

CALIFORNIA AIR RESOURCES BOARD
MONITORING AND LABORATORY DIVISION

Toxics Monitoring Program
Report on a Parallel Carbonyl Monitoring Study
Using C18 and Silica Gel Sampling Media

By

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EXECUTIVE SUMMARY

In 1996, the Monitoring and Laboratory Division (MLD) of the California Air Resources Board (CARB) conducted a one-year study in which carbonyls were monitored using parallel silica gel and C18 cartridges. The purpose of the study was to identify and evaluate any bias between the two methods. Parallel carbonyl samples were collected on silica gel and C18 cartridges at two sites, Bakersfield and Stockton, using separate sampling channels of the air samplers located at each site. A collocated sample was collected into silica gel cartridges on a separate sampler.

The results of the one-year parallel study show a negative bias in the sampling efficiency of the C18 media when compared to silica gel, especially at higher ambient carbonyl concentrations. It was determined that breakthrough is one of the causes for the poor efficiency, and that it was a widespread problem with the C18 sampling method. The specific causes for breakthrough were not established. The effects of environmental factors such as ozone concentration, relative humidity, and ambient temperature were investigated, but they were determined to be ambiguous.

The silica gel sampling media demonstrated superior properties in terms of precision and resistance to breakthrough; however, the method has not been fully validated. The MLD plans to conduct further studies to document the method's performance under the program's sampling conditions.

INTRODUCTION

The Monitoring and Laboratory Division (MLD) has operated a carbonyl (formaldehyde, acetaldehyde, and methyl ethyl ketone) monitoring program since 1988. Samples are collected over a 24-hour period every 12 days at 20 monitoring sites throughout the state. Ambient air is drawn at a flow rate of 0.7 liters per minute (lpm) through a sampling cartridge packed with a solid phase substrate coated with acidified 2,4-dinitrophenylhydrazine (DNPH). The method was adapted from the U. S. EPA's Method TO-11, and from 1988 to 1990, the solid phase was silica gel. In 1990, following EPA's recommendations, the substrate was changed to chromatographic grade C18 in order to reduce interferences by ozone and other pollutants. In January of 1996, the solid phase was changed back to silica gel and an ozone denuder was added to the sampling assembly.

This report presents the results of a one-year study, conducted in 1996, in which carbonyls were monitored using parallel silica gel and C18 cartridges. The purpose of the study was to identify and evaluate any bias between the two methods.

SAMPLING AND ANALYSIS

During 1996, parallel carbonyl samples were collected on silica gel and C18 cartridges at two sites, Bakersfield and Stockton, using separate sampling channels of the XonTech 920 Toxic Air Samplers located at each site. The primary samples were collected into a single silica gel cartridge at Bakersfield and two cartridges connected in series (tandem) at Stockton. The parallel samples were collected on C18 cartridge tandems at both sites. A third sample was collected into a single silica gel cartridge at Bakersfield and a silica gel tandem at Stockton on a collocated sampler. The upstream cartridge in a tandem was designated as the first stage and the downstream cartridge as the second stage. Figures 1 and 2 show a diagram of the sampling scheme.

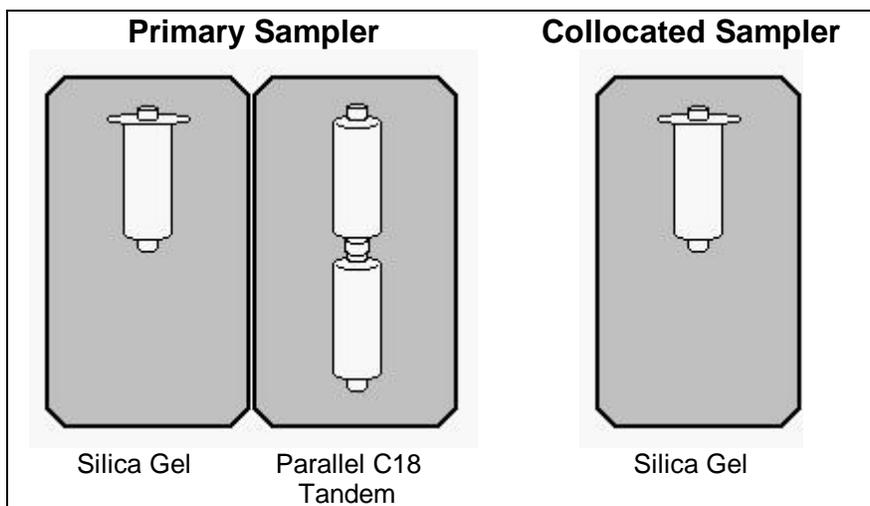


Figure 1. Sampling scheme at Bakersfield.

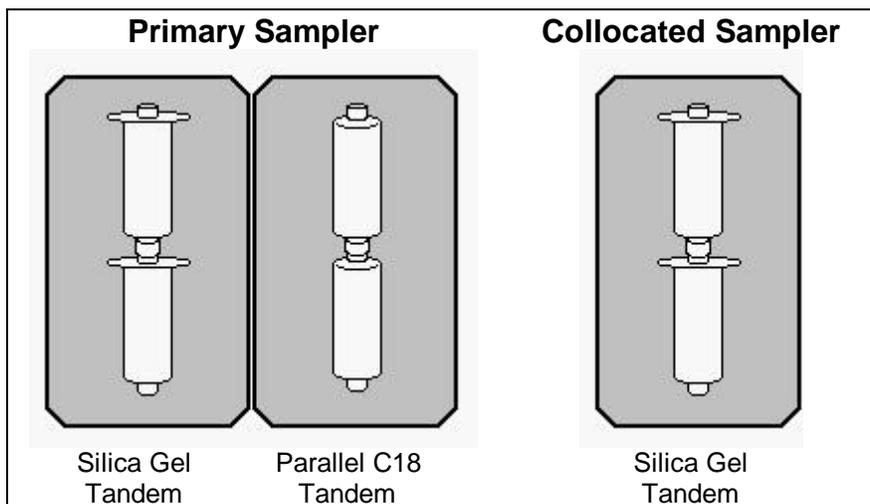


Figure 2. Sampling scheme at Stockton

All samples were analyzed at the MLD laboratory in Sacramento using a high-performance liquid chromatography method. The sampling cartridges were extracted and analyzed individually, and in the cases where samples were collected into paired cartridges, the total concentration was calculated as the sum of the individual concentrations.

QUALITY ASSURANCE

The field samplers were calibrated twice, at six-month intervals, against transfer standard mass flow meters. The accuracy of the calibrations was verified by an independent performance audit conducted by the Quality Assurance Section, which showed that the difference between the flow rate indicated by the samplers and the certified flow rate averaged 0.7% and ranged from -1.4% to 3.2%.

Every tenth sample was analyzed in duplicate, and the average percent difference between formaldehyde duplicates was -0.3% with a standard deviation of 1.9%, and 0% for acetaldehyde, with a standard deviation of 1.5%. A spiked solution was analyzed with each analytical batch. The average spike recoveries were 100% for formaldehyde and 101% for acetaldehyde, with standard deviations of 2% for both compounds. A reagent blank was also analyzed with each batch, and no contamination was detected in any analytical run.

RESULTS

The 24-hour formaldehyde and acetaldehyde concentrations measured by the silica gel and C18 methods are shown in Figures 3 through 6. Also shown in each figure is the relative percent difference of the C18 value compared against the average of the two methods. In

Bakersfield, it was observed that, in general, silica gel yielded higher measurements of both compounds, and the difference between the two methods became larger later in the year as the ambient concentrations increased. A similar trend was observed in Stockton, but there were two major differences: the ambient concentrations were lower at Stockton, and many of the samples from the high concentration season were missed.

Methyl ethyl ketone (MEK) was detected in only 17 of the primary silica gel samples, 9 of the collocated silica gel samples, and 21 of the parallel C18 samples, out of a total of 61 sample sets. Of the samples in which it was detected, most had MEK concentrations below two times the reported limit of detection (LOD) of 0.1 ppb. The average concentrations were 0.17 ppb for the primary silica gel, 0.18 ppb for the collocated silica gel, and 0.18 ppb for the parallel C18. Since the uncertainty of the measurements increases significantly as the concentration levels approach the LOD, resulting in wide discrepancies between parallel measurements, further analyses of the MEK data were not conducted.

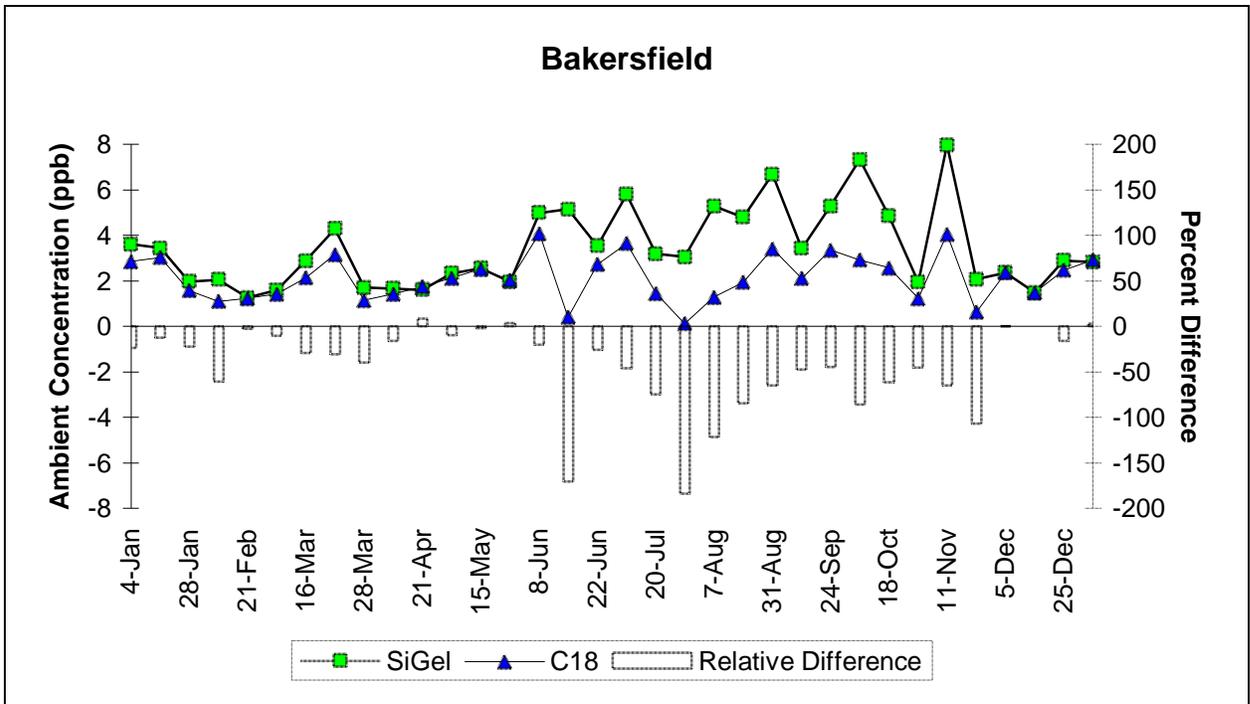


Figure 3. Formaldehyde concentrations at Bakersfield measured by parallel C18 and silica gel sampling methods

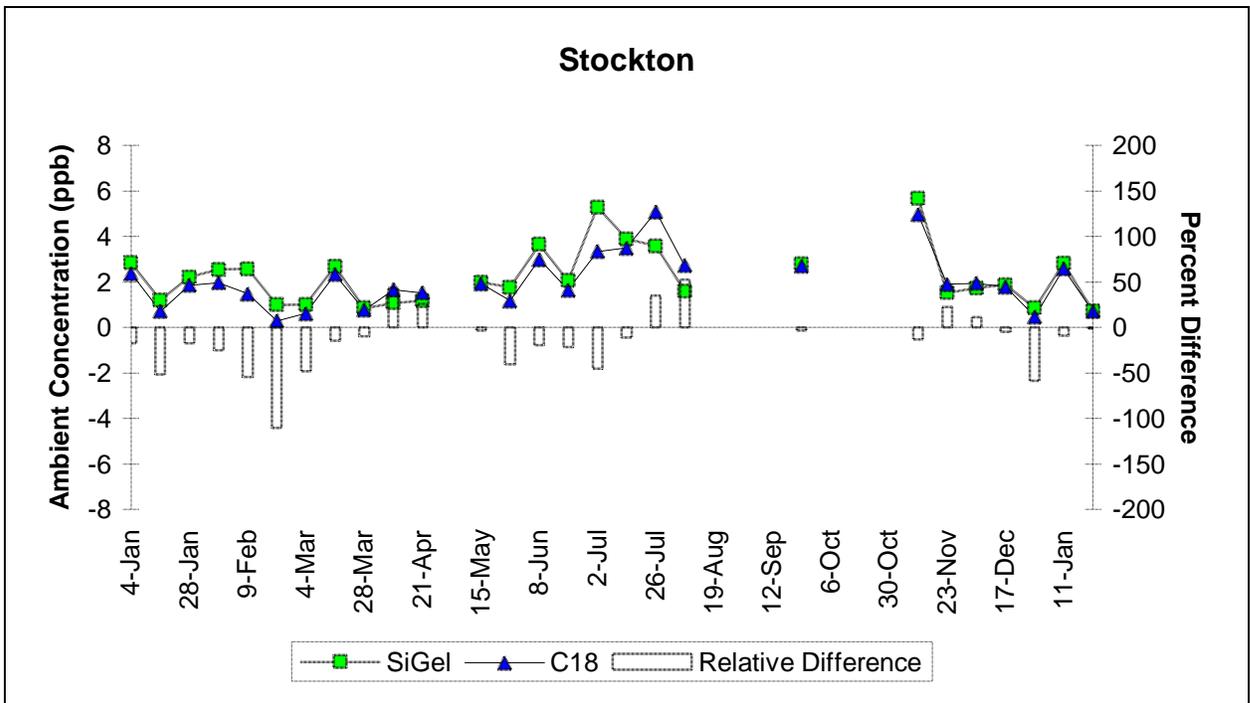


Figure 4. Formaldehyde concentrations at Stockton measured by parallel C18 and silica gel sampling methods

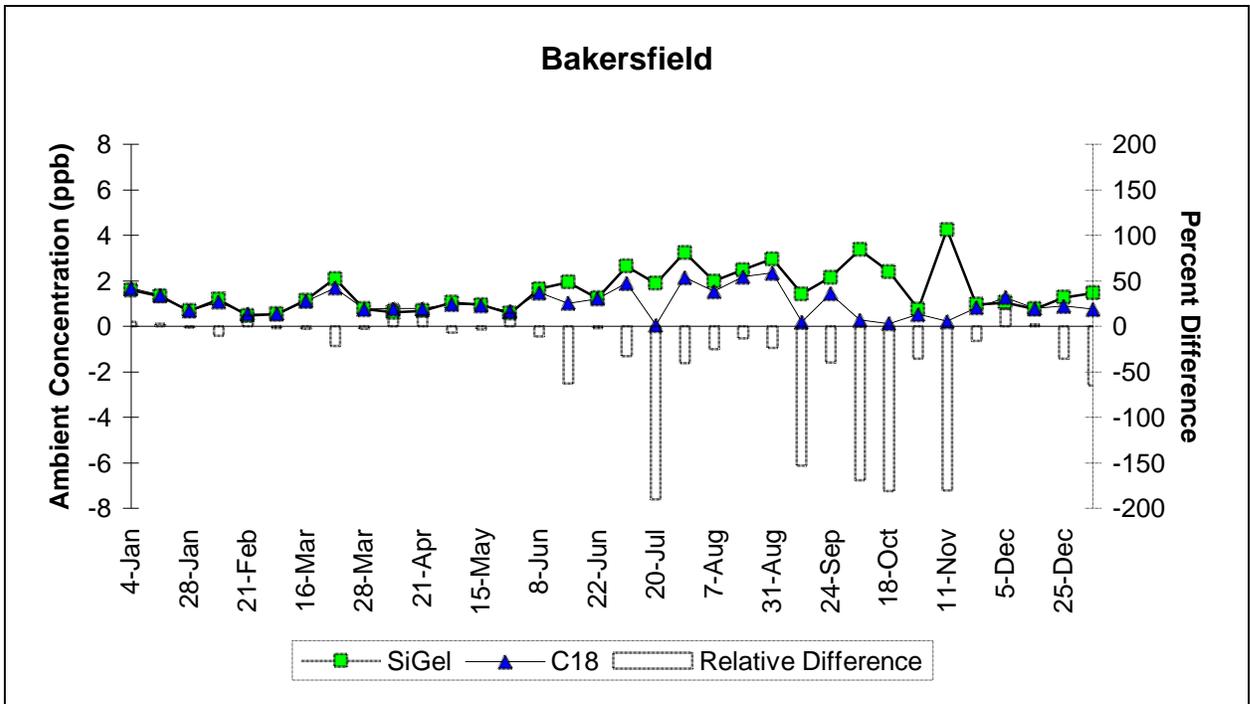


Figure 5. Acetaldehyde concentrations at Bakersfield measured by parallel C18 and silica gel sampling methods.

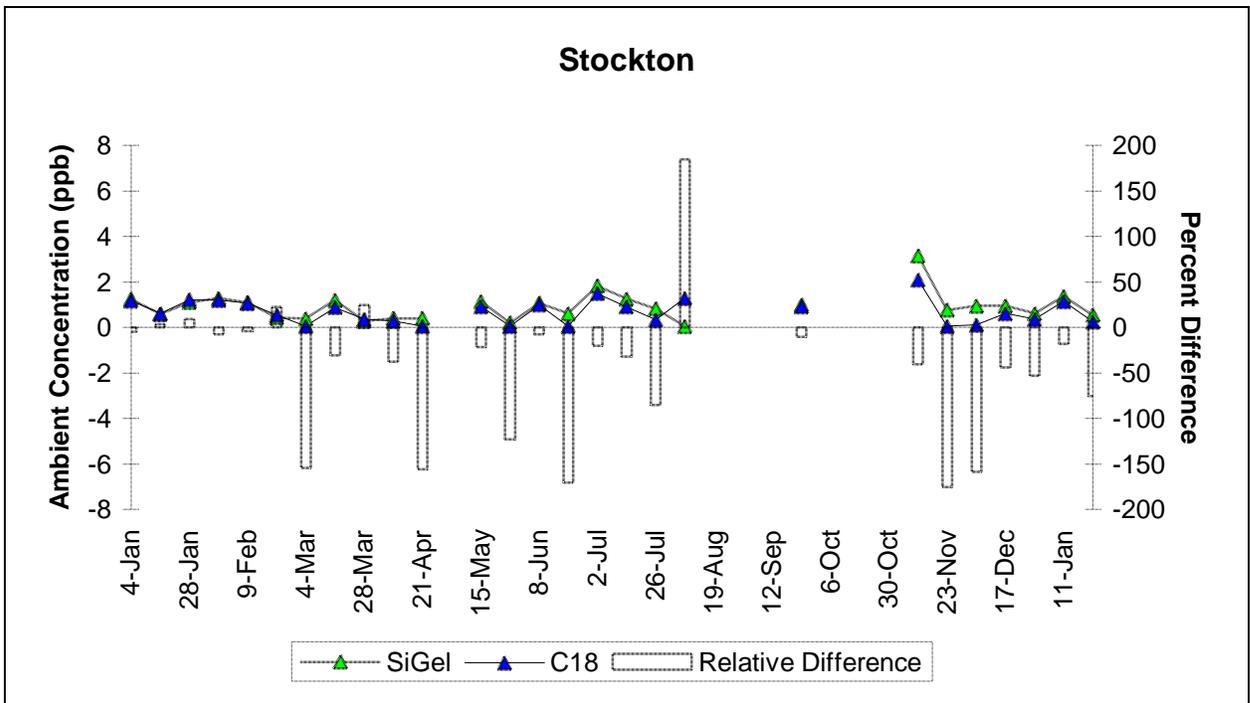


Figure 6. Acetaldehyde concentrations at Stockton measured by parallel C18 and silica gel sampling methods.

A scatter plot of the formaldehyde concentrations measured by C18 versus silica gel (Figure 7) shows a significant number of data pairs lying in close proximity to the 1:1 line, which indicates good correlation between the two sampling methodologies. However, two other features can be observed: 1) several data pairs fall well below the 1:1 line, suggesting failure of the C18 sampling media, and 2) at higher ambient concentrations, C18 measurements level off at about 4 ppb, suggesting saturation of the sampling cartridges. A scatter plot of the acetaldehyde data (Figure 8) shows similar results, with the efficiency of C18 leveling off at about 2 ppb.

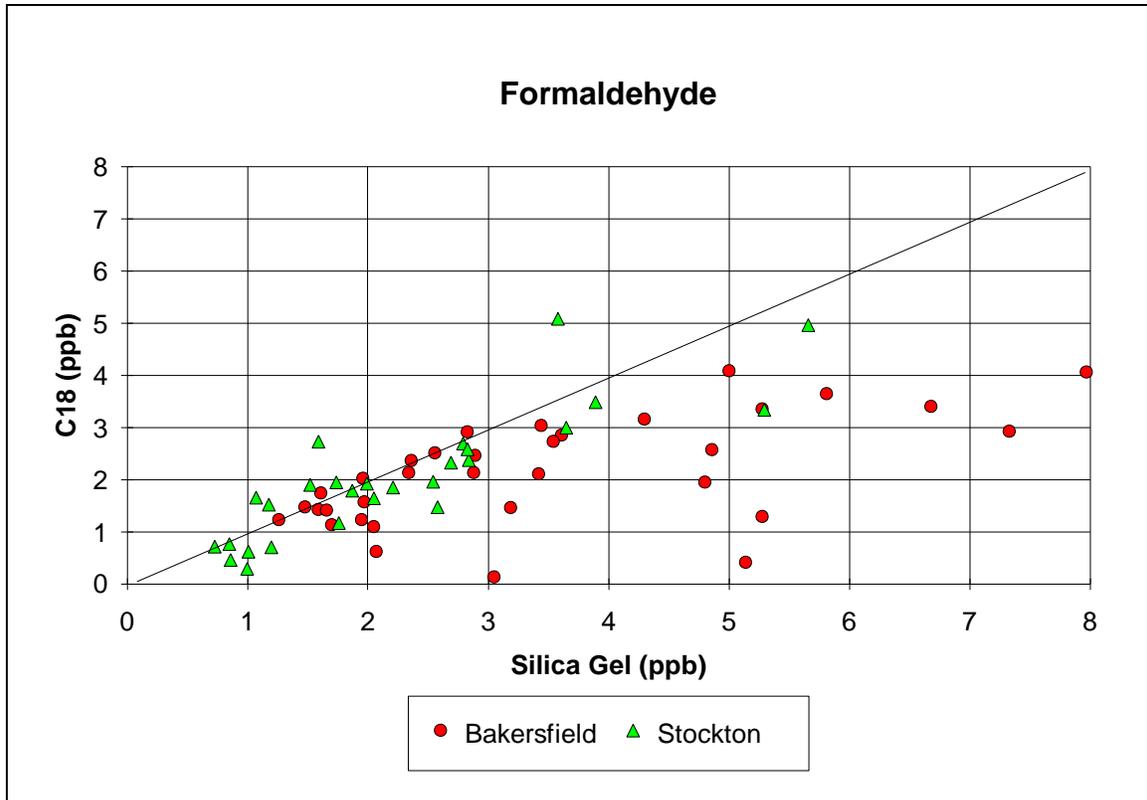


Figure 7. Formaldehyde ambient concentrations measured by C18 versus silica Gel

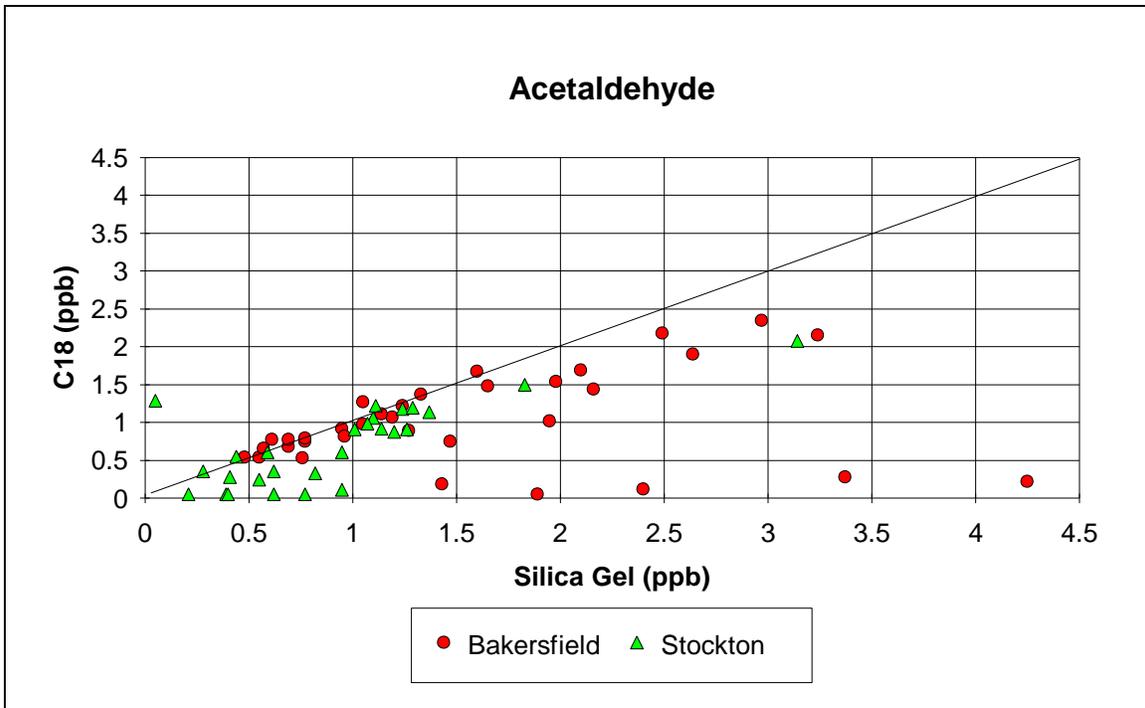


Figure 8. Acetaldehyde ambient concentrations measured by C18 versus silica Gel

Statistical analysis of the relative percent difference between the parallel silica gel and C18 results, where

$$\text{Relative Percent Difference} = \frac{\text{C18 Measurement} - \text{Silica Gel Measurement}}{\text{Average of Both Measurements}}$$

yields average differences of -31.0% for formaldehyde and -39.6% for acetaldehyde, which are evidence of a negative bias in the C18 sampling method. However, the standard deviations of 44.3% and 68.8%, respectively, indicate a great deal of variability between the two methods.

Using the standard deviation of the relative differences between pairs of collocated samples as an indicator of method variability, it can be demonstrated that the silica gel method, with a standard deviation of 18.0, is a more precise formaldehyde sampling method than C18, which showed a standard deviation of 47.9 for collocated cartridges collected during 1995. Likewise, the acetaldehyde silica gel method had a standard deviation of 21.6, compared to 88.0 for collocated C18 measurements also made in 1995. Thus, it can be concluded that the variability observed between the silica gel and C18 results in the study was largely influenced by the variability of the C18 method.

In the effort to determine the cause for the low carbonyl recoveries observed with C18, the effects of ambient ozone concentration, relative humidity, and ambient temperature on the sampling efficiency were investigated but, at best, any correlation was deemed poor and ambiguous.

A close examination of the laboratory results for the individual C18 cartridges showed that, while the formaldehyde concentration was usually much higher in the first stage than the second (as would be expected), about one-third of the samples had concentrations in the second stage which were near the concentration of the first stage (Figure 9), suggesting a failure of the first stage which leads to breakthrough of formaldehyde into the second stage. Breakthrough appears to be independent of the formaldehyde concentration, and it was observed in both, low and high concentration samples.

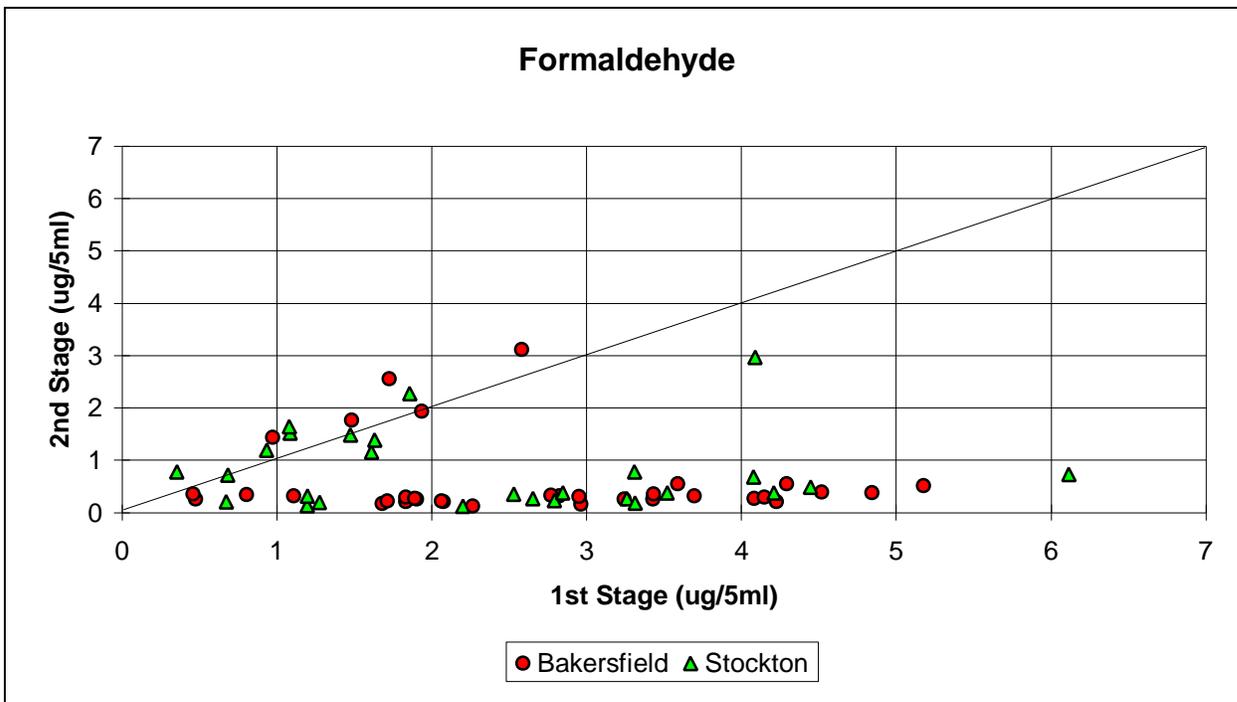


Figure 9. Formaldehyde concentration in second C18 stage versus first stage.

The failure rate for acetaldehyde appears to be greater, with about two thirds of the samples showing significant amounts of breakthrough (Figure 10). By comparison, the analyses of the first and second stage silica gel samples collected in Stockton showed no evidence of breakthrough (Figure 11). Thus, it is speculated that breakthrough was partly responsible for the low recoveries observed with the C18 sampling media.

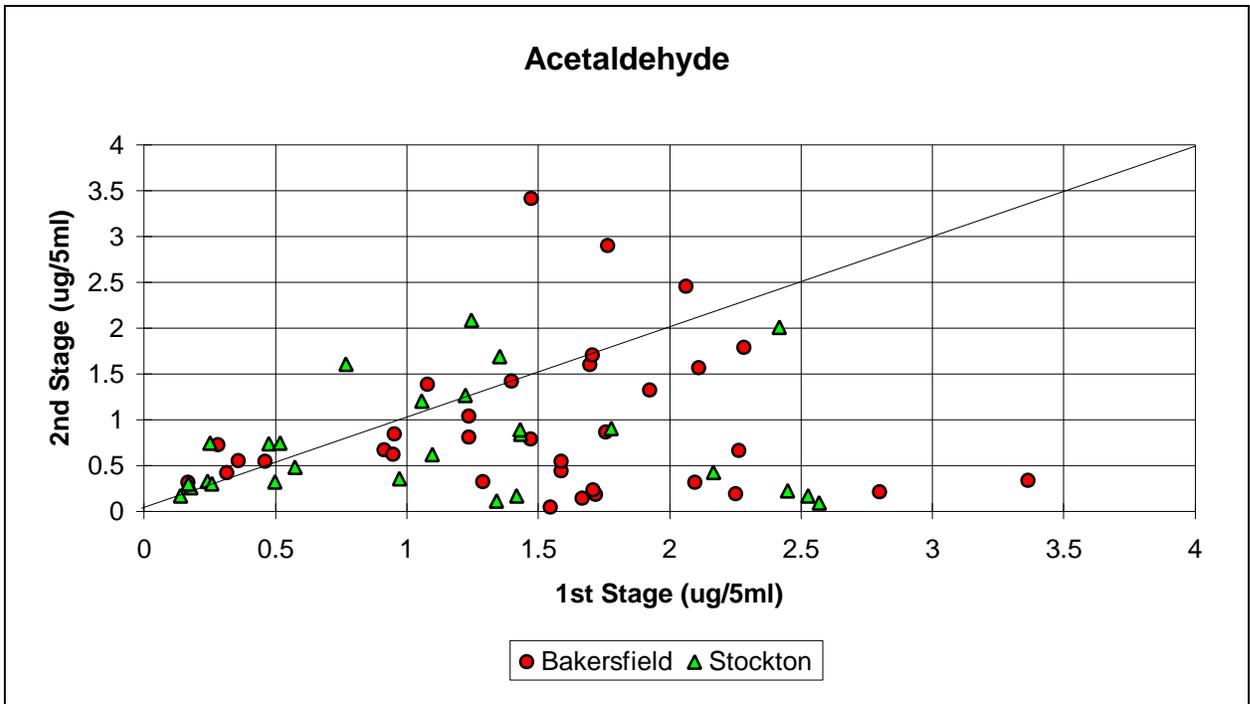


Figure 10. Acetaldehyde concentration in second C18 stage versus first stage.

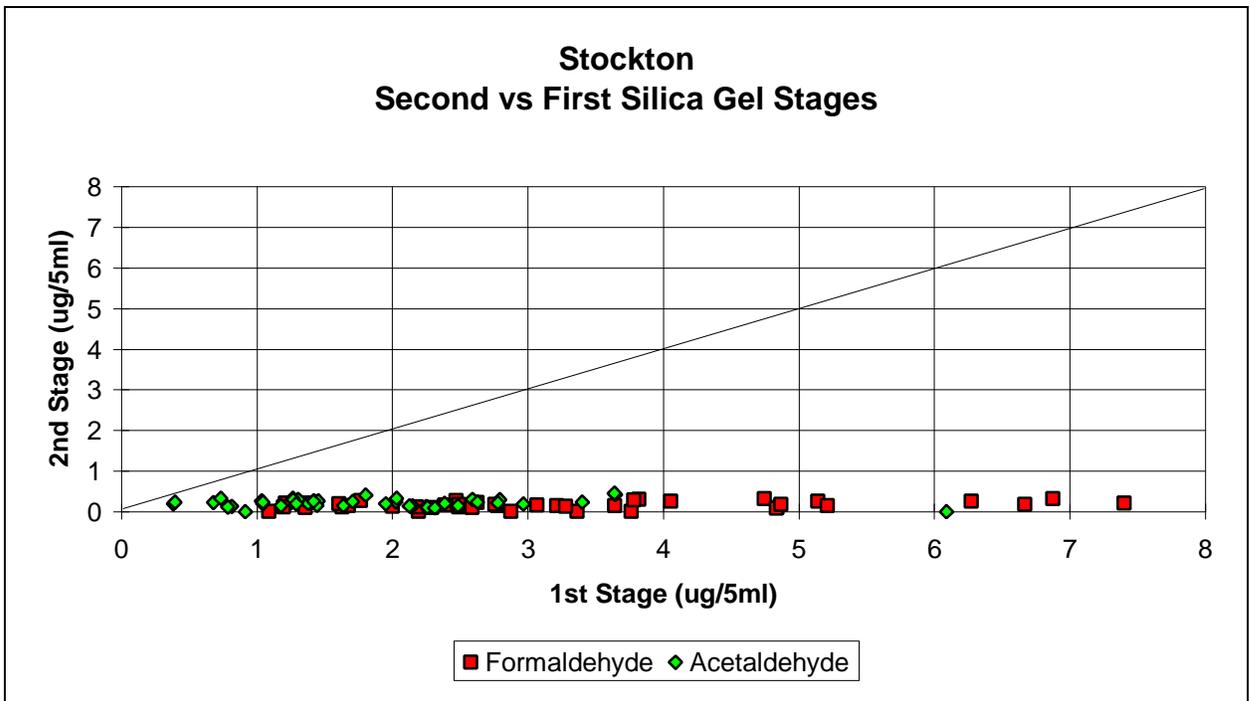


Figure 11. Formaldehyde and acetaldehyde concentrations in second silica gel stage versus first stage.

When the samples containing more than one third of the total formaldehyde mass in the second stage are removed from the scatter plot of C18 vs. silica gel measured concentrations, the correlation improves, especially at concentrations lower than 4 ppb (Figure 12). However, several samples in the higher concentration range still show poor C18 recoveries, which suggests that other factors may have also affected the performance of the C18 media.

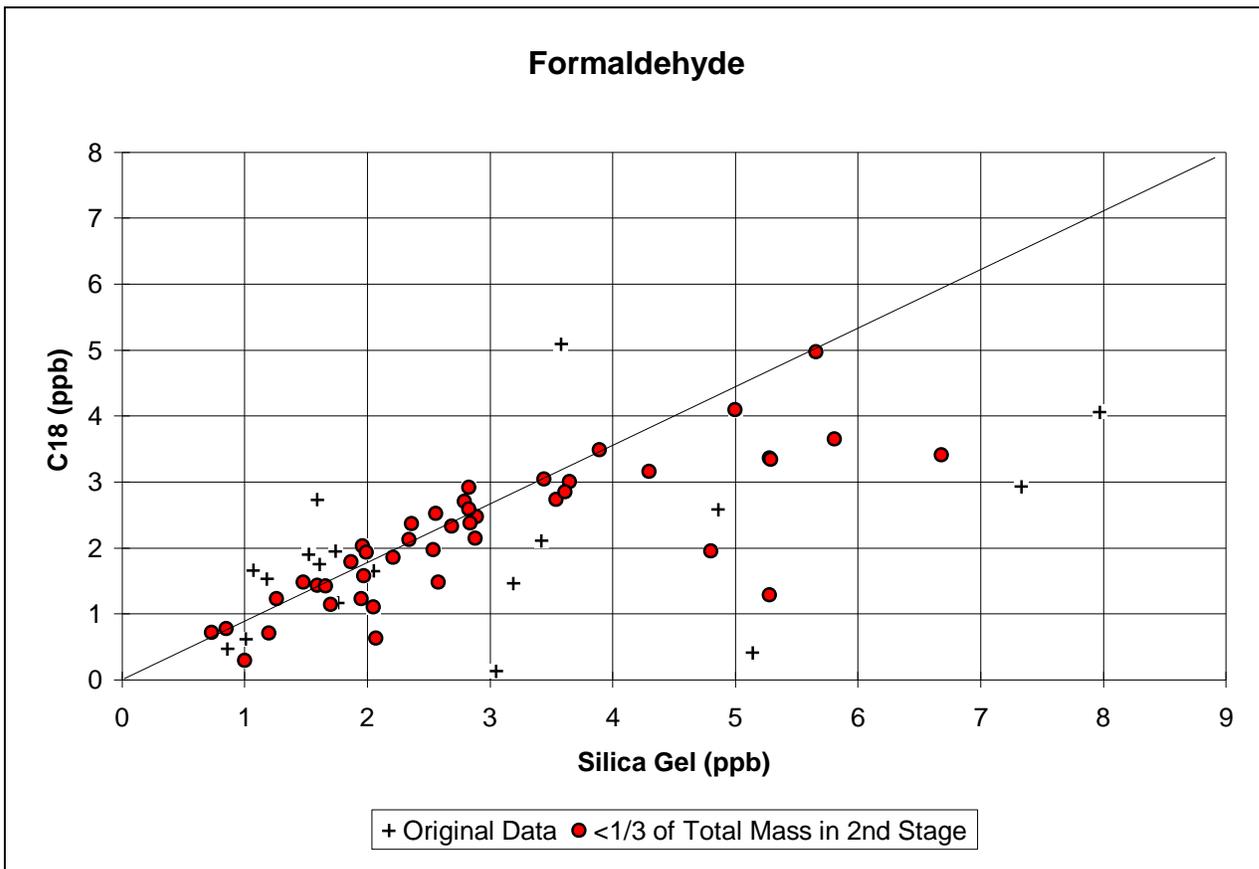


Figure 12. Formaldehyde ambient concentrations measured by C18 versus silica Gel

CONCLUSIONS

The results of the one-year parallel study show an apparent negative bias in the sampling efficiency of the C18 media when compared to silica gel, especially at higher ambient carbonyl concentrations. Breakthrough was a widespread problem with the C18 sampling method, and it was probably one of the causes for the poor efficiency.

The specific causes for breakthrough have not been established. The effects of environmental factors such as ozone concentration, relative humidity, and ambient temperature were investigated, but they were determined to be ambiguous. Factors leading to breakthrough could include: 1) inconsistent packing of the substrate which could lead to channelization of the air flow, 2) inconsistent DNPH coating which could

lead to variable trapping efficiency, 3) sample desorption due to flow rates that exceed the capacity of the cartridge, or 4) mass loading that exceeds the cartridge capacity leading to sample saturation.

During the one-year parallel study, the silica gel sampling media demonstrated superior properties in terms of precision and resistance to breakthrough; however, the method has not been fully validated. The MLD will conduct further studies to document the method's performance under the program's sampling conditions. Specifically, these studies will include: 1) analysis of laboratory and field blanks, 2) determination of collection efficiency, 3) determination of maximum mass loading capacity, and 4) documentation of sample stability under current sampling and storage conditions. Also, monitoring of ambient samples for breakthrough will be re-established at a high concentration site, with the results reported in the laboratory's quarterly quality control report. Finally, the laboratory staff will maintain a record of the sampling cartridge batch numbers, so that if a sampling problem is associated with a batch, the affected samples can be quickly identified.