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R., Air quality model evaluation data for organics .2. C-1-C-14 carbonyls in Los Angeles air. *Environ. Sci. Technol.* **1996,** 30, (9), 2687-2703.
31. Lipari, F.; Swarin, S. J., Determination of Formaldehyde and Other Aldehydes in Automobile Exhaust with an Improved 2,4-Dinitrophenylhydrazine Method. *J. Chromatogr.* **1982,** 247, (2), 297-306.
32. Tejada, S. B., Evaluation of Silica-Gel Cartridges Coated Insitu with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air. *Int. J. Environ. An. Ch.* **1986,** 26, (2), 167-185.
33. Grosjean, D., Formaldehyde and Other Carbonyls in Los Angeles Ambient Air. *Environ. Sci. Technol.* **1982,** 16, 254-262.
34. U.S. Department of Labor, O. S. a. H. A. Method 52: Acrolein and/or Formaldehyde. http://www.osha.gov/dts/sltc/methods/organic/org052/org052.html
35. Zhang, I.; Zhang, L.; Fan, Z.; Ilacqua, V., Development of the personal aldehydes and ketones sampler based upon DNSH derivatization on solid sorbent. *Environ. Sci. Technol.* **2000,** 34, (12), 2601-2607.

36. Dong, J. Z.; Moldoveanu, S. C., Gas chromatography-mass spectrometry of carbonyl compounds in cigarette mainstream smoke after derivatization with 2,4-dinitrophenylhydrazine. *J. Chromatogr. A* **2004,** 1027, (1-2), 25-35.
37. Goelen, E.; Lambrechts, M.; Geyskens, F., Sampling intercomparisons for aldehydes in simulated workplace air. *Analyst* **1997,** 122, (5), 411-419.
38. Huynh, C. K.; Vu-Duc, T., Intermethod comparisons of active sampling procedures and analysis of aldehydes at environmental levels. *Anal. Bioanal. Chem.* **2002,** 372, (5-6), 654-657.
39. Schulte-Ladbeck, R.; Lindahl, R.; Levin, J. O.; Karst, U., Characterization of chemical interferences in the determination of unsaturated aldehydes using aromatic hydrazine reagents and liquid chromatography. *J. Environ. Monitor.* **2001,** 3, (3), 306-310.
40. Weisel, C. P.; Zhang, J. F.; Turpin, B. J.; Morandi, M. T.; Colome, S.; Stock, T. H.; Spektor, D. M.; Korn, L.; Winer, A.; Alimokhtari, S.; Kwon, J.; Mohan, K.; Harrington, R.; Giovanetti, R.; Cui, W.; Afshar, M.; Maberti, S.; Shendell, D., Relationship of Indoor, Outdoor and Personal Air (RIOPA) Study: Study design, methods and quality assurance/control results. *J. Expo. Anal. Env. Epid.* **2005,** 15, (2), 123-137.
41. Seaman, V. Y.; Charles, M. J.; Cahill, T. M., A sensitive method for the quantification of acrolein and other volatile carbonyls in ambient air. *Anal. Chem.* **2006,** 78, (7), 2405-2412.
42. Spaulding, R. S.; Talbot, R. W.; Charles, M. J., Optimization of a mist chamber (cofer scrubber) for sampling water-soluble organics in air. *Environ. Sci. Technol.* **2002,** 36, (8), 1798-1808.
43. Occupational Safety and Health Administration Method 52: Acrolein and/or Formaldehyde. http://www.osha.gov/dts/sltc/methods/organic/org052/org052.html
44. Seaman, V. Y.; Bennett, B. H.; Cahill, T. M., Origin, Occurrence and Source Emission Rate of Acrolein in Residential Indoor Air. *Environ. Sci. Technol.* **2007,** 41, 6940-6946.
45. Destaillats, H.; Spaulding, R. S.; Charles, M. J., Ambient air measurement of acrolein and other carbonyls at the Oakland-San Francisco Bay Bridge toll plaza. *Environ. Sci. Technol.* **2002,** 36, (10), 2227-2235.
46. California Air Resources Board Aerometric Data Analysis and Management system (ADAM), Air Toxics Summary. www.arb.ca.gov/adam/toxics
47. Liu, W.; Zhang, J.; Zhang, L.; Turpin, B. J.; Welsel, C. P.; Morandi, M. T.; Stock, T. H.; Colome, S.; Korn, L. R., Estimating contributions of indoor and outdoor sources to indoor carbonyl concentrations in three urban areas of the United States. *Atmos. Environ.* **2006,** 40, (12), 2202-2214.
48. Cahill, T. M.; Charles, M. J.; Seaman, V. Y. *Development and Application of a Sensitive Analytical Method for Acrolein Determination in Ambient Air*; Health Effects Institute: Boston, MA, in press.
49. Yu, J. Z.; Cocker, D. R.; Griffin, R. J.; Flagan, R. C.; Seinfeld, J. H., Gas-phase ozone oxidation of monoterpenes: Gaseous and particulate products. *J. Atmos. Chem.* **1999,** 34, (2), 207-258.
50. Cahill, T. M.; Seaman, V. Y.; Charles, M. J.; Holzinger, R.; Goldstein, A. H., Secondary organic aerosols formed from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains of California. *J. Geophys. Res-Atmos.* **2006,** 111, (D16).
51. Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Traverse, M., Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 1. Mass Emission Rates. *Environ. Sci. Technol.* **1999,** 33, (2), 318-328.

52. Kirchstetter, T. W.; Singer, B. C.; Harley, R. A.; Kendall, G. R.; Hesson, J. M., Impact of California Reformulated Gasoline on Motor Vehicle Emissions. 2. Volatile Organic Compound Speciation and Reactivity. *Environ. Sci. Technol.* **1999,** 33, (2), 329-336.
53. Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T., Gas-Phase and Particle-Phase Organic Compounds Emitted from Motor Vehicle Traffic in a Los Angeles Roadway Tunnel. *Environ. Sci. Technol.* **1998,** 32, (14), 2051-2060.

Abbreviations

ARB	Air Resources Board
GC-MS	gas chromatography mass spectrometry
meta-	a 1,3- substitution pattern on an aromatic ring.
MDL	minimum detectable limit
MLD	Monitoring and Laboratory Division of the California Air Resource Board
MQL	minimum quantifiable limit
NCI	negative chemical ionization (a type of ion source for mass spectrometry)
ortho-	a 1,2- substitution pattern on an aromatic ring.
para-	a 1,4- substitution pattern on an aromatic ring.
PFBHA	*o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine
SOP	standard operating procedure

APPENDIX 1

Acrolein Sample Collection & Extraction Standard Operating Procedure

Created by: Thomas Cahill
Created on: 4-29-05 Revised on: 12-27-06
Purpose: Collect and determine acrolein and other small carbonyls in the ambient atmosphere using mist chambers and a bisulfite trapping solution.

Hazards: Use all solvents and perform all extractions in the fume hood. Hexane, which is used in the extraction, is flammable and should be considered toxic. Hydrogen peroxide is an oxidizing agent and should be stored away from other organic solvents. Sulfuric acid is a corrosive agent that should be stored with other acids. Be sure to wear protective gear when making solutions of sulfuric acid. Pentafluorohydroxylamine (PFBHA) has not been fully characterized as to its hazards, thus it should be treated as with care as a potential toxicant.

Reagents:

1. Bisulfite solution (0.1 Molar)
   Prepare solution by adding 12.6g of sodium sulfite to 1 liter of HPLC or 18 MΩ-resistance water. Adjust pH to approximately 5.0 by adding 55mL 1.0M H_2SO_4. Allow solution to equilibrate for 24 hours prior to use. The solution appears to be stable for at least 6 months.
   An alternative approach for making larger quantities of the 0.1 M bisulfite solution is as follows:
   "Big Jug of Bisulfite"
   Open a new 4-L bottle of HPLC-grade (or better) water. Add 50.4 g Na_2SO_3 and 21.7 mL pure (18M) H_2SO_4. Shake well and let it sit at least 3 days before using. This creates enough bisulfite solutions for about 200 samples.
2. Pentafluorohydroxylamine (PFBHA) 75mM solution
   Add 0.938g of PFBHA to 50mL methanol. Use the PFBHA as received from manufacturer. The solution appears to be stable for at least 1 month. This creates enough solution for about 110 samples (double tubes).
3. Hydrogen peroxide (H_2O_2)
   Use the 30% as purchased. Keep bottle sealed when not in use to prevent contamination. Do not pipet directly from the source bottle.
4. Internal Standard Solution
   Acrolein-d_4, benzaldehyde-d_6 and acetaldehyde-d_4 are prepared at a concentration of 10ng/μL in acetonitrile. Additional internal standards will be added to the IS mix as they become available. For field sampling, the IS mix will be added to 2 mL screw-cap vial. A separate vial should be prepared for each day of sampling to avoid volatile losses of the solvent of possible contamination. The internal standard mix will be added to the samples prior to collection to account for blow-off, degradation or incomplete derivatization of the analytes.
5. Injection Standard Solution
   Octafluoronaphthalene (10ng/μL), 1,2,3-tribromo-5-fluorobenzene (50ng/μL), dibromonaphthalene (50ng/μL) and hexabromobenzene (100ng/μL) are combined into a single hexane solution containing the stated concentrations. 10μL of the injection standard is

added to a 0.5 mL volume sample just prior to instrumental analysis to quantify any instrumental drift.

6. Calibration Standards
   Calibration standards are mixtures of the carbonyls of interest in acetonitrile. The carbonyl "supermix" has a target analyte concentration of 8 to 10 ng/μL. The calibration mix does not have the injection standards or the internal standards in the solution; these are added in the field and lab extraction steps. Care should be taken to ensure that the calibration mix is rarely opened (to reduce solvent evaporation and contamination) and always chilled since the stability of some of the carbonyls in acetonitrile is not known.

Glassware Cleaning:
All glassware is washed in hot soapy water, rinsed twice with de-ionized water, rinsed once with acetone (to remove soap residues) and baked at 550ºC for 8 hours. After baking, the glassware is either capped (in the case of test tubes and centrifuge tubes) or have the openings covered in aluminum foil. This is designed to reduce glassware exposure to air, which might cause contamination.

Sampling Equipment:

2 mist chambers per sampling train (+ backups in case of breakage)
Medo vacuum pump
DryCal lite (preferred) or rotometer to measure air flow rate
Vacuum tubing and connectors
Snyder column (to act as an aerosol trap and protect pump from any bisulfite solution leakage)
HPLC-grade water (for rinsing mist chambers), ~4 L per day of sampling.
10 to 25 μL syringe or WireTols for measuring internal standards and calibration curves.
Large syringe (preferred) OR pasteur pipets and bulbs for water rinses.
Meteorological measuring equipment (temperature, relative humidity, and wind speed)
Ozone meter
Laboratory notebook

For sampling in remote areas away from line power, the additional equipment is needed:

12v deep cycle battery
Power inverter (300w or greater, one per pump)
Battery recharger

Prior to Field Collection:

a. Measure 10 ml of the 0.1M bisulfite solution into 15 ml vials. These are the "collection" solutions. Prepare enough vials for all the samples (with 2 vials per sample train), reagent blanks, field blanks and calibration curve. Additionally, prepare approximately 15% extra vials in case of breakage.
b. Prepare the "reaction" tubes that will neutralize the bisulfite and derivatize the carbonyls. These are the tubes that contain H_2O_2, PFBHA, sulfuric acid, water and hexane. This mix is stable for a least one week, but try to prepare these solutions as close to your sampling time as possible.

a. If the two mist chambers are going to be combined (no collection efficiency measurement), the add the following to a 50 ml test tube:
   2 mL of 1.8 M H_2SO_4
   200µL of H_2O_2
   400µL of 75mM PFBHA
   5 mL of hexane

b. If the two mist chambers are going to be processed separately (for collection efficiency determination) then add the following to a 30ml test tube:
   1 mL of 1.8 M H_2SO_4
   100µL of H_2O_2
   200µL of 75mM PFBHA
   5 mL of hexane

The choice to combine the two sequential mist chamber solutions or process them separately is a matter of logistics. Processing the two mist chambers separately allows the investigators to determine the collection efficiencies of the analytes for the field samples. However, this results in processing two samples for every mist chamber collection run. Combining the two mist chambers reduces the number of samples that need to be processes by half, but then the collection efficiency cannot be determined for the field samples. A second disadvantage to combining the samples is that the combined sample will have a higher background blank, so the sensitivity of the combined sample is lower. If the mist chamber samples are processed separately, then the blank (which is largely due to reagents) is lower. Since the first mist chamber collects most of the chemical mass, this creates a better signal to noise ratio.

Therefore, combining the two mist chamber solutions is recommended when large numbers of samples need to be processed. The solutions should be processed separately when only a few samples are processed and the expected concentrations are low, such as at background sites.

Operating temperatures: The ideal range of operating temperatures for the mist chambers is between 1°C and 34°C. The upper limit represents the condition where 70% of the acrolein-d_4 internal standard is lost during a 10 minute sample as determined by field studies in Roseville, CA. Ambient temperatures above 34°C result in lower retention of internal standards. Although the data is adjusted by the loss of the internal standard, larger IS loses make quantification less reliable. The lower temperature limit is the result of the aqueous solutions freezing. Due to evaporative cooling, it is possible for solution freezing to occur up to about 1°C. Samples can be collected below 0°C if the solutions start at room temperature and efforts are made to keep the mist chambers above 0°C between sample collection runs (e.g. heat lamps).

Collection & Derivatization:

1. Assemble vacuum pump and flow monitoring system.
2. Fill two mist chambers with 10 ml of the 0.1 M bisulfite solution. Keep the two mist chambers in the same order for all sampling times during the campaign, so label one chamber "A" and always put it as the first mist chamber.
3. Add 100 ng of each internal standard chemical to mist chamber A by adding 10uL of the 10ng/uL solution directly to the collection solution. Allow the collection solution to sit for

10 minutes. If the experiment calls for the determination of collection efficiency, then add the internal standards to both mist chambers since they will be processed separately.

4. Connect the two mist chambers in series making sure that chamber A is first.
5. Turn on the vacuum pump and set the flow rate to approximately 10-20 liters per minute. Record the exact start time and flow rate in the sample log book.
6. Record meteorological conditions such as temperature, relative humidity and wind speed/direction.
7. After 10 minutes, turn off the vacuum pump and record the exact end time in the sample log book. Make any comments relevant to the sampling (e.g. local conditions, any noticeable smells, etc.)
8. Empty both mist chambers into a single 50 mL reaction tube. If the chambers are going to be processed separately, then add the solutions from the two chambers to two different xml reaction tubes being sure to label as either "A" or "B" chambers. Rinse each chamber twice with ~ 5 ml of HPLC or 18 MΩ-resistance water. Add these rinses to the appropriate sample in the reaction tubes.
9. Label the sample on both the test tube and the cap with a sticky label and a pencil. Pencil marks do not come off in organic solvents, so accidental erasure is less likely.
10. Prepare a calibration curve in the field at the same time (within 6 hours) of the sample collection. Add the internal standard mix (10μL of the 10ng/μL solution) to each of 6 collection solution vials. Then add the appropriate amount of the standard solution (which has a target concentration of 8 to 10 ng/μL of the analytes) to each vial (see below). Allow the chemicals to react for 10 minutes and then pour the collection solution into a reaction tube. The amount of standard to add is the following:

0 μL of standard solution	= 0 pg/μL in the final 0.5 ml extract volume
1 μL of standard solution	= 20 pg/μL in the final 0.5 ml extract volume
3 μL of standard solution	= 60 pg/μL in the final 0.5 ml extract volume
10 μL of standard solution	= 200 pg/μL in the final 0.5 ml extract volume
30 μL of standard solution	= 600 pg/μL in the final 0.5 ml extract volume
50 μL of standard solution	= 1000 pg/μL in the final 0.5 ml extract volume

    The concentrations of the standards can be adjusted for the goal of the sampling episode. The calibration standards above work well for ambient sampling. Source sampling will want to have higher concentrations.
11. Store the samples at room temperature for 24 to 96 hours to allow them to react. The samples should be extracted before 96 hours for the best results.

Sample Extraction:

Sample extraction needs to be conducted 24-96 hours after sample collection. For each sample and standard:

1. Shake vigorously and allow the aqueous and hexane layers to separate. Remove the hexane layer and add it to a graduated, 15mL conical glass centrifuge vial by passing the hexane though a sodium sulfate pasture pipet column. The pipet column consists of a short (5½") pasture pipet half filled with granular sodium sulfate. The columns are baked at 550°C for 8

hrs (after which the columns need to stay in a sealed container). This step is designed to remove any traces of water.
2. Conduct an additional extraction by adding another 5 ml of hexane to the sample and processing as in (1).
3. Reduce the volume of the extract to 0.5 mL by nitrogen evaporation. Vortex the centrifuge tube to wash the walls before transferring the solution to an amber GC vial.
4. Add 10μL of the "Injection Standard" solution to each sample and standard to serve as an injection standard.
5. Store samples at 4^{o}C in a sealed container with desiccant until instrumental analysis. The samples are stable for at least 30 days in this condition.

Instrumental Analysis:

The samples are best determined by gas chromatography-negative chemical ionization mass spectrometry due to the electronegative properties of the pentafluorohydroxyl functional group. Note: carbonyls may give rise to more than one peak due to isomers arising from the double bond in the derivatization reagent. Chromatographic separation of different isomers (e.g. methacrolein, methyl vinyl ketone, and crotonaldehyde) is easily accomplished by gas chromatography. Our instrumental conditions are:

1. Instrument: Agilent 6890GC + 5973MS
2. Column: DB-5MS or DB-XLB (30m, 0.25mm I.D., 0.25μm film thickness)
3. Helium carrier gas at a linear velocity of 35 cm/sec.
3. GC Program: Initial temperature 50ºC, increase 5ºC/min to 150ºC, increase 20ºC/min to 260ºC, increase 30ºC/min to 325ºC, hold for 5 min.
4. MS Source temperature = 150ºC, Mode = negative EC/CI, Reagent gas = CH_4

Typically, the PFBHA-derivatized carbonyls ionize to give $[M–20]^-$ as the dominant ion, which represent the loss of hydrofluoric acid (HF) from the molecule. This is typically the quantification ion for our analytes.

APPENDIX 2

Minimum Detection Limits (MDL) for the 5 sampling episodes

Table A2.1. The MDLs are expressed as ng/m^3. Values listed as "NA" indicate that the MDL was not available for that sampling period, which generally indicates that the calibration curve was too poor for quantification of that analyte during that sample period.

Compound	Roseville Summer 1	Roseville Summer 2	Roseville Winter 1	Roseville Winter 2	Putah Creek	average MDL
acrolein(Peak#1)	11.6	26.4	6.3	6.6	36.3	17.4
acrolein(peak#2)	10.2	57.1	9.5	8.8	39.7	25.1
2-methyl-1-propanal	270.9	345.9	160.3	170.2	472.5	284.0
methacrolein	7.6	73.8	1.9	1.7	106.0	38.2
methyl-vinyl-ketone	28.9	157.6	26.2	65.3	311.0	117.8
3-pentanone	111.3	284.9	49.1	129.3	360.2	187.0
2-pentanone	92.9	396.1	53.8	191.7	484.9	243.9
3-methylbutanal	173.0	52.5	19.5	10.6	315.7	114.3
crotonaldehyde	19.2	17.9	17.3	28.9	9.0	18.4
glycolaldehyde	NA	697.5	60.4	NA	630.0	462.6
pentanal	92.1	65.4	59.8	NA	90.9	77.0
5-hexen-2-one	475.4	555.1	376.2	283.3	714.8	481.0
2-methyl-2-butenal	2.8	1.3	1.4	2.2	7.5	3.0
4-hexen-2-one	32.2	19.3	9.6	57.9	14.9	26.8
3-methyl-2-butenal	1.8	3.4	1.0	0.6	2.9	1.9
hexanal	NA	327.3	977.6	345.0	969.6	654.9
2-heptanone	70.2	57.0	19.2	160.3	82.1	77.8
2-furaldehyde	3.5	6.2	12.3	5.1	3.2	6.1
2-hexenal	6.0	10.1	1.0	2.9	22.6	8.5
heptanal	240.6	153.8	52.0	132.0	232.1	162.1
2-octanone	38.2	NA	20.4	50.7	72.1	45.4
2-heptenal	3.4	2.5	1.3	4.1	6.8	3.6
octanal	131.0	99.1	22.4	65.4	190.1	101.6
benzaldehyde	173.7	51.8	6.8	44.4	284.7	112.3
nopinone	108.7	NA	NA	NA	192.5	150.6
nonanal	567.1	202.4	22.0	124.3	495.3	282.2
2-decanone	70.3	NA	44.8	24.7	NA	46.6
1,4-benzoquinone (single-derivative)	NA	NA	19.2	24.1	NA	21.7
o,m-tolualdehyde	4.7	3.8	1.1	2.2	9.0	4.2
p-tolualdehyde	1.7	1.5	0.8	0.6	4.0	1.7
4-decenal	21.2	69.3	NA	NA	NA	45.3
2-ethylbenzaldehyde	1.9	1.3	0.3	0.3	1.7	1.1

decanal	492.8	177.3	97.1	240.8	268.1	255.2
3,4-dimethyl-benzaldehyde	6.9	2.4	0.4	0.6	4.7	3.0
glyoxal	133.4	95.4	109.6	80.2	191.3	122.0
4-methoxy-benzaldehyd	1.7	1.5	0.7	2.3	3.8	2.0
methyl-glyoxal	33.5	22.7	15.5	22.4	74.9	33.8
3-phenyl-2-propenal	18.8	19.0	453.6	0.0	29.1	104.1
2,3-butanedione	12.2	16.9	6.0	24.2	16.0	15.0
2,3-pentanedione	8.6	8.4	1.2	10.3	24.8	10.7
3,4-hexanedione	9.5	NA	5.9	4.8	44.2	16.1
3-hydroxy-benzaldehyde	3.2	7.6	2.4	4.0	1.5	3.7
2,4-pentanedione	22.9	24.5	4.3	12.2	77.5	28.3
2,3-hexanedione	2.6	1.6	2.0	4.2	15.5	5.2
3,5-heptanedione	6.5	17.9	0.9	8.5	8.7	8.5
glutaraldehyde	NA	211.0	NA	106.5	568.1	295.2
1-naphthaldehyde	20.9	NA	20.1	78.8	53.0	43.2
1,4-benzoquinone (double-derivative)	NA	NA	50.6	16.6	NA	33.6
pinonaldehyde	9.3	7.1	8.1	15.9	12.2	10.5

APPENDIX 3

On-road sample results

The inherent assumption of collecting samples at the North Sunrise ARB station was that this site would be impacted by vehicles from the nearby roads. Given the focus on roadway emissions, we thought it might be worth collecting some samples on the roadways themselves. A total of 8 "on road" samples were collected on July 17 during the second summer Roseville sampling episode. These results were then compared to the results from the stationary site.

The sample collection system and spiking procedure was the exact same as the stationary site at the ARB station except that the vacuum pump was powered with a 300 watt power invert that drew power from car power supply. Also, a 1.5 m long PTFE tube was attached to light bar of the Jeep and served as the air intake. The Jeep was then driven on both freeways and surface streets to collect air while driving around for 10 minutes. The samples were all collected in pairs where one sample was collected driving away from Douglas and Interstate 80 and the other was collected on the return trip. Unfortunately, there was a fairly strong breeze on this day that may cause rapid mixing of the air mass on the road. The exact conditions for each of the samples were:

On-road #1:
I-80 westbound from Douglas Blvd to Winter street. Started 10:32, duration 10 minutes. Distance covered 10.6 miles. Speed approximately 65 MPH. I stayed in the second lane from the left when possible. (next to fast lane). There is moderate traffic but it is moving well.

On-road #2
I-80 eastbound from Winter Street to Douglas Blvd (return trip). Started 10:48, duration 10 min 30 seconds. Distance covered = 10.4 mi. Traffic same as westbound (moderate, but moving fast).

On-road #3
Douglas Blvd from North Sunrise to (next big road after Barton, has a shopping center and a Taco Bell). Start 11:10, duration 10 minutes. Distance covered 5.1 mi. Generally in fast lane on Douglas. I was first out of the lights for about ½ the distance (missed everyone stepping on the gas). Last 1/3 of distance was rather open (in Granite Bay). I added about 4 ml of water to the column before starting.

On-road #4
Douglas Blvd from (Barton + a little) to N Sunrise. This is the return from #3. Distance 5.1 mi. Duration = 10 minutes, 30 seconds. Start 11:28. I chipped the top of the lower MC, so there is some ground glass powder in the sample. It should not affect anything. I added 4-5 ml of water to the column before sampling.

On-road #5
I-80 East from Douglas. Start 14:20, duration 10 minutes. Distance covered 10.9 mi. I made it to Newcastle Road. The traffic cleared out a little after Penryn. Traffic moving at 65-70 MPH.

On-road #6

I-80 (return from #5) Newcastle to Douglas. Distance = 10.9 mi. Duration = 11min, 30 sec. There was a backup at Douglas, hence the longer time.

On-road #7
Roseville ramble. West Douglas to railyard (wind from railyard), south to Cirby, east to Sunrise. I added water to the lower MC. It is hot and dry out there! Start 15:06. Distance = 3.2 mi, time 10 minutes.

On-road #8
Sunrise Blvd. Start at Cirby, go south for two minutes, U-turn and head north. Pass Douglas and end at Automall Drive. Start 15:24. Duration 10 minutes, distance covered 4.4 miles. I added water to the lower chamber.

These samples were stored and processes along with the samples collected at the ARB station on the same day.

The results from this limited set of samples showed a very good agreement between the concentrations collected at the ARB station and the "on-road" samples collected at similar times (Figures A3.1 and A3.2). The only chemicals that showed any on-road enrichment were the *m,o*-tolualdehydes and the *p*-tolualdehydes. Unfortunately, the data are near the minimum detectable limit, so the data are a little more scattered than with other chemicals. This supports the notion that these aromatic aldehydes are the result of a direct emission from motor vehicles, which is also supported by the emission source samples presented in Appendix 4. Most of the other chemicals that were regularly detected showed no enrichment in the on-road samples. However, many of these chemicals have clear, non-vehicle sources such as 2-furaldehyde, so the consistency between the ARB station and the on-road collection was expected.

While the consistency between the stationary sampler and the on-road sampler may not have identified many chemicals that could be attributed to direct vehicle emission, the consistency of the results does help to demonstrate the consistency of the method under different conditions, such as mobile and stationary sample collection. This helps to validate that the samples collected with a 12V DC power supply and a power inverter were comparable to the ones collected with line power supplies. Also, it shows the consistency while using different sets of mist chambers since the on-road samples were collected with a different sampler than the ARB station samples.

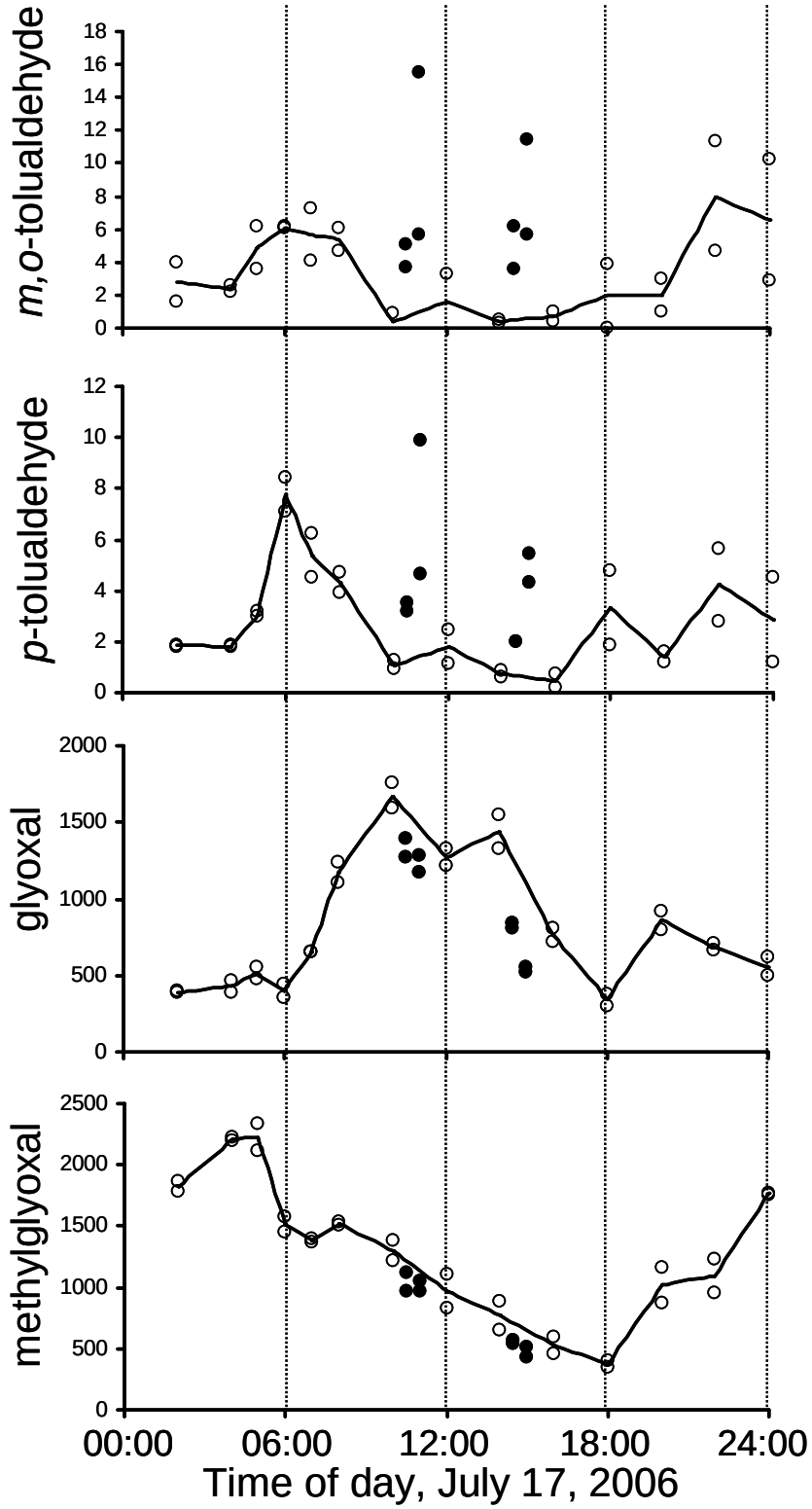


Figure A3.1. Comparison of the carbonyl concentrations (ng/m^3) collected at the ARB north Sunrise station (open circles) and the "on-road" samples (solid circles).

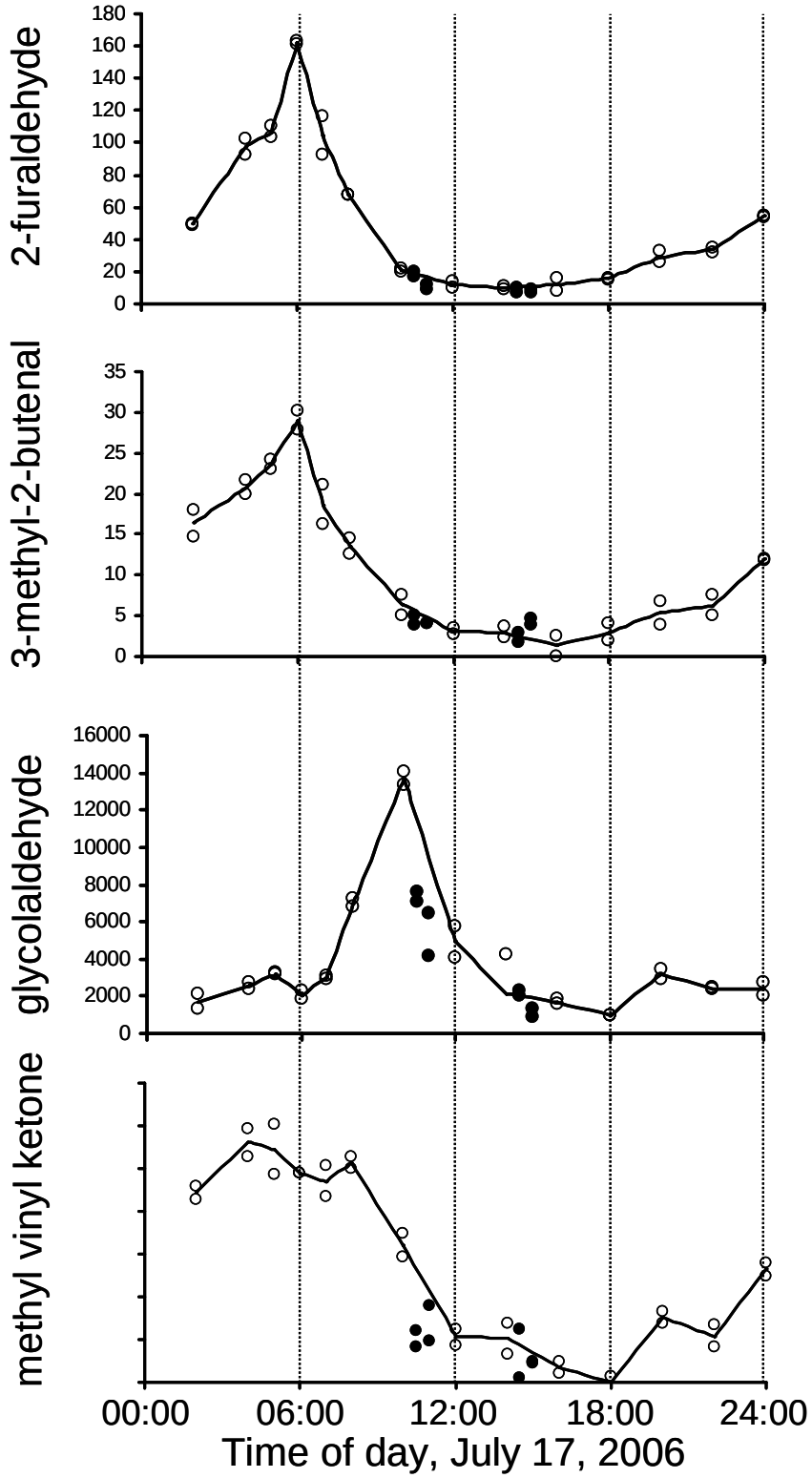


Figure A3.2. Comparison of the carbonyl concentrations (ng/m^3) collected at the ARB north Sunrise station (open circles) and the "on-road" samples (solid circles).

APPENDIX 4

Emission Source Samples

One of the major aspects of this research project was to determine the diurnal cycles of acrolein and relate it back to its presumed source, which was expected to be motor vehicles based on the location of the site adjacent to a busy freeway and several large surface streets. However, it is useful to double-check the field assessment by collecting some samples right from the expected sources. Therefore, a small side projected collected samples from three idling vehicles designed to represent some typical vehicles as well as two fires that used soft wood (Douglas Fir) or hard wood (Blue Oak) as the fuel.

Typical research projects to characterize emissions sources are far more complicated and thorough than this un-funded side project. Vehicle characterization often relies on the use of a dynamometer and a specific drive cycles. Combustion emission characterizations are often conducted in sealed chambers with dilution and residence time chambers. Neither of these systems were available to conduct this sampling, so this samples will be less accurate than a thorough source characterization experiment. However, even this "quick and dirty" source characterization will provide considerable information about the different chemicals from some of the suspected primary emission sources in the field study.

Methods:

The source samples were collect with the same mist chamber system as described in the standard operating procedure (Appendix 1), except that a simple residence time chamber (RTC) was hooked up between the source sample and the mist chamber. The RTC was a sealed 30 L stainless steel chamber which would give an air residence time of approximately 2 minutes at our standard air sampling rates. The intake tube was 0.6 m of ¼" stainless steel tubing, which entered the RTC at the top of the chamber. The other end of the intake tube was placed in the source (up the tailpipe of the car or 3" to 10" above the flame of the fire). The outlet line from the RTC was ~1.5 m for PTFE tubing. The outlet air was pulled from the bottom of the RTC. The RTC was purged with each source for 5 minutes prior to sample collection and air flow through the RTC was maintained between sample collection events. Unlike most source characterization experiments, there was no dilution of the air stream from the source to the samples, so the samples are expected to be very concentrated. An ambient sample was collected before the source sample so that the emission samples can be corrected for the ambient air concentrations.

The exact sampling conditions for the 5 sources are presented in the field note log (Appendix 5) but they are also summarized below:

Sampling item 1: Vehicle source sample (Jeep Wrangler)

Year and Model: 1995 Wrangler
Engine type and size: gasoline, 4 L, 6 cylinders
Idle conditions: warm idle
Odometer: 95,636 miles
Previous sample: ambient (blank)

Comments: I drove the Jeep 5+ miles at freeway speeds before conducting the test. The RT was purges with exhaust for 5 minutes prior to the first sample collection. The intake was

inserted up the tailpipe to sample only exhaust. The steel intake line to the RT was quite warm, but the Teflon line was cool. There was some condensation of water in the Teflon line. There was no change in the solution temperature in the MCs, it was still cool. I kept the pump pulling exhaust through the RTC in between samples, so it was always read for another sample to start. I could not see any difference in flow rates with and without the RT attached to the samplers.

Sampling item 2: Vehicle source sample (Ford Mustang)

Year and Model: 1986 Mustang

Engine type and size: gasoline, 5 L, 8 cylinders (new catalytic converters installed last year)

Idle conditions: warm idle (run for 5+ miles on freeway 113 before sample collection)

Odometer: 218,629 miles

Sample duration: 10 minutes

Previous sample: Jeep Wrangler

Comments: Same collection procedure as the Jeep. The exhaust was a little cooler than the Jeep. I can smell the exhaust more than the Jeep.

Sampling item 3: Vehicle source sample (Toyota Corolla)

Year and Model: 1997 Corolla

Engine type and size: gasoline, 1.76 L

Idle conditions: warm idle (Reiko drove it ~1 mile over here and it idled a while before the first sample was collected)

Odometer: 47,913 miles

Sample duration: 10 minutes

Previous sample: Ford Mustang

Comments: Same collection procedure as before. Reiko was here to help and to see the method in action. This was Reiko's car. The exhaust was very cool; there was some condensation in the tailpipe itself. The smell of exhaust was stronger than either the Jeep or the Mustang, which is a little surprising since this car has few miles than either of the other two cars.

Sampling item E: Field Blank

This is a standard field blank. No air was pulled through the chambers.

Sampling item F: Wood smoke (Douglas fir)

Duration: 10 minutes (first one) 3 minutes after that

Previous sample: field blank

Comments: The wood was well dried Douglas fir 2 X 2 that was cut up and put in a Webber Kettle. The fire was started with newspaper. The fire was made on a metal grate and the vents below it were open, so it got plenty of air under it. The steel intake was positioned about 3 to 6 inches above the top of the flame. The intake tube got hot. The first sample was collected 9 minutes after fire ignition, so it was in a steady flame stage. Once again, the chamber was purged for 5 minutes before collecting the first sample and the pump was used to pull air through the RTC in between samples. The first sample was very nasty looking and the solution was brown color, so I cut the sample collection time down to 3 minutes for the next of the sample to prevent overloading the derivatization reagent and the instrument. The last sample was collected during the smolder phase.

Sampling item G: Wood smoke (Blue Oak)

Duration: 3 minutes

Previous sample: Douglas Fir wood smoke

Comments: The wood smoke samples were collected like the previous samples. Sample collection was uneventful. The samples are a distinct gray color. The mist chamber nozzles were dark with soot from the smoke.

Results:

The results of the three different vehicles gave some unexpected results in that the newest car with the fewest miles gave the highest concentrations of chemicals (Tables A4.1 and A4.2). This car had the strongest odor during sample collection as noted in the field notes, so the higher concentration of chemicals was also collaborated by our sense of smell during sample collection. Equally unexpected, the Jeep Wrangler had non-detectable concentration of acrolein and all other chemicals after the data had the ambient air concentrations subtracted from the emission concentrations. Therefore, the first conclusion is that there is a very high degree of variability in emission concentrations between different vehicles.

The dominant chemicals in the vehicle emission samples were the aromatic aldehydes, namely benzaldehyde, *o,m,p*-tolualdehydes and dimethylbenzaldehydes. These chemicals compromised 75.1% and 57.9% of the total chemical mass collected and quantified in the Ford Mustang and Toyota Corolla samples respectively (Table A4.1). Given that gasoline has a high concentration of aromatic compounds (benzene, toluenes, etc.), it appears that these compounds are arising from partly-combusted gasoline. These results are intuitive and were expected.

The acrolein emissions from the vehicles was highly variable based on the vehicle tested. The Jeep had acrolein concentrations below the limit of quantification for all three samples. The Ford Mustang had a low acrolein emission rate with tailpipe concentrations of 4,200 ± 1,400 ng/m^3, which represented approximately 2.1% of the quantified carbonyl mass. This concentration was lower than expected since the tailpipe concentration was only 7-fold higher than the highest ambient sample in the summer and about 21-fold higher than the highest ambient winter sample. While both the Jeep and the Ford had low acrolein emissions, the Toyota had very high acrolein emissions at 690,000 ± 8,100 ng/m^3, which is about 17.1% of the carbonyl mass collected and quantified. The Toyota had higher concentrations of almost all chemicals. This may be due to the fact that this was the only car that was not driven at freeway speeds before sampling, so it may represent more of a "cold start" condition than the other two cars. However, the sample concentrations did not appear to change during the 30+ minutes of idling as the samples were collected.

The wood smoke samples were very dirty samples that were visibly brown upon collection. Therefore, there may be more carry-over between sample collection runs than with the cleaner samples. While there may be more carry-over between replicates, this was not expected to change the concentrations of the major chemical species due to the very high mass loading in the samples. The main result of the wood smoke samples, other than concentrated wood smoke it very dirty, is that furaldehyde was the most abundant chemical detected in all of the samples representing 27.6% to 43.1% of the mass fraction quantified (Table A4.1). The absolute concentrations were in the 1,300,000 to 3,800,000 ng/m^3 range (or 1.3 to 3.8 mg/m^3) (Table A4.3). This confirms that furaldehyde is produced in large amounts in wood fires, which

was expected. This is the main tracer of biomass burning in this project, thus it was useful to see it confirmed with the types of wood that people in the region are likely to burn. The rest of the chemical mass in wood smoke is spread out over a number of chemicals including acrolein. The mass fraction of acrolein was 13.5% and 6.3% in the fir and oak wood samples respectively, thus wood fires are capable of releasing significant amounts of acrolein. This was also observed in the field sampling campaign where the winter time acrolein concentrations correlated well with furaldehyde and peaked in the early evenings on cold nights. The absolute concentrations above the flames were very high, but this was expected. While most compounds were detected in the smoke samples, the aromatic aldehydes that were dominant in the vehicle samples were very minor in the fir and oak smoke samples with mass fractions of 4.8% and 1.5% respectively.

The source samples confirmed the suspected sources of the chemicals in the field sampling campaign with the aromatic aldehydes arising from vehicles and 2-furaldehyde, and a lot of minor chemicals, coming from wood smoke. Furthermore, the samples showed that wood smoke releases more acrolein on a mass fraction basis than two of the three vehicles tested. The source samples also showed tremendous variation between the three vehicles tested, which suggests that additional vehicle characterization is needed to determine what the average emissions from a vehicle fleet would be.

Table A4.1. Emission profiles from three vehicles and two types of fires as expressed as the relative abundance (in %, $n = 3$) of the chemicals detected and quantified. The data has not been corrected for the efficacy of the methods, thus the ketones are under-represented by this analysis. The ambient air concentrations have been subtracted from the emission data. Chemicals listed as "---" were not detected in two of the three replicates at concentrations that were above ambient air concentrations. None of the Jeep samples were consistently above the ambient air concentrations.

	1995 Jeep Wrangler	1986 Ford Mustang	1997 Toyota Corolla	Fir fire	Oak Fire
acrolein	---	2.1	17.1	13.5	6.3
2-methyl-1-propanal	---	---	0.4	0.3	0.1
methacrolein	---	4.4	6.8	1.1	0.7
methyl-vinyl-ketone	---	4.0	6.2	6.8	3.3
3-pentanone	---	---	0.1	0.2	0.1
2-pentanone	---	0.2	0.7	0.9	0.7
3-methylbutanal	---	---	0.1	0.2	0.2
crotonaldehyde	---	0.9	2.6	4.0	2.1
glycolaldehyde	---	0.3	0.1	0.9	0.5
hydroxyacetone	---	---	0.1	4.7	2.7
5-hexen-2-one	---	---	0.3	0.0	0.2
2-methyl-2-butenal	---	0.1	0.4	0.7	0.5
4-hexen-2-one	---	0.2	0.1	0.6	0.4
3-methyl-2-butenal	---	---	0.2	0.4	0.2
hexanal	---	---	0.4	0.6	---
2-heptanone	---	0.1	0.6	0.3	0.2
2-furaldehyde	---	0.2	0.4	27.6	43.1
2-hexenal	---	---	0.2	0.3	0.2
heptanal	---	0.1	0.2	1.3	0.4
2-octanone	---	0.2	0.0	0.4	0.1
2-heptenal	---	---	0.0	0.2	0.0
octanal	---	---	---	1.0	---
benzaldehyde	---	38.9	24.6	3.5	1.1
nonanal	---	---	0.0	1.0	0.0
2-decanone	---	0.1	0.2	0.5	0.1
1,4-benzoquinone	---	---	0.0	0.7	0.5
o,m-tolualdehyde	---	24.0	20.3	0.5	0.2
p-tolualdehyde	---	8.8	10.7	0.2	0.1
2-ethylbenzaldehyde	---	0.5	0.1	0.1	0.1
decanal	---	---	0.1	0.4	---
3,4-dimethylbenzaldehyde	---	3.4	2.3	0.1	0.1
glyoxal	---	0.2	1.1	3.3	1.7
4-methoxybenzaldehyde	---	---	0.1	0.0	0.0
methyl-glyoxal	---	0.0	0.7	6.5	12.3
3-phenyl-2-propenal	---	0.9	0.3	8.1	10.4
2,3-butanedione	---	1.0	0.2	5.2	8.2
2,3-pentanedione	---	---	0.1	0.7	0.9
3,4-hexanedione	---	8.9	1.5	0.5	0.3
3-hydroxybenzaldehyde	---	0.1	0.2	1.4	1.2
2,4-pentanedione	---	0.1	0.1	0.2	0.2
2,3-hexanedione	---	0.3	0.1	0.2	0.1
3,5-heptanedione	---		0.1	0.2	0.1
glutaraldehyde	---		0.1	0.2	0.1
1-naphthaldehyde	---	0.3	0.1	0.6	0.1

Table A4.2. The average concentration (ng/m^3, n = 3) and standard deviation of three non-diluted tailpipe emissions from three different vehicles. The data has not been corrected for the efficacy of the methods, thus the ketones are under-represented by this analysis. The ambient air concentrations have been subtracted from the emission data. Chemicals listed as "---" were not detected in two of the three replicates at concentrations that were above ambient air concentrations. None of the Jeep samples were consistently above the ambient air concentrations. The data has been rounded to two significant digits of accuracy.

	1995 Jeep Wrangler	1986 Ford Mustang	1997 Toyota Corolla
acrolein	---	4,200 ± 1,400	690,000 ± 8,100
2-methyl-1-propanal	---	---	---
methacrolein	---	9,100 ± 640	270,000 ± 7,800
methyl-vinyl-ketone	---	8,100 ± 3,200	250,000 ± 9,800
3-pentanone	---	---	4,500 ± 750
2-pentanone	---	370 ± 250	29,000 ± 4,000
3-methylbutanal	---	---	6,200 ± 1,400
crotonaldehyde	---	1,800 ± 220	110,000 ± 38,000
glycolaldehyde	---	590 ± 140	3,400 ± 1,600
hydroxyacetone	---	---	6,000 ± 3,300
5-hexen-2-one	---	---	10,000 ± 3,200
2-methyl-2-butenal	---	310 ± 25	17,000 ± 1,900
4-hexen-2-one	---	360 ± 3.5	4,400 ± 3,400
3-methyl-2-butenal	---	---	9,200 ± 3,400
hexanal	---	---	16,000 ± 3,100
2-heptanone	---	280 ± 87	24,000 ± 11,000
2-furaldehyde	---	450 ± 28	16,000 ± 2,900
2-hexenal	---	---	8,600 ± 8,300
heptanal	---	160 ± 10	6,200 ± 250
2-octanone	---	320 ± 58	860 ± 280
2-heptenal	---	---	190 ± 130
octanal	---	---	1,700 ± 400
benzaldehyde	---	80,000 ± 15,00	990,000 ± 260,000
nonanal	---	---	1,900 ± 340
2-decanone	---	260 ± 71	6,800 ± 2,900
1,4-benzoquinone	---	---	2,100 ± 330
o,m-tolualdehyde	---	49,000 ± 9,300	810,000 ± 150,000
p-tolualdehyde	---	18,000 ± 3.800	430,000 ± 60,000
2-ethylbenzaldehyde	---	930 ± 250	4,800 ± 1,400
decanal	---	---	2,800 ± 520
3,4-dimethylbenzaldehyde	---	8,700 ± 4,200	92,000 ± 56,000
glyoxal	---	370 ± 57	43,000 ± 17,000
4-methoxybenzaldehyde	---	---	2,000 ± 2,500
methyl-glyoxal	---	88 ± 56	29,000 ± 15,000
3-phenyl-2-propenal	---	1,900 ± 640	13,000 ± 5,800
2,3-butanedione	---	2,000 ± 500	9,500 ± 490
2,3-pentanedione	---	---	2,600 ± 38
3,4-hexanedione	---	18,000 ± 14,00	62,000 ± 35,000
3-hydroxybenzaldehyde	---	150 ± 1.9	9,300 ± 17
2,4-pentanedione	---	150 ± 30	3,600 ± 220
2,3-hexanedione	---	550 ± 290	2,400 ± 210
3,5-heptanedione	---	---	3,100 ± 210
glutaraldehyde	---	---	3,500 ± 630
1-naphthaldehyde	---	560 ±290	2,300 ± 1,300

Table A4.3. The average concentration (ng/m^3, n = 3) and standard deviation of non-diluted wood smoke samples collected 3" to 6" above two types of fires. Note that the fire conditions changed over the three sample replicates (flame vs smolder phase) so the variation between replicates is greater than normal. The data has not been corrected for the efficacy of the methods, thus the ketones are under-represented by this analysis. The ambient air concentrations have been subtracted from the emission data. Chemicals listed as "---" were not detected in two of the three replicates at concentrations that were above ambient air concentrations.. The data has been rounded to two significant digits of accuracy.

	Fir fire	Oak Fire
acrolein	630,000 ± 380,000	550,000 ± 200,000
2-methyl-1-propanal	12,000 ± 5,100	8,600 ± 11,000
methacrolein	52,000 ± 22,000	58,000 ± 14,000
methyl-vinyl-ketone	320,000 ± 210,000	290,000 ± 74,000
3-pentanone	10,000 ± 8,000	11,000 ± 1,700
2-pentanone	44,000 ± 31,000	58,000 ± 16,000
3-methylbutanal	10,000 ± 7,100	19,000 ± 7,900
crotonaldehyde	190,000 ± 100,000	180,000 ± 75,000
glycolaldehyde	41,000 ± 31,000	46,000 ± 33,000
hydroxyacetone	220,000 ± 240,000	240,000 ± 230,000
5-hexen-2-one	2,200 ± 2,100	21,000 ± 990
2-methyl-2-butenal	31,000 ± 16,000	41,000 ± 6,500
4-hexen-2-one	28,000 ± 13,000	39,000 ± 4,100
3-methyl-2-butenal	17,000 ± 3,200	14,000 ± 3,100
hexanal	28,000 ± 38,000	---
2-heptanone	13,000 ± 14,000	14,000 ± 9,100
2-furaldehyde	1,300,000 ± 180,000	3,800,000 ± 1,100,000
2-hexenal	15,000 ± 4,200	17,000 ± 1,000
heptanal	62,000 ± 37,000	32,000 ± 9,100
2-octanone	21,000 ± 4,600	11,000 ± 11,000
2-heptenal	7,100 ± 6,400	610 ± 73
octanal	48,000 ± 40,000	2,300 ± 2,300
benzaldehyde	160,000 ± 110,000	100,000 ± 47,000
nonanal	45,000 ± 34,000	3,400 ± 1,500
2-decanone	23,000 ± 11,000	8,600 ± 850
1,4-benzoquinone	35,000 ± 15,000	41,000 ± 4,600
o,m-tolualdehyde	23,000 ± 9,400	20,000 ± 5,300
p-tolualdehyde	9,200 ± 3,700	7,100 ± 3,100
2-ethylbenzaldehyde	5,300 ± 2,500	6,400 ± 460
decanal	20,000 ± 12,000	---
3,4-dimethylbenzaldehyde	6,300 ± 2,700	8,800 ± 1,000
glyoxal	160,000 ± 82,000	150,000 ± 200,000
4-methoxybenzaldehyde	920 ± 470	740 ± 190
methyl-glyoxal	300,000 ± 66,000	1,100,000 ± 260,000
3-phenyl-2-propenal	380,000 ± 240,000	910,000 ± 110,000
2,3-butanedione	240,000 ± 150,000	720,000 ± 200,000
2,3-pentanedione	32,000 ± 20,000	78,000 ± 10,000
3,4-hexanedione	24,000 ± 8,500	29,000 ± 4,400
3-hydroxybenzaldehyde	65,000 ± 25,000	100,000 ± 35,000
2,4-pentanedione	12,000 ± 6,600	14,000 ± 1,800
2,3-hexanedione	8,000 ± 4,100	12,000 ± 1,900
3,5-heptanedione	7,800 ± 4,100	11,000 ± 2,000
glutaraldehyde	10,000 ± 3,900	12,000 ± 1,900
1-naphthaldehyde	29,000 ± 27,000	11,000 ± 8,500

APPENDIX 5

Complete Field Notes & Sample Log

Saturday June 17, 2006, preparation for Putah Creek Sampling

I prepared the reaction tubes (~85 of them) today. I prepared the "**double reaction tubes"** that will have both mist chambers (and washes) emptied into the same reaction tube. The reaction tubes consisted of:

2mL HPLC-grade water

200μL of H_2O_2

400μL of PFBHA (75mM solution in methanol)

4mL hexane (trace grade)

All mixed into a 50mL test tube with a PTFE lined lid (which had been water washed before use).

I also prepared fresh spiking solutions by adding 10μL of stock acrolein-d_4 and benzaldehyde-d_6 solutions as well as 100μL of the stock acetaldehyde-d_4 solution to 880ul of acetonitrile (as to give 1 mL total volume). I prepared three separate vials so we can used a different vial each day as to reduce drift due to evaporative losses.

Lastly, I prepared the "carbonyl supermix #1" from the five concentrated stock solutions. This supermix has chemical concentrations ranging from about 8 to 10 ng/μL.

Sunday June 18, 2006

Left Davis at 04:40 for the Putah Creek site. I arrived at the site at about 05:20. Site setup took about 50 minutes, so the first samples were collected at 06:10. The standards and reagents were stored in an ice chest. Ozone, temperature, relative humidity, wind speed and direction were recorded during each sample. Two sets of mist chambers were used. Setup "A" used mist chambers #7 followed by #8 while setup "B" consisted of chambers #5 and #6. Each setup was powered by a Medo pump connected to a power inverter and a deep-cycle 12V battery. The same battery powered both pumps, but each pump had its own power inverter to reduce load. Each sample was spiked with the labeled standards 10 minutes before sample collection. Samples were collected according to the SOP.

The sample log is as follows (transcribed from field notes):

Sample period	Actual start time	Temp (°C)	RH (%)	O_3 (ppb, 3 measures)	Wind speed & direction	comments
June 18, 2006						
06:00	06:10	19.4	52	31	5.1 west	Top chambers were not rinsed prior to first sample.
08:00	08:00	24.9	52	33, 34, 36	3.5 west	Everything OK, gusty down valley wind
10:00	10:01	28.3	42	37, 38, 41	2-3 west	Gusts to 6.5, spilled 1 to 2 ml of the top bisulfite solution of sampler A
12:00	12:01	30.9	43	58, 63, 64	1.3 east	Wind calmed and switched direction.
Blanks	12:37					Prepared two field blanks
14:00	14:02	36.0	32	53, 57, 58	1.3 to 5.4	Variable wind direction from west and north

16:00	16:01	37.4	24	62, 63, 64	2.3-4.1 west	Samples A and B may have been mixed up.
18:00	18:00	30.8	32	57, 58, 57	3-11 west	Gusty down valley wind. I found that the small amber vials with the black caps slowly leaks when stored on their side. We switched to the test tubes only for the bisulfite storage.
20:00	20:00	26.3	36	48, 50, 49	3-12 west	
22:00	22:00	22.9	41	49, 42, 50	6-16 west	Cap from spiking solution fell on ground. Nothing seen in cap afterward. A fly got into the vial of Sample B. This sample was compromised and not extracted.
24:00	23:54	20.5	42	53, 44, 44	5-17.5 west	A tiny bit of spillage of A (lower chamber) after sampling.
June 19, 2006						
02:00	01:56	18.3	56	42, 40, 39	3-24.2 west	Big gusts from the west
04:00						Missed sample time
06:00	05:57	15.8	68	40, 34, 38	0-0.2 calm	Dropped syringe on ground. No apparent contamination. Rinsed three times with good water.
08:00	08:00	17.6	73	31, 35, 32	<1 calm	No problems. After sampling, I gave the columns a good washing with DI water followed by a rinse with HPLC water. I found two Ritz cracker wrappers behind the samplers.
10:00	10:02	25.5	47	43, 45, 46	1.3-3.1 SE	Switched deep cycle battery. There is a very small bug in sample A (smaller than an aphid).
12:00	12:01	27.4	40	54, 54,56	<0.5 calm	Few wind gusts from SE.
Blanks	12:35					Prepared two field blanks.
14:00	14:00	33.3	31	62, 63, 63	1.3-2.5 SE	
16:00	15:52	34.9	28	67, 71, 69	0.8-2.2 east	
18:00	17:55	31.9	32	70. 69, 69	1.1-3.6 east	
20:00	19:55	25.9	50	49, 50, 51	0.1-0.4 east	A small amount of sample solution from top chamber of A was spilled.
22:00	21:55	20.4	62	50, 51, 51	0-1 west	
24:00	23:55	19.8	65	50, 49, 49	1-5 east	
June 20, 2006						
02:00	01:55	19.4	67	45,45,46	1.4-6.2 west	
04:00	03:55	19.1	74	45, 44, 45	0-5 west	
06:00	05:55	17.5	80	40, 35, 38	0-5.6 east	Spike solution was spilled a little bit. Condensation very prevalent. Small bug in sample A.
08:00	07:58	21.5	64	36, 37, 38	1.2-3.0 west	Gusts to 9.8+. Started to use the new daily spike SLN. Gave the MCs a good DI water wash /HPLC water rinse after sampling.
10:00	09:56	21.5	64	52, 52, 52	<0.5 calm	At 10:31, conducted the "30 minute" sample test in duplicate. These were additional, non-standard samples.
12:00	11:55	31.9	30	56, 56, 56	0.5-2.5 east	
Blanks	12:20					Prepared two field blanks
14:00	13:53	33.6	32	60, 60, 61	1.5-2.6 east	
16:00	15:54	36.9	23	60, 61, 63	1.1-4.4 east	
18:00	17:55	34.9	28	78, 78, 78	0-2.1 east	Small amount of sample spilled from bottom chamber of B
20:00	19:55	28.6	39	58, 57, 59	0.3 calm	
22:00	21:55	23.9	51	46, 46, 46	0.3-0.7 east	Sample B lost because of bug.
24:00	00:01	23.8	50	48, 47, 47	0.5-1.1 east	

June 21, 2006						
02:00	02:01	22.3	56	41, 41, 41	0.4-2.0 west	Single sample due to lack of reaction tubes.
04:00	04:00	20.9	59	38, 38, 38	0-1.4 east	Single sample due to lack of reaction tubes. Spike solution spilled a little and cap fell on the ground. No noticeable contamination.
06:00	06:00	20.1	62	37, 35, 36	0-0.6 east	Single sample due to lack of reaction tubes.

Wednesday, June 21, 2006;

Calibration of mist chamber flow rates using the "DryCal DC-lite" primary flow meter (Bios International, serial #5917, Butler, NJ). The flows were measured in an identical fashion as the field collection, namely batter power (one battery with two power inverters and two pumps running at the same time) and 10 ml of solution in the mist chambers. The pumps were paired up with the proper mist chamber setup to maintain consistency. I also measured the flow rates using line power like we will have at Roseville and Parlier.

For setup A (MC #7 followed by MC #8):

Battery flow rates:	17.08	17.20	17.28	17.28	17.33	17.35 L/min
Line power flow rates	19.17	19.19	19.24	19.26	19.24	19.26 L/min

For setup B (MC #5 followed by MC #6):

Battery flow rates:	20.96	20.96	20.99	20.98	21.06	21.04 L/min
Line power flow rates	23.68	23.68	23.71	23.64	23.68	23.74 L/min

Thursday June 22, 2006:

I started to extract the Putah Creek samples as per the SOP. I extracted only the first day of the Putah Creek samples.

Saturday, June 24, 2006:

I finished the extraction of the Putah Creek samples. They are now all on the GC-MS.

I prepared the reaction tubes (see recipe on first page) and some bisulfite tubes using the "acidified sodium sulfate" method rather than the sodium bisulfite powder directly as was done at Putah Creek. The preliminary results are showing greater internal standard loss than before which can only be attributed to either 1) the differences in preparing the bisulfite solution or 2) the fact that the spiking standard is in acetonitrile. I do not suspect that the latter reason is likely since the carbonyls have 10 minutes to bind to the bisulfite before being put in the mist chambers. Therefore, I am going back to the old bisulfite formation method that has given good IS recoveries in the past.

Sunday, June 25, 2006:

Start sampling at the ARB site in Roseville. The address for the site is 151 North Sunrise Blvd, suite 510. This site is on the roof of the building and it is about 200m from Interstate-80 (I-80). Since we are interested in vehicle emissions, we decided to monitor traffic on I-80 when

collecting our samples to give an indication of traffic. We started counting the number of vehicles (cars + trucks + motorcycles) during a 30 second sample. Only eastbound traffic was counted on the first day (since it is easier to see those lanes) but we started counting both directions during the night of the first samples. Sampling started at 06:00 on June 25, 2006.

The sample collection setup is the same as the Putah Creek sampling but we are using line power to drive the vacuum pumps rather than batteries. We used the ARB met instrumentation for the temperature, wind, RH and ozone measurements. Their equipment is nice compared to our field devices.

The sample log is as follows (transcribed from field notes):
EB = east bound traffic on I-80 (vehicles per 30 second count).
WB = west bound traffic on I-80 (vehicles per 30 second count)
Vehicles = cars + trucks + motorcycles (anything that moves under its own power)
Wind speed is in knots!

Sample period	Actual start time	Temp (°C)	RH (%)	O_3 (ppb)	Wind speed (knots) & direction (degrees)	EB (veh)	WB (veh)	comments
June 25, 2006								
06:00	06:00	19.9	58.9	86.5	2.9-3.5, 101°			No problems, rinsed all chambers with spiked bisulfite. Traffic on I-80 is light (Sunday at 6:00 am- no surprise there)
08:00	07:55	21.5	55.6	27.2	2.7-3.5, 150°	24	sim	Light and fast traffic
10:00	09:55	26	45	39.6	6.8, 130°	20		There is a "sewer" smell on the roof during this sampling time
12:00	11:53	30.8	39	55.7	0.8, calm	30	sim	The sewer odor is still present. Evaporation is becoming significant, but it also cools the mist chamber solutions. It is very hot due to reflected light. (hotter than met reading).
Blanks	12:00							
14:00	13:53	35.0	29.9	79.8	4.7, 245°	51		Traffic moving well. I added 5 ml of water to the bottom MCs to account for evaporation. There is pretty heavy traffic on Sunrise Blvd. Prepared reagent blank and 10 ul Cal at 14:30.
16:00	16:01	37.3	27.5	95.5	4.9, 221°	34		Erin was getting trained and was going to take over for the first evening shift.
18:00	18:02	37.9	25.6	84	5.65, 219°	less	45	Added 5 ml of water to lower MCs, 3x rinse of both upper MCs instead of 2x. Did not clean bottom of top MC.
20:00	20:00	34.3	34.9	84.0	5.3, 172°	33	33	Smells like food.
22:00	21:59	30.2	42.3	46.7	9.0, 151°	19	12	Snyder column broke. Wind blew it off of stand as it was resting while rinsing.
24:00	---	---						Missed it.
June 26, 2006								**A "SPARE THE AIR" day**
02:00	01:59	25.7	39.7	35.0	5.0, 130°	1	4	Small chip in synder column "B"
04:00	03:56	24.8	43.5	33.2	2.4, 125°	6	3	

06:00	05:59	23.2	50.3	85.3	3.0, 140°	19	30	
08:00	07:59	24.9	47.5	28.0	2.0, 175°	39	31	Smells like emissions
10:00	09:55	27.2	45.5	42.6	5.7, 146°	41	44	They are re-paving the parking lot to the south. I can smell the tar. I think I smelled the "sewer" odor again. There is a fair amount of activity at the construction site across Sunrise Blvd. They are in the "earth moving" stage with lots of heavy equipment.
12:00	11:54	31.9	36.1	61.5	5.6, 195°	43	48	I can still smell tar. I am also smelling Chinese cooking (hot oil). The air conditioning units are dripping water onto the roof
Blanks	12:37							Prepared 2 field blanks, one reagent blank and the Cal 10µl standard.
14:00	13:54	35.4	32.5	92.9	3.9, 204°	37	40	Added 5 ml of water to the lower chambers to counteract evaporation. I still smell tar and cooking oil. People are removing the root tiles on the nearby building. The temperature on the roof in the shade at ground level was 40.9°C. That is hot!
Note	15:00	36.4				32	31	At 15:00h, the ambient ozone reached 101.1 ppb. At 15:09, there was a traffic jam in the west-bound I-80. The vehicle count was 32 vehicles/30 seconds, but the traffic was moving slowly (<20 mph)
16:00	15:52	37.9	26.5	103.8	2.0, 160°	39	28	Traffic jam in the westbound I-80 lanes at the Douglas merge. Traffic <10mph. Ozone was 107 after I was done rinsing the chambers. Also, I am not feeling very good.
18:00	18:03	38.2	21.7	94.1	3.7, 179°	59	35	Added 5 ml of water to lower chambers to account for evaporation.
20:00	20:00	34.6	25.9	57.9	7.5, 188°	29	24	
22:00	22:03	29.4	31.1	41.4	3.75, 143°	20	15	
24:00	24:00	27.8	35.0	34.5	4.9, 118°	4	6	
June 27, 2006								
02:00	---							Missed it, alarm failed
04:00	---							Missed it, alarm failed
06:00	05:59	24	53.2	84.5	1.6, 336°	28	42	Roofers are tearing off the roof right next to us.
08:00	07:55	22.3	59.1	9.8 (?)	5.1, 129°	55	58	Roofers are pulling off tiles and putting down plastic. They are stirring up a lot of dust (The PM people will want to know about that!). I smell tar again; there are still people repaving the parking to in front of RiteAid. Ozone meter gave a ridiculously low ozone value. I re-checked it after finishing the samples and I got a value of 18.8 (at 08:21)
10:00	09:55	27.2	42.3	35.2	5.3, 134°	32	54	I smell the tar and "sewer smell" again. I also smelled cooking while I

								was rinsing the columns.
Cal	10:35							I prepared a calibration curve and a reagent blank on the roof. The smell of tar is significant so our "reagent blank" may not be as clean as it should be.
12:00	11:53	30.3	31.3	52	3.5, 31°	32	25	Smell of oriental food
Blanks	12:30							Smell of tar hangs in the air, so I am not sure that they are going to be the best "blanks". They will certainly be cleaner than the samples. I will not use these for MDL determination.
14:00	13:52	33.3	29.7	58.1	5.4, 180°	55	54	There is a high thin cloud layer that is cutting down on sunlight intensity. Evaporation from MCs is becoming significant.
Exp	14:28	32.0	30.1	50.5	5.3, 167°			Experimental 30 minute samples started. I added 10 ml of water and 10 ml of spiked bisulfite to the lower MCs. The water was added to counteract evaporation during this long sample. I am more interested in the loss of the labeled standards over 30 minutes compared to the normal 10 minute sample than I am about the resulting concentrations. I powered down the pumps after 20 minutes to allow solution trapped in the snyder columns to drain back into the MCs, but everything was still running fine before I did this.
16:00	15:58	32.6	30.4	65.0	7.8, 199	49	35	WB slight backup of cars. Slight smell of tar. 5ml of water added to lower MCs.
18:00	17:58	32.5	17.6	59.0	6.67, 150	54	40	5ml of water added to lower MCs
20:00	19:58	29.0	27.5	50.2	7.9, 163	42	24	Smells like cooking oil
22:00	22:00	26.1	33.6	45.5	8.2, 120	17	17	
24:00	24:00	24.1	39.2	47.6	6.12, 165	10	10	
June 28, 2006								
02:00	02:00	22.4	41.4	44.5	7.5, 128	1	2	
04:00	04:01	20.9	48.0	39.0	5.0, 130	3	4	Column B slid onto syringe and cracked it in half.
06:00	06:55	19.7	57.4	28.4	3.7, 150	26	43	Sample time off by one hour (alarm was off by an hour).

Total number of samples: 66 (two failed QA/QC), Blanks and calibrations not counted.

Saturday July 8, 2006

Preparation for Roseville II or Putah Creek II. I prepared 200 bisulfite tubes and 100 reaction tubes (recipe on first page), so that is enough materials for the whole sampling time. I also prepared new labeled spiking solutions (one for each sampling day) and opened a new ampule of the carbonyl supermix and transferred it to a screw cap vial.

I was unable to get the key for the Roseville ARB site, so I am going to re-sample Putah Creek since I desperately need a control site and the previous sampling effort was a bust due to contamination and bisulfite solution problems. This sampling event does not fulfill any ARB contractual obligations, but I think it is necessary to understand the behavior of acrolein in Roseville. After all, you need to know what the baseline is before you can assess any enrichment from urban activities.

Sunday July 9, 2006, Putah Creek Episode II.

I drove out to Putah Creek and set up the site. Sampler A is MC #7 followed by #8 and Sampler B is #5 followed by #6 like all the previous sampling events. All the samplers and ozone meter were powered by batteries. Each MC sampler had its own power inverter. The ozone meter was run off a separate battery or the same battery as the samplers, but at a slightly different time (during the spiking phase) as to avoid excessive power drain. The ozone meter requires about 10 minutes to warm up before it gives consistent measurements.

I decided to add a sampling time at 07:00 to try to capture the early morning spike that was observed at Roseville. I do not expect it at this site, but I want enough samples to PROVE it isn't there.

The thermometer was hung in a tree about 5 feet above the ground. It was shaded by an aluminum tee-pee that was open on one side to allow for good air circulation.

Sampling commenced at 06:00 on July 9, 2006.

The sample log is as follows (transcribed from field notes):
DV = down valley wind (from the west), UV = up valley wind (from east)

Sample period	Actual start time	Temp (°C)	RH (%)	O_3 (ppb, 3 measures)	Wind speed (km/h) & direction	comments
July 9, 2006						Sunday
06:00	06:01	21.8	63	44, 44, 43	2 – 5 DV	Tom collecting samples. Sampler A = MC #7 and #8, Sampler B = MC #5 and #6. I rinsed all mist chambers with spiked bisulfite before the first sample. Sample 06:01B looks strange in the test tube. Something is causing the aqueous solution to bead up on the walls (as if oily)
07:00	06:56	23.0	61	41, 41, 42	5.2 – 7.4 DV	
08:00	07:55	25.6	56	39, 40, 42	1 – 3 DV	No problems
10:00	09:55	31.4	41	43, 44, 44	1.9 – 2.3 DV	No problems
12:00	11:55	37.5	34	85, 85, 85	3.2 – 5.4 UV	Wind changed direction and the temperature increased along with the ozone readings. I added 5 ml of extra water to the lower MCs, but it was not needed.
Blanks	12:28					Prepared two field blanks and one 10µl calibration solution. Note: I forgot to prepare a reagent blank today, so I made a second one on the last day to make up for it.
14:00	13:56	39.1	31	96, 89, 103	1.6 – 5.2 UV	
16:00	15:58	45.5?	21	63, 68, 63	0.9 – 3.1 UV	Lisa collecting samples. I am not sure I believe the temperature reading. This sample was collected by an undergrad student, so they may not have noticed if something was wrong (e.g.

						sunlight leaking in the side of the tee-pee.)
18:00	18:00	39.9	21	62, 70, 64	0.1 – 0.5 DV	Mist chamber #6 was broken. From now on, Sampler A = #7 followed by #3 Sampler B = #8 followed by #2
20:00	19:58	31.8	30	61, 61, 61,	0.1 – 0.6 UV	
22:00	21:55	27.6	36	59, 50, 51	0.3 – 1.1 DV	
24:00	00:25	24.1	24	47, 49, 49	0 – 2.0 DV	Sample collection a little late.
July 10, 2006						Monday
02:00	02:04	22.3	46	44, 44, 45	0 – 0.5 DV	Nick collecting samples
04:00	04:05	20.8	55	38, 41, 37	0 – 7.5 DV	
06:00	06:05	19.4	67	33, 33, 34	4.8 – 9.6 DV	
07:00	06:55	19.6	69	28, 33, 29	1.6 – 6.1 DV	
08:00	07:58	21.9	59	34, 34, 34	4.4–10.2 DV	Tom collecting samples
10:00	09:54	29.9	42	38. 37, 39	Calm <0.5	
Note	11:15					Prepared a calibration curve (0, 1, 3, 10, and 30 µL of supermix). I skipped the 100µl standard since nothing at Roseville was that high.
12:00	11:55	33.6	34	54, 53, 51	2.3 – 5.0 UV	
Blanks	12:30					Prepared the two field blanks. Field blanks mixed up during extraction. I think I extracted one blank into two centrifuge tubes. I combined the two tubes that I thought belonged together, but check the labeled spike values carefully. This mix-up may also involve the 02:00A sample.
14:00	13:56	35.6	32	63, 63, 60	1.9 – 3.6 UV	
16:00	16:02	39.0	29	63, 64, 64	3.7 –4.4 DV	Erin collecting samples. Wind gusts to 6.4.
18:00	18:00	34.5	31	58, 57, 57	4.0 – 6.5 DV	Lots of gusts. Some leakage in Sample A when shaking.
20:00	20:00	28.4	40	41, 41, 41	4.1 – 5.8 DV	
22:00	21:57	25.6	44	36, 36, 36	5.2 – 7.5 DV	
24:00	24:00	23.4	50	33, 33, 32	4.0–8.0 DV	Nick collecting samples. Glass flask left on Chamber A for sample. Sample still retrieved, but then the sample spilled ~ 10 ml. Just a bad sample! I agree- half the hexane layer was missing!
July 11, 2006						Tuesday
02:00	02:00	21.6	55	33, 33, 32	1–5.5 DV	Battery to ozone meter and light died. Using last battery to run ozone meter after samples were collected. No light (full moon)
04:00	04:05	19.9	68	32, 28, 32	5–9.6 DV	One vial of solution (pre sampling) spilled on outside of column B. Both batteries dead. Attempting to retrieve fresh batteries before next sample.
06:00	06:00	18.6	70	26, 26, 28	7.3–11.0 DV	
07:00	06:55	18.1	72	27, 26, 26	4.7–11 DV	Small bug in sample B
08:00	07:56	21.0	58	29, 30, 29	4.0–8.2 DV	Tom collecting samples.
10:00	09:54	27.4	43	32, 33, 34	2.1–5.0 DV	Prepared 10µL calibration standard at the same time. No rinse of top chamber of sampler B. There is a small piece of foreign material in the MC. The chamber was well washed with HPLC water.
12:00	11:55	31.9	32	43, 43, 43	1.9–5.2 DV	The wind is still coming down valley. On other

						days, the wind would have switched directions by now.
Blanks	12:30					Prepared two field blanks and two reagent blanks. I forgot the reagent blank on the first day, so the second reagent blank today was to make up for the missed one.
14:00	13:51	33.9	31	50, 52, 53	5.2–9.8 DV	
16:00	16:01	34.9	27	46, 59, 48	4.9–8.8 UV?	Lisa collecting samples. The wind is reported from the east, but I think that the directions are mixed up. The ozone meter was not at equilibrium yet.
18:00	17:58	30.1	30	42, 47, 43	5.0–12.2 DV	
20:00	20:00	25.4	31	39, 43, 41	3.8–6.2 DV	
22:00	22:02	20.8	38	36, 42, 38	0.1–0.6 UV	
24:00	24:00	18.5	55	40, 38, 39	0–3.2 DV	Nick collecting samples.
July 12, 2006						Wednesday
02:00	02:00	16.6	63	37, 35, 38	0–7.2 DV	Gusts eastwards
04:00	04:00	15.0	69	36, 34, 36	5.6–12.4 DV	
06:00	06:00	14.1	74	34, 33, 33	1.2–7.9 DV	
07:00	06:55	14.9	72	34, 31, 34	0.2–1.1 DV	

Total number of samples: 81 (one was lost in the field), Blanks and calibrations not counted.

Thursday July 13, 2006

I started extracting the samples from the first sampling day according to the SOP. Any problems or comments during the extraction process are noted above in the sample log in RED. The samples were placed on the GC-MS immediately after extraction was complete. The injection standard solution has changed a little. It now contains octafluoronaphthalene, tribromofluoroebenzene, dibromonaphthalene and hexabromobenzene and it is prepared in toluene to reduce evaporation during pipetting into a large number of samples. These injection standard compounds elute over a wide range of times in the chromatogram and serve as excellent time markers.

Friday July 14, 2006

I extracted the second day of Putah Creek samples.

Saturday July 15, 2006

I extracted the last day of Putah Creek samples and started preparation for Roseville Episode II (aka "Return of the Heat Wave" based on weather forecasts). I prepared 160 bisulfite tubes, after which I ran out of solution. I prepared another liter of solution, but I want it to equilibrate for a day before I put it in vials. I also prepared 48 double reaction tubes (see recipe on first page). I ran out of right-sized test tubes. The rest of the tubes were just liberated from today's extractions. I washed them and put them in the furnace. I also prepared a fresh batch of injection standards. I added 3-chloro-2,4-pentanedione to the labeled spike mix. Therefore, the labeled mix now consists of 10 ng/µL of acrolein-d_4, benzaldehyde-d_6, and 3-chloro-2,4-pentanedione and 100 ng/µL of acetaldehyde-d_4. I also opened a new ampule of the carbonyl supermix and transferred it to a screw-cap 2ml vial. The rest of the equipment was packed up and ready to go.

Sunday July 16, 2006, Roseville ARB Episode II "Return of the Heat Wave"

This was another early morning (left Davis at 04:03). I got to Roseville ARB and setup the apparatus. I washed all the mist chambers with spiked bisulfite solutions and 60 ml of HPLC-grade water. I used the same MCs as was used in the Putah Creek II sampling even after the breakage, namely Sampler A is MC #7 followed by #3 while Sampler B is MC #8 followed by #2. The Hi-Vol sampler is running, so I moved the MCs as far away from the Hi-Vol while still being on the platform.

The plan is to collect hourly samples from 04:00 to 08:00 when the early morning spike in acrolein concentrations is observed and then every other hour for the rest of the day. Sampling commenced with the 06:00 sample on 7-16-06.

The sample log is as follows (transcribed from field notes):
EB = east bound traffic on I-80 (vehicles per 30 second count).
WB = west bound traffic on I-80 (vehicles per 30 second count)
Vehicles = cars + trucks + motorcycles (anything that moves under its own power)
The values in parenthesis indicate the number of TRUCKs in the counted vehicles. In other words, how many of the vehicles counted were trucks.
Wind speed is in knots!

Sample period	Actual start time	Temp (°C)	RH (%)	O_3 (ppb)	Wind speed (knots) & direction (degrees)	EB (veh)	WB (veh)	comments
July 16, 2006								**Sunday**
06:00	05:55	22.5	59.9	NA	0.71, erratic	9(0)	5(1)	Tom collecting samples. No problems. No noticeable smells or activity near site. No ozone value available due to calibration routine.
07:00	06:55	22.7	51.0	28.8	1.6, 161°	7(0)	12(2)	No problems.
08:00	07:55	23.8	53.1	35.5	1.0, erratic	21(0)	16(0)	No problems.
10:00	09:55	27.1	43.6	48.7	4.1, 306°	48(1)	52(4)	Nice breeze from I-80
12:00	11:55	32.3	34.3	68.9	7.6, 296°	49(0)	41(1)	Added 5 ml of water to lower MCs. There is a nice breeze directly from I-80.
Blanks	12:31							Prepared 2 field blanks.
Note	13:00							Prepared 1 reagent blank and the Cal 10ul STD for the day
14:00	13:54	36.1	26.7	76	6.4, 311°	47(1)	38 (1)	Erin collecting samples. Added 5 ml of water to lower columns. 50.6°C on sampler thermometer
16:00	16:00	38.25	15.1	71.5	4.74, 281°	35(1)	39(0)	Slow traffic west bound. Collection time ± 15 sec. No extra water added to MCs. 49.4°C on sampler thermometer
18:00	18:02	39.2	4.35	60.7	5.5, 300°	29(0)	33(0)	Added 4 ml of water to lower chambers. Some spillage in collecting samples, especially B. sampler thermometer 45.1°C
20:00	19:58	38.3	3.6	43.5	2.6, 302°	27(0)	30(1)	Sampler thermometer 36.1°C
22:00	22:00	33.8	19.5	12.7	1.6, 16°	20(1)	14(2)	
24:00	24:00	28.0	33.7	36.8	2.4, 65°	17(0)	7(1)	Nick collecting samples

								Sampler thermometer 25.9°C
July 17, 2006								**Monday**
02:00	02:00	26.4	38.0	38.2	5.3, 87°	3(1)	2(1)	Sampler thermometer 24.9°C
04:00	04:03	25.1	45.0	18.0	1.0, 245°	4(3)	5(2)	Sampler thermometer 22.1°C
05:00	05:02	24.4	49	-6	2.4, 356°	7(2)	14(1)	Sampler thermometer 21.9°C Sample 05:00B leaked when shaken in the lab.
06:00	05:56	23.2	50.5	CAL	3.1, 313°	36(2)	37(0)	Tom collecting samples. Mike Poore collected 3 canister samples at 06:01.30 for the intercomparison. Sunrise occurred between 06:10 and 06:15.
07:00	06:54	23.7	46.7	3.5?	1.1, 340°	44(3)	47(2)	West bound traffic slow. Ozone meter gave a low reading. A follow-up reading at 07:20 was also low at 7.8. At 07:33, it was 8.6ppb.
08:00	07:54	26.3	39.3	16.4	1.5, 300°	52(6)	55(2)	West bound traffic still slow. Ozone meter still giving low values. Sampler thermometer 30.6C
Note	08:33							Prepared calibration curve from 0, 1, 3, 10 and 30 µL of the carbonyl supermix. This also cover the reagent blank for the day (= Cal 0). The cal curve was prepared on the roof (to avoid contamination indoors)
10:00	09:54	30.0	34.9	43.2	3.4, 342°	36(2)	35(2)	
Note								Collected four on-road samples on I-80 (n=2) and Douglas blvd (n=2) See separate log for these samples.
12:00	11:59	35.5	18.6	63.7	6.8, 319°	37(4)	42(2)	Sampler thermometer reads 48.8C Added 5 ml of water to lower chambers.
Blanks	12:34							Prepared two field blanks. It is HOT on the roof top!
14:00	13:56	39.2	7.65	66.5	4.3, 310°	39(1)	37(6)	Erin collecting samples. Added 5ml to lower chambers. Sampler thermometer 53.3C
16:00	16:00	41.4	4.68	61.4	6.9, 308°	40(3)	25(4)	Slow WB traffic, sampler thermometer 51.9C. Added 5 ml of water to lower chambers
18:00	18:00	41.5	3.95	50.5	6.2, 298°	36(1)	31(2)	Added 5 ml of water to lower chambers.
20:00	19.58	39.6	15.7	64.2	3.2, 165°	20(1)	23(4)	
22:00	21:58	33.9	27.3	55.2	4.1, 125°	10(0)	13(1)	
24:00	00:01	30.5	36.8	46.7	2.0, 62°	16(1)	2(1)	Nick collecting samples. Sampler thermometer 28.4C
July 18, 2006								**Tuesday**
02:00	02:00	26.7	49.8	33.0	4.75, 122°	5(1)	2(0)	Sampler thermometer = 25.6, Small spillage of the top chamber, second rinse of sampler A, < 2 ml.

04:00	04:00	25.8	43.4	36.2	4.0, 125°	3(2)	4(2)	Sampler thermometer = 24.4
05:00	05:00	24.7	45.9	?	5.6, 122°	11(1)	6(1)	Sampler thermometer = 23.5
06:00	06:00	25.2	45.4	Cal	2.5, 112°	22(3)	30(2)	Sampler thermometer = 23.6
07:00	06:55	24.7	53.6	14.4	3.3, 130°	48(7)	47(2)	Cahill collecting samples
08:00	07:55	25.6	53.9	24.5	4.6, 124°	43(3)	35(6)	
10:00	09:57	29.3	35.3	47.9	6.8, 148°	39(5)	27(2)	I may have accidentally stopped the sampler at 10:05 instead of 10:07. Check to see if these results are low.
Note								Went to Roseville rail yard to collect samples downwind of repair facility. See special log below.
12:00	11:55	33.4	28.1	67.5	5.6, 205°	42(3)	58(3)	I smell Asian food. Sampler temp = 41.3C. The breeze keeps the temperature down (or at least it does not feel as bad.)
Blanks	12:35							Prepared the two field blanks, one reagent blank and one 10µl calibration standard.
14:00	14:00	37.4	22.1	99.8	5.3, 234	33	35	Lisa collecting samples. Added 5 ml of water to lower MCs.
16:00	16:00	16:57	17.6	112.8	3.7, 218	52	31	Added 5 ml of water to lower MCs. Spilled a little from the bottom of column A. Westbound traffic moving slowly
18:00	17:55	38.4	13.9	83.9	7.1. 195	56	27	Added 5 ml water
20:00	20:03	35.7	21.9	72.0	4.6, 182	32	16	Added 5 ml water
22:00	21:57	32.6	26.9	53.3	3.1,131	14	13	
24:00	24:00	29.3	39.5	44.9	6.8, 150	8(1)	4(1)	Sampler temp =28.1
July 19, 2006								
02:00	02:00	26.8	40.2	36.9	6.5, 130	4(1)	1(0)	Sampler temp 26.6
04:00	04:00	26.5	36.4	37.8	4.2, 142	3(1)	3(1)	Sampler temp 26.3
05:00	05:00	26.3	36.4	Cal	4.75, 136	17(8)	8(3)	Sampler temp 26.1
06:00	06:00	26.2	35.5	cal	6.0, 150	25(2)	22(4)	Sampler temp 26.4
07:00	07:00	26.2	35.2	32.2	3.6, 149	47(2)	48(0)	Sampler temp 27.9

On-road samples:

These samples used MC # 5 and #10 powered by pump "A" and a power inverter plugged into the cigarette lighter. The MCs were mounted at a slight angle to allow the snyder column to sit on top, but it was not really needed since no mist was escaping anyway. The outside air was pulled through a 2 m length of Teflon tubing that was tied (nylon string) to the light bar of my Jeep. The tubing extends about 10 cm in front of the light bar, so we should not have any effect of the string on the sampling. The sample collection is the same at the fixed site except: 1) The time between the bisulfite spike and the start of sample was not always 10 minutes, but ranged from about 5 to 10 minutes depending on how fast the samples could be turned around, and 2) the water rinses of the column were not measured by a syringe, but were "eye-balled" in the interest of speed. Therefore, the volume of water will vary a little, but this really does not matter much since water is not a reagent and its volume (even in the fixed samples) is not critical.

The goal is to sample the roads around the ARB site. I want to sample both I-80 and the surface streets where there is stop lights to stop cars. I assume cars at freeway speeds are more efficient than start-and-stop traffic conditions on surface streets.

In-car #1:
I-80 westbound from Douglas Blvd to Winter street. Started 10:32, duration 10 minutes. Distance covered 10.6 miles. Speed approximately 65 MPH. I stayed in the second lane from the left when possible. (next to fast lane). There is moderate traffic but it is moving well.

In-car #2
I-80 eastbound from Winter Street to Douglas Blvd (return trip). Started 10:48, duration 10 min 30 seconds. Distance covered = 10.4 mi. Traffic same as westbound (moderate, but moving fast).

In-car #3
Douglas Blvd from North Sunrise to (next big road after Barton, has a shopping center and a Taco Bell). Start 11:10, duration 10 minutes. Distance covered 5.1 mi. Generally in fast lane on Douglas. I was first out of the lights for about ½ the distance (missed everyone stepping on the gas). Last 1/3 of distance was rather open (in Granite Bay). I added about 4 ml of water to the column before starting.

In-car #4
Douglas Blvd from (Barton + a little) to N Sunrise. This is the return from #3. Distance 5.1 mi. Duration = 10 minutes, 30 seconds. Start 11:28. I chipped the top of the lower MC, so there is some ground glass powder in the sample. It should not affect anything. I added 4-5 ml of water to the column before sampling.

In-car #5
I-80 East from Douglas. Start 14:20, duration 10 minutes. Distance covered 10.9 mi. I made it to Newcastle Road. The traffic cleared out a little after Penryn (sp?). Traffic moving at 65-70 MPH.

In-car #6

I-80 (return from #5) Newcastle to Douglas. Distance = 10.9 mi. Duration = 11min, 30 sec. There was a backup at Douglas, hence the slower time.

In-car #7
Roseville ramble. West Douglas to railyard (wind from railyard), south to Cirby, east to Sunrise. I added water to the lower MC. It is hot and dry out there! Start 15:06. Distance = 3.2 mi, time 10 minutes.

In-car #8
Sunrise Blvd. Start at Cirby, go south for two minutes, U-turn and head north. Pass Douglas and end at Automall Drive. Start 15:24. Duration 10 minutes, distance covered 4.4 miles. I added water to the lower chamber.

Rail yard Samples, July 18, 2006:

I talked to a Placer county air pollution control district person this morning and he mentioned that they get 1200ppb NO at the rail yard, so I decided to burn up the last few extra samples sampling the rail yard. There is a reasonable south-west breeze, so I located at Church street between Ash and Circuit streets. This site is DIRECTLY downwind of the main repair facility. I am about 40m from the nearest idling train. I am 25 m (paced distance) from the fenceline. The smell of diesel fumes is strong, but not overpowering; the wind must dilute it somewhat. This location was chosen for the maximum impact, so it is not a random (or typical) condition.

The sample collection was the same as the in-car samples yesterday. (MC #5 followed by #10, powered by an inverter). All three samples were collected at the same spot. This also means that I can spike the next sample while the current one is running. This speeds-up the process.

Sample #1: Start 10:50. Duration 10 minutes, no problems.
Sample #2: Start 11:05. Duration 10 minutes, no problems.
Sample #3: Start 11:19. Duration 10 minutes. I somehow forgot to add the bisulfite to the top chamber. I added water about 4 minutes into the sample. I added the bisulfite after collection (to maintain the proper reagent ratios). I do not think this will have a major impact since the bottom chamber was running fine and it does most of the collection.

July 20, 2006:

I started the Roseville extractions today. Everything went smoothly. I used the injection standard 3.1 that contains octafluoronaphthalene, tribromofluorobenzene, dibromonaphthalene and hexabromobenzene.

July 21, 2006:

Extractions continue. There are A LOT of samples that need extracting.

July 22, 2006:

Extractions completed. All samples are on the machine and are being run.

Total Samples from Roseville Episode II:

88 “normal” samples
8 “in car” samples
3 Rail yard samples
Total: 99 samples (excluding calibration standards, field blanks and reagent blanks)

Measure flow rates of new MC combinations using the DryCal lite. The MCs have 10 ml of water in them to simulate a sample. I tested the two pumps under load and they effectively had the same slow rate. Pump A averaged about 0.1 L/min less than Pump B. Pump C seemed to behave and gave values about 0.15 L/min less than Pump B. This pump was not used since it failed in the field once. It seems to be OK now, so it would be good as a backup.

Sampler A: (#7 followed by #3)
Line power = 14.28, 14.29, 14.30, 14.30, 14.30 Avg = 14.29 L/min
Battery power = 13.08, 13.08, 13.07, 13.10, 13.08 Avg = 13.08 L/min

Sampler B: (#8 followed by #2)
Line power = 15.80, 15.80, 15.77, 15.78, 15.72 Avg = 15.77 L/min
Battery power = 14.67, 14.66, 14.62, 14.59, 14.60 Avg = 14.62 L/min

In-Car sampler (mobile): (#5 followed by #10)
Battery power = 21.89, 21.90, 21.87, 21.87, 21.78 Avg = 21.86 L/min

Summary for Summer 2006 ARB acrolein sampling:

Putah Creek Episode I:	0 useable samples (contamination and bisulfite solution problems)
Roseville Episode I:	66 valid samples (two failed QA/QC)
Putah Creek Episode II:	81 valid samples (one lost in the field)
Roseville Episode II:	88 valid samples (tentative pending QA/QC evaluation)
Total	235 samples (excluding blanks, calibrations, etc.)

Roseville site map (from Google Earth).

Local view- Many Asian restaurants to the south in the shopping complex. Sunrise Blvd to the west.

Expanded view: I-80 to the west and Douglas Blvd to the south. The Roseville rail yard is far to the west.

Winter Acrolein Sampling I
Return to Roseville

12-14-06

I reassembled the sampling equipment and cleaned the glassware. I re-baked the bisulfite and the reaction tubes to make sure that organic material had condensed on the glassware during storage. The tubes were stored capped so they should have still been clean, so this was just a precaution.

I also started to prepare the sampling solutions. I prepared a big, 4-L jug of the bisulfite solution right in the HPLC water bottle by adding 50.4 g of sodium sulfite and 21.7 ml of pure sulfuric acid (18 M). The solution is best to allow it to sit a couple of days before using it. I also prepared the 75 mM PFBHA solution in methanol. This was achieved by adding 0.938 g of PFBHA (molar mass = 250g/mol) to a volumetic flask and then adding purge-and-trap grade methanol to bring the volume up to 50 mL.

12-15-06

Today was the day that I prepared the sulfite and reaction tubes for sampling. I estimate that I will need 78 sample tubes for the samples and field blanks. Add another 12 for reagent blanks and standards and a few duplicates in case of breakage. Therefore, I think I will need 100 sample vials. I prepared 110 reaction tubes to allow for additional intercomparisons between the mist chamber method and the canister method. This may also allow me to run a few extra-long test samples in the chilly conditions of winter when evaporative losses should be less. I may need these to get a low MDL.

The reaction tubes were the "double" reaction tubes consisting of:

2 ml of 1.8 M H_2SO_4
200 µL of H_2O_2
400 µL of 75 mM PFBHA
5 mL of hexane.

The H_2O_2 was from a new, unopened bottle as was the hexane (trace grade). The acid solution was prepared from new HPLC water and recently-purchased 18M H_2SO_4 bottle. The PFBHA solution was prepared yesterday (see above). I shook all the reaction tubes to mix the reagents and test for leaks. I found three leaky tubes that were subsequently discarded. That brings the total of good reaction tubes to 107.

I prepared 220 of the 10mL 0.1M bisulfite reaction tubes.

I also picked up a key for the Roseville site from 13th and T street office.

12-16-06

Last day of preparation. I created a new set of the internal standard solutions by adding 10µL of the concentrated internal standard stock solutions to 0.97 mL of acetonitrile so the final volume will be 1 mL and the final concentration will be about 10 ng/µL). The internal standards were: acrolein-d_4, benzaldehyde-d_6 and acetaldehyde-d_4. I opened a new ampule of the carbonyl supermix for the carbonyl standards and transferred it to a screw-capped vial for easy use in the field. NOTE: I forgot that acetaldehyde needed a 10-fold greater concentration for the spiking solution, so the concentration I used was 10-fold too low, so it is unlikely that we will observe

this internal standard. Luckily it is not used very much and does not affect the acrolein quantification.

I took care of miscellaneous items needed for field sampling (print out data sheets and sample labels) and then loaded up the Jeep.

12-17-06

Start of field sampling. I left Davis at about 04:20 and arrived in Roseville at about 05:00. I unpacked the critical materials and setup the samplers on the roof. Sampler setup "A" consists of MC #3 followed by #2. Sampler setup "B" was mist chamber #7 followed by #8.

I washed all four mist chambers will a spiked bisulfite solution to cover up any active sites and to wash out any contaminants that got in the chambers during transport. The bisulfite rinse was followed by two water rinses like a normal sample. I barely got everything ready for the 06:00 sampling time.

The sample log is as follows (transcribed from field notes):
EB = east bound traffic on I-80 (vehicles per 30 second count). West bound traffic cannot be seen anymore due to a new building.
Vehicles = cars + trucks + motorcycles (anything that moves under its own power)
Wind speed is in knots!

Sample period	Actual start time	Temp (°C)	RH (%)	O_3 (ppb)	Wind speed (knots) & direction (degrees)	EB (veh)	comments
Sunday Dec 17, 2006							**Sunday**
06:00	06:02	2.2	74	4.1	2.3 @ 86°	---	Tom collecting samples. Rinsed MCs with spiked bisulfite solutions before use. There is frost on the platform. There was no evaporation from the MC solutions. Setup A = MC #3 and 2 Setup B = MC #7 and #8.
08:00	07:53	0.61	80	3.8	2.1 @ 108°	18	I can no longer see westbound traffic due to a new building and a high K-rail that hides smaller cars. I also smelled a trace of wood smoke, but not as much as during sample prep. The water I spilled at 06:00 has frozen. The sun has risen, but the platform is still in shadow.
10:00	09:55	6.1	69	17.3	7.3 @ 141°	38	No problems. The weather is clear, sunny and cold.
Cal and reagent blank	10:43						Prepared reagent blank and 10µL carbonyl supermix standard on the roof. They were allowed to react for 10 minutes before being put in the reaction tubes.
Field Blank	11:08						Added the field blanks to the MCs. They were spiked with the

							IS like normal samples.
12:00	11:54	8.1	60.4	21.8	2.8 @ 146°	33	No problems. I smelled French fries during sampling.
Experimental 30 min sample	12:28	8.5	57.4	23.4	1.8 @ 110°	59	This is the start of a 30 minute sample to try to improve sensitivity by a longer sampling time. It worked OK in the summer and we should have even lower evaporative losses now due to the lower temperature. Almost no water is being lost over 10 minute sampling period. I could smell Chinese food when starting the sample. There was not much evaporation, but a fair amount of the lower MC solution was transferred to the upper chamber.
14:00	13:55	9.5	49.8	29.7	2.7 @ 207°	37	No problems.
16:00	15:51	9.7	53.3	25.4	6.6 @ 296°	55	The sun angle getting low. It will go down soon. Sun went down at 16:38.
18:00	17:50	7.2	67.6	10.2	4.6 @ 315°	32	Temperature dropping fast. It is going to be a cool night.
20:00	20:07	5.4	69.2	4.0	2.53 @ 323°	24	Erin collecting samples
22:00	21:56	3.76	75.2	3.1	2.0 @ 346°	11	
24:00	23:59	2.06	79.25	3.1	1.75 @ 9°	9	
Monday Dec 18, 2006							
02:00	01:59	0.45	82.57	1.8	3 @ 351°	1	Column nozzles kept freezing closed, especially B. Hence it did not collect for the entire 10 min. Some solution froze inside column.
04:00	04:05	-0.35	80.45	Cal	1.2 @ 310°	4	
06:00	05:55	-1.1	82.6	1.7	2.1 @ 317°	23	Tom collecting samples. Sample B froze up after 5 minutes. Sample A was functional for the full 10 minutes. I moved the halogen lamp close to the samplers to keep them warm. The weak breeze during the night was from the north-west. These samples are going to be clean!
Note:							At -2.3°C, the halogen lamp can keep the bottom two chambers thawed if left on all the time. The top two still ice over. Thanks to Ken's heat gun, I thawed the MCs and washed them with a lot of water. The BAMs data for the evening showed particulate values of 20 to 40 overnight and 10 to 20 yesterday.
8:00	07:55	-0.5	74.7	2.6	1.1 @ 54°	60	No problems with freezing this time due to the halogen lamp and the start of sunrise.

Calibration curve	08:42						I prepared a calibration curve consisting of 0, 1, 3, 10 and 30 μL of the carbonyl supermix and the 10μL of the internal standard mix. The curve was prepared on the roof but allowed to react for 10 minutes indoors before being transferred to the reaction vials. I do not prepare samples/standards indoors due to contamination concern from the potent air fresheners used indoors.
10:00	09:51	2.0	64.7	4.7	4.6 @ 306°	45	It is a clear and sunny (but cold) day. At 11:00 am, the sky was cloudless.
Field Blanks	10:12						Prepared two field blanks. I smelled a diesel truck while cleaning setup B.
12:00	12:00	8.2	45.1	16.7	4.6 @ 327°	37	These samples were collected along side Mike Poore's sample. I smelled cooking about when Mike opened his canister. It went away a few minutes later.
Experimental 30 min sample	12:32	9.7	42.6	16.7	8.8 @ 313°	41	I started another set of 30 minute samples at the same time as yesterday. I added about 5 mL more water to the lower chambers.
Note							This is quite possibly the worst possible weather for air pollution sampling. The air is clear with a northwest wind. There is no inversion whatsoever and the cool temperatures will suppress photochemistry. Even rain would have been more interesting…
14:00	13:52	11.95	28.3	25.7	10.6 @ 323°	46	strong NW wind.
16:00	16:05	11.35	31.74	22.05	10.5 @ 319°	43	Lisa collection samples
18:00	18:05	8.91	38.29	4.34	4.48 @ 329°	49	
20:00	20:00	6.05	50.5	2.75	2.2 @ 102°	26	
22:00	21:55	4.57	63.9	2.91	5.71@ 116°	29	
24:00	00:05	2.66	72.3	7.7	0.63@137°	6	Erin collecting samples
Tuesday Dec 19 2006							
02:00	01:55	1.21	66.0	8.2	3.13 @ 97°	11	No freezing issues
04:00	03:48	1.2	74.1	9.7	3.15 @ 104°	5	No freezing issues
06:00	05:55	0.09	72.1	3.8	2.0 @ 45°	25	Tom collecting samples. I turned on the halogen lamp during the spiking step to keep things warm, but the apparatus was not frosty/frozen. There were no freezing issues.
Note:							The Hi-Vol looking sampler is running today. It may kick out some brush dust that we might

							see.
08:00	07:53	0.76	74.4	9.8	2.7 @ 84°	54	No problems
Cal and reagent blank	08:20						I prepared a reagent blank and one 10μL calibration standard on the roof.
10:00	09:51	6.3	63.8	16.4	5.9 @ 123°	37	No problems
Field Blanks	10:27						Weather is mostly clear with a few high clouds. There is a thin brown haze layer to the north, so we may have some air pollution today.
12:00	11:51	8.6	52.0	27.3	7.6 @ 185°	42	I smell cooking and there is an AC repairman on the roof. He left the hatch to the building open and I am smelling perfume/air freshener.
Experimental 30 min sample	12:22	9.2	51.6	25.8	6.4 @ 183°	41	I can smell frying. I am not sure if it is the Asian food places or the hotdog place. I added about 5 mL of water to each of the lower chambers. There is a strong south breeze. I still smelled frying at the end of the sample.
14:00	13:51	10.8	49.6	29.7	5.6 @ 190°	49	No problems
16:00	15:50	10.3	48.4	26.5	3.0 @ 251°	65	No problems
18:00	17:51	7.9	64.9	3.8	2.9 @ 328°	47	I smell cooking again.
20:00	19:53	5.6	69.6	3.7	2.4 @ 100°	38	Erin collecting samples
22:00	21:58	4.1	72.2	4.8	4.8 @ 98°	15	
24:00	23:57	3.8	72.9	8.9	1.6 @ 83°	3	
Wed Dec 20 2006							
2:00	01:57	3.5	72.5	12.0	2.0 @ 91°	4	
4:00	03:56	2.1	75.8	cal	2.1@ 350°	2	
6:00	5:50	1.3	77.6	2.9	1.7 @ 51°	31	End sample collection

Wednesday, Dec 20, 2006

Today was the clean-up day from the last sampling episode. It basically consisted of cleaning and repacking the field sampling equipment. I also started to clean the glassware, but it will take some time to clean all the used bisulfite tubes. I also prepared the injection standards according to the SOP. I made six separate vials of INJ STD solutions. One for each day of extractions in the winter episodes (3 for episode I and 3 for episode II). The vials were sealed with Teflon tape, put in a larger amber gar and frozen. Besides, all the chemicals are very stable so the main objective is not to lose solvent to evaporation.

Thursday, Dec 21, 2006

Start extracting the samples from Winter Roseville I. Extractions proceeding according to the SOP without any problems. New reagents were used for the extractions. The injection standard mix (10μL) was added to each sample. The samples were placed in a large gar with sodium sulfate.

Friday, Dec 22, 2006

Continued extracting the Roseville I samples. Extractions proceeded without incidence. The extracts are stored in a sealed gar on anhydrous sodium sulfate and are stored in the freezer.

Saturday, Dec 23, 2006

Finished extracting the Roseville I samples. The following is a list of potential problems:

Sample 12-19-06: 04:00 B. Sample test tube cap was cracked and it may have leaked. There was salt encrusting the crack, but no observable difference in sample volume.

Sample 12-19-06: 12:00 B. Sample extract contacted glove while capping the vial. This may result in post-derivatization contamination.

Sample 12-20-06: 06:00 A. Sample lost. GC vial had a glass chip out of the bottom, so the sample leaked out.

The extracts are stored in a sealed gar on anhydrous sodium sulfate and are stored in the freezer. The gar was purged with nitrogen gas before being sealed. All vials were stored in an upright fashion to prevent leaks.

Winter Acrolein Sampling II
Return to Roseville

Thursday Jan 4, 2007

I prepared 20 reaction tubes and 40 bisulfite tubes for the source samples. The reaction tubes were prepared with new PFBHA solutions. I also prepared a large jug of bisulfite solution for the main sampling event in Roseville. I also prepared 4 vials of internal standard mixes, so we have three vials for the Roseville sampling and one for emission sampling.

I also went to Walmart to get a metal residence time chamber for the emission sampling. The idea behind the residence time chamber is to give the exhaust (or smoke sample) time to cool down before being pulled into the mist chambers. I settled on a 30 L stainless steel steamer, so the residence time of air under sampling conditions is 1.5 to 2 minutes depending on the mist chambers used. I drilled two holes in the top for the inputs and outputs. The input was at the top of the chamber while the output used a ¼" stainless steel tube to take air from near the bottom of the chamber. I cleaned out the chamber with water and propanol and then sealed the chamber with Teflon tape (both as a gasket between the top and the body of the steamer and on the outside). A quick test under vacuum revealed that the chamber was fairly (if not completely) air tight. The intake tube (0.6 m of ¼" stainless steel tubing) was affixed to the intake to the chamber and a PTFE co-polyermer was used as the output line (~1.5 m of ¼" tubing). The RT chamber is ready for action.

Friday, Jan 5, 2007

Source sampling events. The objective here is to determine the gaseous carbonyl profiles from our two suspected sources, namely vehicles and wood smoke. Preliminary tests conducted by Vince have already indicated that furaldehyde is a good biomass combustion tracer, but I want to confirm this in a formal and rigorous fashion. These samples were all taken at home for convenience.

Sampling item A: Ambient sample taken through residence time chamber (effectively a blank)

Duration 10 minutes
Mist chambers used: #3 followed by #2
Start time: 10:29 am (only one sample collected)
Previous sample: none
Comments: This was the first sample for the RT chamber. The weather is sunny, cool and a strong north wind. It is another clean day where I can see the Sierra Nevada from Davis, so this will be a good background sample. Sample collection followed the SOP exactly except for the presence of the RT chamber on the front end.

Sampling item B: Vehicle source sample (Jeep Wrangler)

Year and Model: 1995 Wrangler
Engine type and size: gasoline, 4 L, 6 cylinders
Idle conditions: warm idle
Odometer: 95,636 miles
Sample duration: 10 minutes

Sample #1 start time: 11:01
Sample #2 start time: 11:17
Sample #3 start time: 11:33
Previous sample: ambient (blank)
Comments: I drove the Jeep 5+ miles at freeway speeds before conducting the test. The RT was purges with exhaust for 5 minutes prior to the first sample collection. The intake was inserted up the tailpipe to sample only exhaust. The steel intake line to the RT was quite warm, but the Teflon line was cool. There was some condensation of water in the Teflon line. There was no change in the solution temperature in the MCs, it was still cool. I kept the pump pulling exhaust through the RTC in between samples, so it was always read for another sample to start. I could not see any difference in flow rates with and without the RT attached to the samplers.

Sampling item C: Vehicle source sample (Ford Mustang)
Year and Model: 1986 Mustang
Engine type and size: gasoline, 5 L, 8 cylinders (new catalytic converters installed last year)
Idle conditions: warm idle (run for 5+ miles on freeway 113 before sample collection)
Odometer: 218,629 miles
Sample duration: 10 minutes
Sample #1 start time: 12:20
Sample #2 start time: 12:35
Sample #3 start time: 12:50
Previous sample: Jeep Wrangler
Comments: Same collection procedure as the Jeep. The exhaust was a little cooler than the Jeep. I can smell the exhaust more than the Jeep.

Sampling item D: Vehicle source sample (Toyota Corolla)
Year and Model: 1997 Corolla
Engine type and size: gasoline, 1.76 L
Idle conditions: warm idle (Reiko drove it ~1 mile over here and it idled a while before the first sample was collected)
Odometer: 47,913 miles
Sample duration: 10 minutes
Sample #1 start time: 13:24
Sample #2 start time: 13:45
Sample #3 start time: 14:04
Previous sample: Ford Mustang
Comments: Same collection procedure as before. Reiko was here to help and to see the method in action. This was Reiko's car. The exhaust was very cool; there was some condensation in the tailpipe itself. The smell of exhaust was stronger than either the Jeep or the Mustang, which is a little surprising since this car has few miles than either of the other two cars.

I cleaned out the RTC with water and propanol. There was some condensed water from the three vehicle tests, so 2/3rd of this solution was added to a reaction tube. (that was all that could fit). I then purged the RTC for 1.5 h with ambient air before the collecting the next sample.

Sampling item E: Field Blank

This is a standard field blank. No air was pulled through the chambers.

Sampling item F: Wood smoke (Douglas fir)

Duration: 10 minutes (first one) 3 minutes after that
Sample #1 start time: 19:20 (10 minutes)
Sample #2 start time: 19:33 (3 minutes)
Sample #3 start time: 19:40 (3 minutes)
Previous sample: field blank

Comments: The wood was well dried Douglas fir 2 X 2 that was cut up and put in a Webber Kettle. The fire was started with newspaper. The fire was made on a metal grate and the vents below it were open, so it got plenty of air under it. The steel intake was positioned about 3 to 6 inches above the top of the flame. The intake tube got hot. The first sample was collected 9 minutes after fire ignition, so it was in a steady flame stage. Once again, the chamber was purged for 5 minutes before collecting the first sample and the pump was used to pull air through the RTC in between samples. The first sample was very nasty looking and the solution was brown color, so I cut the sample collection time down to 3 minutes for the next of the sample to prevent overloading the derivatization reagent and the instrument. The last sample was collected during the smolder phase.

Sampling item G: Wood smoke (Blue Oak)

Duration: 3 minutes
Sample #1 start time: 20:37
Sample #2 start time: 20:43
Sample #3 start time: 20:49
Previous sample: Douglas Fir wood smoke

Comments: The wood smoke samples were collected like the previous samples. Sample collection was uneventful. The samples are a distinct gray color. The mist chamber nozzles were dark with soot from the smoke. I drove into the lab to wash the MCs and put them in the furnace to clean off all the carbon.

Saturday, Jan 6, 2007

More preparation for the Roseville sampling. I prepared the reaction tubes (~ 100 of them) and the bisulfite tubes (~180 of them). I don't quite have enough bisulfite tubes to conduct the whole sampling episode, so I will have to clean the first day's tubes and re-fill them. I also noticed that the tubing from the wood smoke tests smelled of fire, so I replaced it to avoid any possible contamination even though it is down-stream of the samplers. I also took apart the mist trap, washed it in soapy water, and re-assembled it with a new glass wool packing. Lastly, I will use pump "C" for the field sampling to avoid any wood smoke traces from re-volatilizing from the pump.

Sunday, January 07, 2007

Start of Roseville winter #2 sampling episode. I left Davis at about 04:05 and arrived in Roseville at about 04:40. I unpacked the critical materials and setup the samplers on the roof.

Sampler setup "A" consists of MC #3 followed by #2. Sampler setup "B" was mist chamber #7 followed by #8, which is the exact configuration as last time.

I washed all four mist chambers will a spiked bisulfite solution to cover up any active sites and to wash out any contaminants that got in the chambers during transport. The bisulfite rinse was followed by two water rinses like a normal sample.

We are low on the Wiretrol disposable micropipets (and I was unable to get any on Friday since neither VetMed nor the chem. stores had them). I will leave the Wiretrol micropipets for the students and I will use a gas-tight 25 µL syringe to measure the spikes, which is probably more accurate but a greater hassle to use due to pre and post washing.

The sample log is as follows:
EB = east bound traffic on I-80 (vehicles per 30 second count).
Vehicles = cars + trucks + motorcycles (anything that moves under its own power)

Sample period	Actual start time	Temp (°C)	RH (%)	O_3 (ppb)	Wind speed (knots) & direction (degrees)	EB (veh)	comments
Sunday Jan 7, 2007							**Sunday**
06:00	05:56	2.3	80.8	3.6	0.74 @ calm	5	Tom collecting samples. Rinsed MCs with spiked bisulfite solutions before use. Setup A = MC #3 and #2 Setup B = MC #7 and #8.
08:00	07:50	1.35	82.1	2.7	2.1 @ 72°	19	Sunrise occurred just before sample collection. There is now a thin layer of frost on the deck.
Cal and reagent blank	08:27						I prepared a reagent blank and one 10µL calibration standard on the roof.
10:00	09:52	6.9	67.2	17.1	5.1 @ 141°	33	No problems
Field Blanks	11:08						Two field blanks were prepared. The weather is clear and sunny. There is a little of a haze layer. It looks fairly typical of a slightly hazy winter day. Note: Field blank A broke in transport, so the sample was lost.
12:00	11:52	9.0	59.6	22.6	2.4 @ 144°	28	No problems
Experimental 30 min samples	12:25	10.0	56.8	23.8	2.7 @ 147°	41	I started set of 30 minute samples. I added about 5 mL more water to the lower chambers. I can smell perfume on the roof, so I bet there is a building vent releasing the stuff.
14:00	13:50	11.8	50.0	29.8	2.6 @ 185°	58	I think I may have smelled wood smoke.
16:00	16:01	13.31	45.55	16.8	1.42 @ 300°	32	Erin collecting samples. She has a cold, so she cannot smell much.
18:00	18:03	10.5	57.65	4.15	2.39 @ 126°	24	
20:00	19:55	6.51	72.3	3.51	1.72 @ 137°	20	
22:00	21:52	6.05	75.0	12.25	2.75 @ 86°	16	
24:00	00:10	4.27	80.13	5.0	1.2 @ 103°	5	Nick collecting samples

Monday Jan 8, 2007							**Monday**
02:00							Missed it
04:00	04:01	2.75	81.0	cal	1.75 @ 79°	3	
06:00	06:00	2.47	80.43	5.3	3.97 @ 84°	15	
08:00	07:52	2.2	80.0	4.6	4.4 @ 87°	59	Tom collecting samples
Calibration curve	08:50						I prepared a six point calibration curve (0, 1, 3, 10, 30 and 100 μL of the carbonyl supermix) outside. I had to use the syringe to measure the larger calibration volumes, so I extensively washed the syringe afterwards (20 water pumps from two jars) to prevent carryover to the next internal standard.
10:00	10:00	8.4	67.5	17.7	4.7 @ 158°	19	**Mike Poore spiked Sampler A with gas-phase acrolein from a canister.** The amount of the spike was deliberately not known to avoid bias on my part. Sampler B will be used for subtraction to determine the mass added to A. The gas-phase spike was added during the first 4 minutes of the ten minute sample.
Field Blanks	11:07						Two field blanks were prepared. Note that these blanks follow Mike's spiked sample. If field blank is high, then it might be due to carryover. I washed the chambers well, but there may still be carryover. The weather is clear and sunny. There is a little of a haze layer. It was a little frosty and foggy in the morning.
12:00	11:51	11.0	57.6	25.6	6.8 @ 149°	46	I smell fry cooking when the sample started.
Experimental 30 min samples	12:29	11.7	55.6	27.1	6.4 @ 153°	47	I started set of 30 minute samples at the same time as yesterday. I added about 5 mL more water to the lower chambers. I can smell fry cooking still in the air. Sample A has a long fiber in it that looks like a cat hair. I may have blown off my shirt during mist chamber rinsing.
14:00	13:54	12.9	54.1	28.8	6.4 @ 157°	44	I still smell fry cooking.
16:00	15:50	14.1	50.2	29.6	3.4 @ 161°	55	Westbound traffic is slow (judging by how slow the trucks are moving). Sun angle is getting low.
18:00	17:55	12.2	58.3	6.8	2.45 @ 165°	42	Erin collecting samples
20:00	19:55	8.21	72.2	6.02	1.3 @ 77°	19	
22:00	21:57	6.21	79.2	4.93	3.2 @ 91°	20	
24:00	23:55	5.84	80.7	8.2	2.4 @ 76°	7	Nick collecting samples

Tuesday, Jan 9, 2007							**This was a "spare the air day" due to particulate matter.**
02:00	02:05	4.4	81	2.15	2.1 @ 113°	1	
04:00	03:56	4.0	79.5	cal	1.9 @ 98°	4	
06:00	05:55	3.15	79.7	5.43	2.36 @ 83°	24	
08:00	07:54	2.88	79.3	2.08	1.8 @ 128°	56	Tom collecting samples. There is a smell in the air like morning camp food. There is a nice haze layer today.
Cal and reagent blank	08:21						I prepared a reagent blank and one 10μL calibration standard on the roof.
10:00	09:52	8.3	60.7	5.8	2.2 @ 308°	35	
Field Blanks	10:27						Two field blanks were prepared. The weather is clear and sunny with a nice haze layer. There was low fog over fields as I drove in. This will be a good day to sample.
12:00	11:51	11.2	63.4	16.3	2.2 @ 319°	39	I can smell tar from the roadwork on N Sunrise Blvd.
Experimental 30 min samples	12:22	12.9	60.1	15.4	2.9 @ 7°	38	I started set of 30 minute samples. I added about 5 mL more water to the lower chambers. I think I can smell both tar and cooking. I also think I smelled some sewer odors, so I wonder if there is a building vent putting out strange stuff.
14:00	14:00	14.6	49.1	21.7	5.4 @ 300°	51	**Mike Poore spiked Sampler A with gas-phase acrolein from a canister.** The amount of the spike was deliberately not known to avoid bias on my part. Sampler B will be used for subtraction to determine the mass added to A. The gas-phase spike was added during the first 8 minutes of the ten minute sample.
16:00	16:22	15.42	45.0	8.5	2.2 @ 309°	31	Erin collecting samples. Westbound traffic slow. Sample collected a little late.
18:00	18:01	12.84	56.5	2.82	3.0 @ 335°	41	
20:00	19:56	8.9	68.8	3.6	1.75 @ 92°	36	
22:00	21:51	7.0	76.45	0.84	1.9 @ 43°	27	
24:00	00:25	5.45	80.3	2.52	1.6 @ 83°	5	Nick collecting samples. Sample a little late.
Wednesday, Jan 10, 2007							
02:00	01:55	5.82	76.1	8.1	3.7 @ 100°	2	
04:00	04:05	4.95	75.3	cal	3.4 @ 72°	4	
06:00	6:10	5.67	67.45	6.51	6,2 @ 105°	15	
08:00	7:50	5.82	67.0	2.2	1.75 @ 321°	37	End of sample collection

Wednesday Jan 10, 2007:

I started to extract the samples today. The source samples were first in line. They were extracted according to the SOP except for the following deviation: The samples were reduced to 1 mL total volume rather than the normal 0.5 mL. The wood samples were a bright yellow color and I was afraid to inject too much junk onto the instrument. These samples will be analyzed LAST to avoid them from contaminating the instrument. These samples are going to be NASTY! I took pictures of the vehicle and wood smoke samples to document the appearances of the samples. I am not sure if these pictures will turn out due to problems with the flash reflecting off of the sample test tubes. By the end of the day, all the source samples were extracted.

Nick finished off the field sampling and returned the equipment to the laboratory. I started cleaning the equipment and packing it away.

Thursday, Jan 11, 2007:

I extracted the first day of Roseville samples today. All went according to the SOP. The samples were reduced to 0.5 mL that is called for the SOP unlike the source samples. The only important note is that Field Blank A was lost in transport, so there is only one field blank for the Jan 7, 2007 sampling day.

Friday, Jan 12, 2007:

I extracted the second day of Roseville samples. The extractions were uneventful except that I spilled about 10% of sample 1-9-07, 14:00B while handling the sample vial.

Saturday, Jan 13, 2007:

I finished off the last of the extractions today. Everything went according to plan except that I had to start using a new bottle of Sigma Chromosolv hexane for the extraction of the last 11 samples. This is a new supplier of the solvent due to trouble ordering solvents. Since this reagent is using during the post-derivatization extraction, it should not be able to contribute any derivatized impurities to the sample. Besides, this is the highest purity grade of solvent that this distributor makes, so it should be good.

It was also a mad rush to clean up everything and get it packed away for the trip back to Phoenix.

APPENDIX 6

Calculations for converting the raw instrumental response into atmospheric concentrations.

This appendix shows the process by when the atmospheric concentrations of the carbonyls are calculated from the instrumental response.

The first step in the quantification procedure is to prepare a set of calibration standards. These standards were prepared in the field by adding a known amount of the analyte chemicals to the same bisulfite and reaction solutions as are used for the samples. The 59 analyte chemicals are prepared a single mixture of acetonitrile where the target concentration of each analyte was approximately 10 ng/ul. Although the target concentration for all analytes was 10 ng/ul, the actual concentrations varied a little with the exact measurements of the analytes during the preparation of the solution. The exact concentration of each analyte was recorded and used for the quantification. Different volumes of the standard mixture were used to generate the set of calibration solutions. For example, the fist standard had a target concentration of 10 ng of each chemical per sample, so 1 μL of the standard mixture was added to this sample. The second standard had a target concentration of 30 ng of each analyte per sample, so 3 μL of the standard mixture was added to the sample. The standards used in this study had the following concentrations: 10, 30, 100, 300, and 1000 ng of analyte per sample. In addition, one sample was prepared as a reagent blank where no analyte solution was added to the sample. This standard also is the calibration "0" standard which was used in the calibration curve.

The calibration solutions also had a set of internal standards added to them. Unlike the analyte concentrations, the internal standards were designed to have the same concentrations (100 ng per sample) in all the calibration solutions and the field samples. The internal standards consisted of acrolein-d_4, benzaldehyde-d_6 and acetaldehyde-d_4. These internal standards were used to calculate the relative response factor for the analytes. Acrolein-d_4 was used to calculate the relative response factor for the three and four carbon aldehydes with the exception of glyoxal and methylglyoxal. Acetaldehyde-d_4 was only used for the relative response factor calculation of acetaldehyde. Due to the poor retention of the labeled standard, acetaldehyde was not quantified or reported for this project. Benzaldehyde-d_6 was used as the internal standard for all the other analytes, which were the larger and less volatile compounds. The internal standards were added to the calibration solutions in the field and to all the field sample solutions prior to collection.

The last aspect of the calibration solutions was the addition of injection standards that were added to the calibration solutions and samples after sample extraction and before instrumental analysis. These chemicals were used to normalize instrumental response, verify instrumental function and to calculate the loss of the internal standards during sample collection. They were not used for the quantification of any analytes. Like the internal standards, the injection standards had the same amount of chemical mass added to each sample and calibration solution, namely 100 ng per sample. A summary of the calibration solutions are given in table A6.1 below.

Table A6.1. Composition of the calibration solutions

Standard name	Concentration of analytes (ng per sample)	Concentration of Internal standards (ng per sample)	Concentration of injection standards (ng per sample)
Cal 0 (reagent blank)	0	100	100
Cal 1	10	100	100
Cal 3	30	100	100
Cal 10	100	100	100
Cal 30	300	100	100
Cal 100	1000	100	100
Field blank	0	100	100
Samples	0	100	100

The standard solutions and samples were stored together during derivatization and were extracted at the same time. All the samples for a given sampling episode were analyzed during the same instrumental analysis run. The sample queue (in order) consisted of 1) the all the calibration solutions, 2) the samples and blanks with a repeated standard every 6 samples to ensure instrumental stability and 3) a final analysis of all the calibration solutions at the end of the run. Therefore the sample analyses were "bookended" by two calibration curves and standards were intermixed with the samples. The results from all the standard analyses were combined to create a single calibration curve for the quantification of the analytes.

The raw instrumental response for the analytes, internal standards and injections standards was the peak area as measured by integrating the area of the quantification ion of each analyte under the peak in the chromatogram. The integration was conducted by Agilent Chemstation software that was provided as part of the gas chromatograph-mass spectrometer instrumentation. The quantification ions are generally the most abundant ion (also called the base ion) in the mass spectra. Occasionally, the second or third most abundant ion is used for quantification is the most abundant is a common "background" ion.

The raw peak area of the analyte and its corresponding internal standard are used to calculate the relative response factor. This is simply the peak area of the analyte ($A_{analyte}$) divided by the peak area of the internal standard ($A_{internal\ standard}$), or

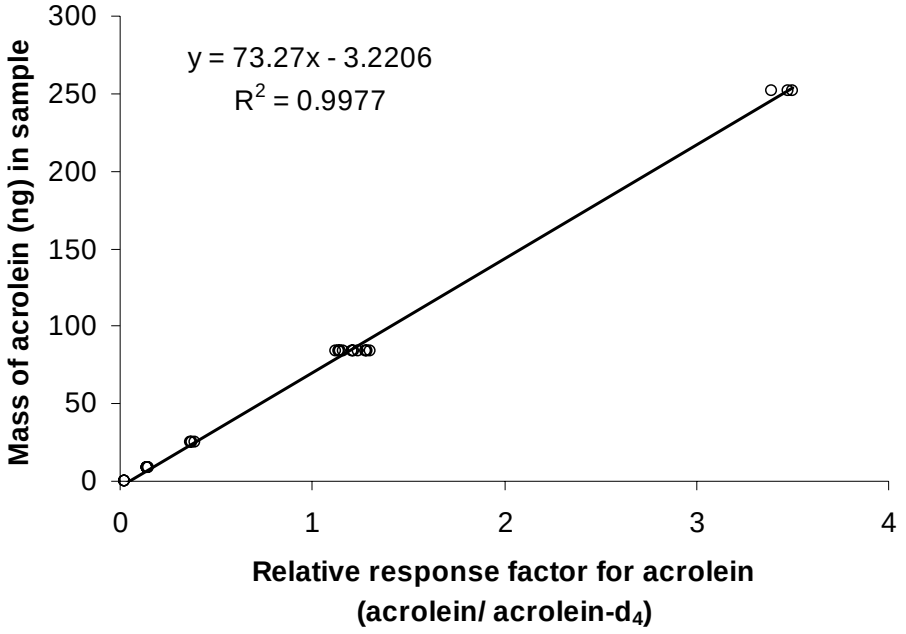
$$\text{Relative response factor} = A_{analyte}/A_{internal\ standard}$$

The relative response factor normalizes the analyte area to account for instrumental drift or poor derivatization or losses during extraction. The relative response factor is a unitless measure.

The next step of the quantification procedure is to construct a calibration curve. The calibration curve converts the raw peak area in the chromatogram into nanograms of analyte in the sample. For each analyte, the mass of the analyte in the standard solutions (x-axis) is plotted against the relative response factors for the analyte (y-axis). A linear regression line is then fitted to the data for the calibration curve to obtain an equation of the line that relates the amount of chemical to the relative response factor. Statistically speaking, the mass of the analyte should be on the x-axis since it is a controlled parameter while the relative response factor is the variable that should be plotted on the y-axis. However, calibration curves are frequently plotted

with the amount of chemical on the y-axis and the relative response factors on the x-axis so that the regression equation for the line (in the form of y = *m*x + *b*) gives the expression to calculate the amount of the chemical directly without any algebraic manipulations. The two ways of plotting the data give the exact same numerical results and they only differ in a small statistical technicality. Figure A6.1 below shows the calibration curve for acrolein for second winter-time sampling episode in Roseville. All the standards run during a sample queue are combined to create a single calibration curve.

Figure A6.1. The calibration curve for acrolein from the second winter sampling episode. The curve shows that the instrument was stable and consistent during the sample run since the standards gave similar responses for the first, middle and final analysis runs.



The next step in the quantification procedure is to "blank subtract" the results. The average mass in the blank sample was calculated from the 6 field blanks and this mass was subtracted from all the field samples. This accounts for any contamination resulting from impurities in reagents, contamination during sample handling or carry-over in the mist chambers.

The last step in the quantification procedure is to calculate the air concentrations. This step simply divides the mass of analyte in the sample (in ng) by the volume of air collected by the sampler. The volume of air processed by the mist chambers during the 10 minute samples ranged from 0.138 to 0.192 m^3 depending on which mist chambers were used to collect the samples. Therefore, the air concentrations are simply (ng of analyte)/(volume of air) to get ng/m^3, which are the units that the data is reported.

The equation used to calculate the air concentration of any given chemical is:

Concentration (ng/m^3) =

$= ((m(A_{analyte}/A_{internal\ standard}) + b) - (average\ field\ blank))/V_{air}$

Where:

$A_{analyte}$ is the raw peak area of the analyte

$A_{internal\ standard}$ Is the raw peak area of the internal standard for the analyte

m is the slope of the regression line from the calibration curve

b is the intercept of the regression line from the calibration curve

"average field blank" is the average of the mass (in ng) present in the 6 field blanks of that sampling episode

V_{air} is the volume of air collected in m^3