

**Appendix FF**  
**Analysis of Carbonyl Data from 1995-2002 to Determine**  
**the Correlation Between Ozone and Aldehyde Concentrations**  
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The purpose of the project was to examine the correlation between ozone and aldehydes, in particular formaldehyde, to determine whether the formaldehyde is secondary or emitted. Overall, the ozone and aldehyde data separated by monitor and year only appeared to be well correlated at a few monitors during a few years, and these correlations did not appear to follow any particular pattern. There was very little improvement in the correlation between ozone and formaldehyde on days with high ozone or for samples with high or low aldehyde concentrations.

However, when the 24-hour samples were divided into wind bins based on resultant wind direction and compared to a map of formaldehyde sources, a pattern in the value of  $R^2$  did seem to appear for each monitor. The Texas City monitor gave the best example of changes in the value of  $R^2$  aligning with sources near the monitor. In directions where there were large sources located near the Texas City monitor, the value of  $R^2$  dropped, and for directions where there were no significant formaldehyde sources, the correlations were much better. All of the other monitors showed a similar relationship between changes in the value of  $R^2$  and the location of formaldehyde sources, although there were a few exceptions to this pattern for several of the monitors. This relationship indicated that there was definitely some formaldehyde in the air that had been created as a secondary product during ozone formation, but that there was also formaldehyde in the air that had been emitted from sources in the HGA area.

### **Introduction**

The purpose of this analysis was to examine aldehyde concentration data in relation to co-located ozone concentration data to determine the extent of the correlation between the two sets of data, in particular the correlation between ozone and formaldehyde. Formaldehyde can be both formed in and emitted into the air, so knowing how the formaldehyde measured by air monitors was produced is of interest when designing formaldehyde regulations. The process of ozone formation involves the conversion of carbonyls to formaldehyde, so a strong correlation between formaldehyde and ozone indicates that the formaldehyde measured by a monitor is probably secondary in nature. When there is a weak correlation between ozone and formaldehyde, it is likely that the formaldehyde measured at the monitor has been emitted from a nearby industrial or urban source. Wind direction data was used in the final part of this analysis to associate uncorrelated data with nearby industrial formaldehyde sources.

### **Description of Analysis**

#### *The data set*

All of the available aldehyde data collected after 1995 at monitors in the Houston-Galveston (HGA) and Beaumont-Port Arthur areas were pulled from the carbonyl data sets in the MOTHER database. The aldehyde measurements available in MOTHER were made using air

parcels collected over two different intervals; some of the measurements were made using air collected in cartridges over a three-hour period and some of the measurements were made using air collected in cartridges over a 24-hour period. After December 25, 1998, all of the aldehyde data were collected as 24-hr samples, so the three-hour samples only span the years from 1995 to 1998, while the 24-hour samples span the entire period between 1995 and 2002. The only sites that collect both three-hour and 24-hour samples are the Clinton and Deer Park monitors; for both of these monitors, the two types of samples do not overlap, since only three-hour samples are collected at these two monitors before December 25, 1998 and only 24-hour samples are collected after that date.

The aldehyde data was merged with hourly ozone data by date and time for data collected at co-located monitors, and any aldehyde data that did not have co-located ozone data was deleted. The resulting data set contained aldehyde and ozone measurements for six CAMS sites, all of which are located in the HGA area. Information about these sites is given in **Table 1**.

**Table 1**  
**Co-located Aldehyde and Ozone data available in the HGA area**

Airs Number	Site Name	Sample Length	Collection Dates	Number of Samples
481671002	Texas City	24-hr	8/25/95-8/20/97	58
482010024	Aldine	24-hr	8/16/00-3/29/01	54
482010026	Channelview	24-hr	11/21/01-3/21/02	21
482010055	Bayland Park	24-hr	1/6/99-7/29/00	60
482011035	Clinton	3-hr, 24-hr	8/24/95-3/27/02	3hr - 231 24hr - 184
482011039	Deer Park 2	3-hr, 24-hr	6/3/98-3/27/02	3hr - 44 24hr - 201

The specific aldehyde compound that was the focus of this analysis was formaldehyde, although acetaldehyde was also examined. These compounds were measured for all of the three hour and 24-hour samples. The total of all aldehyde compounds measured for each sample was also used in the analysis. For samples collected before January 1, 1999, formaldehyde and acetaldehyde were the only aldehydes measured, but for samples collected during and after 1999, several other aldehydes were measured, including propionaldehyde, butyraldehyde, and isovaldehyde. As a result, the total aldehyde for samples collected during 1998 and earlier is the sum of only acetaldehyde and formaldehyde, while the total aldehyde concentration used for samples after 1998 includes the concentrations of all of the aldehydes measured and can be significantly greater than the sum of just formaldehyde and acetaldehyde.

#### *Analysis methods*

A different analysis was performed on the aldehyde and ozone data depending on the sample length. For the three-hour data, the mean concentration of ozone was calculated using the three ozone measurements taken during the collection of each aldehyde sample; for the 24-hour data, the peak ozone measurement collected during the interval of the aldehyde sample was determined. These average or peak ozone values were plotted versus the aldehyde concentrations to determine the extent of the correlation between the ozone and aldehyde data. The degree of

correlation was found by creating a line of best fit for the data and looking at the  $R^2$  and/or adjusted  $R^2$  value for that line. The value of  $R^2$  can vary between one and zero, with a value of one indicating a perfect correlation and a value of zero indicating no correlation; the adjusted  $R^2$  value is similar to  $R^2$ , but it contains an adjustment for sample size that results in a lower adjusted  $R^2$  values for smaller samples.

The first set of correlation plots shows all of the data collected for each year, regardless of monitor or collection interval. The graph for 1999 is given in **Figure 1** as an example of this type of plot. For the second set of correlation plots, the data were divided up by collection interval and monitor and sorted by date. One plot was created for each monitor and the data for each year of collection at that monitor were plotted with different symbols and fitted with separate lines to determine the correlation for each year at each monitor. An example of this type of graph for the Clinton monitor is given in **Figure 2**. The third set of graphs showed ozone vs. high formaldehyde and total aldehyde and ozone vs. low formaldehyde and total aldehyde for all of the data. To determine the cut-off point for high values, histograms were created for all of the data for each compound (formaldehyde and total aldehyde). The high value cut-off was assigned based on which value on the histogram appeared to be greater than approximately 90 percent of the measurements. Correlation plots were also created for aldehyde samples where the peak or average ozone value exceeded either the one-hour standard or the eight hour standard, and the graph for the samples with ozone concentrations greater than the one hour standard is given in **Figure 3**.

The final set of correlation plots looked at the data collected at each monitor based on the resultant wind direction for the sample. To calculate the resultant wind direction, wind speed and direction data were merged with the aldehyde and ozone concentration data. For each aldehyde sample where wind data was collected, the resultant wind direction was determined by using vector addition of all of the hourly wind directions weighted by wind speed. In order to provide enough measurements for each wind direction, all of the resultant wind directions were assigned to one of eight wind bins. Each of the wind bins are 45 degrees wide; bin 1 begins at  $337.5^\circ$  and ends at  $22.5^\circ$ . The other bins are numbered through eight and follow bin 1 in a clockwise direction around the compass. Once each measurement was assigned to a bin, correlation plots were created for each bin, with the data divided up by collection interval and monitor.

For the final part of the analysis, the correlations by wind bin described in the previous paragraph were used to determine possible industrial contributors to formaldehyde levels. All of the sources and air monitors in the Houston area were plotted on a map using Surfer. The plot of the sources was classed, so that the biggest emitters have the biggest symbols, and are colored red; the lowest emitters are the smallest and are colored blue. Formaldehyde emissions data was obtained from the point source database for VOCs, version 12. All of the other industries located in Houston that either do not emit or do not report formaldehyde emissions are included on the maps as the small, black rings. The latitude and longitude boundaries for each of the maps extend to  $\sim 0.2$  degrees on each side of the monitor. These boundaries are set in this way so that all of the sources shown on the map are less than or equal to approximately 15 miles away from the monitor. Only sources within 15 miles of the air monitoring sites were used because formaldehyde is a highly reactive chemical and emissions from a source farther away than 15

miles probably would have dissipated or reacted away before reaching the monitor. On each of the source maps, the monitor of interest has been circled. The maps for the six monitors are given in **Figures 4 through 9**.

## Results and Conclusions

### *Correlation results*

For each of the correlation plots, values of  $R^2$  were determined that related ozone concentrations to aldehyde concentrations. All of these  $R^2$  values are presented in the following tables. **Tables 2, 3, and 4** contain the  $R^2$  values for the ozone v. formaldehyde, ozone v. acetaldehyde, and ozone v. total aldehyde data, respectively, sorted by monitor and year. The bold values in each of these tables indicate the degree of correlation between ozone and the given compound for all of the data regardless of monitor, year, or collection interval.

**Table 2**  
 **$R^2$  Values for Ozone v. Formaldehyde by Site and Year**

Airs Number	1995	1996	1997	1998	1999	2000	2001	2002	Overall
481671002	0.4645	0.0062	0.0002						0.0025
482010024						0.5104	0.007		0.4749
482010026							0.8672	0.0728	0.2508
482010055					0.4241	0.0124			0.3621
482011035	0.4616	0.2384	0.1937	0.3935	0.6357	0.2214	0.1469	0.8804	0.1078
482011039				0.2814	0.5712	0.2238	0.0511	0.036	0.0826
Overall	0.4292	0.0972	0.049	0.3846	0.4479	0.2322	0.1118	0.0884	<b>0.0681</b>

**Table 3.**  
 **$R^2$  Values for Ozone v. Acetaldehyde by Site and Year**

Airs Number	1995	1996	1997	1998	1999	2000	2001	2002	Overall
481671002	0.2582	0.024	0.0059						0.177
482010024						0.3372	0.0037		0.0014
482010026							0.7671	0.3709	0.398
482010055					0.1006	0.0435			0.0684
482011035	0.1172	0.3317	0.2544	0.0083	0.4491	0.2074	0.2696	0.6315	0.177
482011039				0.1037	0.3861	0.0992	0.2619	0.0238	0.1188
Overall	0.0127	0.0806	0.1284	0.1547	0.2303	0.1432	0.2203	0.0732	<b>0.0694</b>

**Table 4**

**R<sup>2</sup> Values for Ozone v. Total Aldehyde by Site and Year**

Airs Number	1995	1996	1997	1998	1999	2000	2001	2002	Overall
481671002	0.4279	0.0126	0.0004						0.0046
482010024						0.6086	0.0004		0.4827
482010026							0.8213	0.1998	0.3652
482010055					0.2978	0.0138			0.2519
482011035	0.3304	0.3099	0.2698	0.3269	0.584	0.2371	0.2672	0.7423	0.2258
482011039				0.1825	0.4338	0.2726	0.1657	0.2252	0.22
Overall	0.1596	0.0989	0.096	0.3911	0.3111	0.2949	0.1958	0.1237	<b>0.1617</b>

**Table 5** contains the R<sup>2</sup> values for the plots of ozone vs. high and low formaldehyde and total aldehyde, along with the values for ozone exceedance days. The high value cut-off points of 10 ppbC and 20 ppbC were assigned to formaldehyde and total aldehyde, respectively, based on the histograms described in the previous section.

**Table 5  
R<sup>2</sup> Values for High Ozone or Carbonyl Samples**

Compound	1hr Ozone Exceedance	8hr Ozone Exceedance	High Carbonyl	Low Carbonyl
Formaldehyde	0.4995	0.0745	0.032	0.0367
Acetaldehyde	0.0082	0.0307		
Total Aldehyde	0.3823	0.0775	0.0306	0.1325

**Table 6** contains the R<sup>2</sup> values for ozone v. formaldehyde data sorted by collection interval, monitor, and wind bin. The values of R<sup>2</sup> for ozone v. acetaldehyde and ozone v. total aldehyde sorted by collection interval, monitor, and wind bin will not be given in this report (see Future Work section). This table also contains the adjusted R<sup>2</sup> values for the 24-hour data, which are listed as the second number in each cell; the adjusted R<sup>2</sup> values are included for this data because some of the monitors don't have a lot of data for each bin and the adjusted R<sup>2</sup> value is a more accurate measure of correlation for these small data sets.

**Table 6**  
**R<sup>2</sup> Values for Ozone v. Formaldehyde**  
**by Collection Interval, Site, and Wind Bin**

Interval	Airs Number	Octant 1	Octant 2	Octant 3	Octant 4	Octant 5	Octant 6	Octant 7	Octant 8
3-hr	482011035	0.3638	0.3918	0.4033	0.5443	0.1244	0.5648	0.1031	0.5411
3-hr	482011039	0.7508	0.7554	0.0023	0.3692	0.0584	NA	NA	NA
24-hr	481671002	0.9777 0.9703	0.8628 0.7942	0.3325 0.2769	0.0052 0	0.2648 0.1980	0.9736 0.9472	NA	0.1711 0
24-hr	482010024	0.8101 0.7830	0.0556 0	0.6764 0.6301	0.0818 0	0.7901 0.7201	NA	0.9506 0.9011	0.4421 0.2561
24-hr	482010026	0.435 0.3543	NA	NA	0.4736 0.2981	NA	NA	NA	NA
24-hr	482010055	0.0125 0	0.5625 0.4167	0.7581 0.7178	0.5719 0.5390	0.2768 0.2166	0.7239 0.5858	NA	0.0079 0
24-hr	482011035	0.4409 0.4177	0.0854 0.0373	0.0593 0.0005	0.6061 0.5967	0.2362 0.2171	0.2083 0.1666	NA	0.334 0.2230
24-hr	482011039	0.1951 0.1504	0.0362 0.0203	0.2272 0.1996	0.2403 0.2248	0.2056 0.1887	0.3389 0.2728	0.0111 0	0.1398 0.0323

*Conclusions for ozone v. aldehyde by monitor and year*

The results of the correlation analysis for the data divided by monitor and year do not conclusively prove that the aldehydes measured in these samples are either secondary or emitted throughout a given year at a given monitor. There are several years at several monitors that have R<sup>2</sup> values above 0.5, which indicates that the data is more correlated than it is random, but these reasonably high R<sup>2</sup> values do not follow any discernable pattern. Also, the formaldehyde and acetaldehyde data appear unrelated in that a low correlation for formaldehyde in a given year at a given monitor does not necessarily mean that the correlation is low for acetaldehyde for that same year and monitor. The overall correlations for each compound using the total data set are very low.

*Conclusions for ozone v. aldehyde for high and low values*

Previous research performed by Carl Berkowitz, et al., using data collected during the TexAQS 2000 study at the Williams Tower monitor indicated that the correlation between formaldehyde and ozone when ozone concentrations are high is very good (almost 90%) (Berkowitz, Plume Characteristics, 2003). To see if this result was confirmed in the carbonyl data used for this analysis, ozone was plotted versus formaldehyde, acetaldehyde, and total aldehyde on days when the ozone concentration was in excess of 125 ppb and when the ozone concentration was greater than 85 ppb but less than 125 ppb. None of the R<sup>2</sup> values for ozone greater than 85 ppb and less than 125 ppb were greater than 0.1, which indicates that there is no correlation for these data. For ozone concentrations above 125 ppb, the correlation with formaldehyde is fairly good, but the slope of the line that fits the data is negative, which would indicate that ozone concentration drops as formaldehyde concentration increases, which is not the expected result. Based on these

$R^2$  values, it is apparent that these data do not reproduce the results found by Berkowitz for high ozone days. There are enough significant differences between the Berkowitz data and the data used for this analysis, such as the monitor position and the frequency of the data collected, that it is not surprising that the results are not similar.

Ozone was also plotted versus both high and low formaldehyde and total aldehyde to see if these data led to higher or lower  $R^2$  values than those for the entire data set. The  $R^2$  values given in **Table 5** for these plots indicate that, if anything, the data are less correlated when separated into high and low concentrations than when the data set is taken as a whole.

#### *Conclusions for ozone vs. formaldehyde by wind bin*

The final part of the aldehyde analysis described in this report involved dividing up the formaldehyde samples based on the resultant wind direction into one of eight wind bins, or octants. A histogram showing the distribution of the 24-hour samples over the wind octants for the six air monitors is given in **Figure 10**. This histogram can be used to show the number of measurements in each wind octant for each monitor and can also be used to show patterns in the distribution of samples over the wind octants. Based on the data in this histogram, it is apparent that for all of the monitors except Channelview, a majority of the samples were collected when the wind was blowing primarily out of the east to south, which corresponds to octants three, four, and five.

For this part of the analysis, the 24-hour data and the three-hour data were not combined. The reason for this is that over two-thirds of the three-hour samples were collected at night (after 8 pm or before 5am). This presents two problems, the first of which is that samples taken at night would be unlikely to contain much new secondary formaldehyde because ozone is not being formed in large quantities at this time. The second problem is that these samples taken at night generally have much lower average ozone concentrations than the daytime peak concentrations used for the 24-hour samples, but the aldehyde concentrations are in the same range of values for the daytime and nighttime samples. This means that when the three-hour and 24-hour samples are combined, the  $R^2$  values for each wind octant are artificially driven lower by the lack of cohesion in the two sets of data. Since the three-hour samples were all collected before 1998 and at only two monitors, the focus of the following analysis will be on the 24-hour samples.

The  $R^2$  values obtained from the correlation plots for data separated by collection interval, monitor and octant are presented in **Table 6**. For each of the monitors, the  $R^2$  values were compared with the source maps to see if low correlations tended to coincide with directions where sources were located. Since the Channelview monitor has very little data and  $R^2$  values for only two of the wind octants, it is difficult to analyze the agreement between the locations of sources around this monitor and the variations in  $R^2$  values. For this reason, no further analysis will be done for this monitor.

The Texas City monitor provides an especially good example of the coincidence of formaldehyde sources and low  $R^2$  values. The map for the Texas City monitor, which is given in **Figure 4**, shows that there are several formaldehyde sources located primarily to the south and southeast of the monitor. This group of sources includes two sources that are in the highest class of emitters. There are also two large emitters located to the northwest of the monitor. Based on

this map, wind coming from the directions of these sources should contain emitted formaldehyde and the  $R^2$  values for these wind octants should be low, while the wind coming from all of the other octants should contain primarily secondary formaldehyde and the correlations for these octants should be good. The  $R^2$  values for this monitor support this hypothesis. Correlations are very good for wind from the north and northeast, octants one and two; the  $R^2$  values drop for wind out of the east, octant three, and the lowest correlation occurs for wind out of the southeast, octant four, which would pass over one of the large emitters. The  $R^2$  values continue to be low for wind from the south, octant five, which would pass over the other large emitter in that area. The correlation is good for winds from octant six, which contains no formaldehyde sources. There is not enough data to get an  $R^2$  value for octant seven, but the  $R^2$  value for octant eight is the second lowest, since wind from this direction could have passed over two large emitters located to the northwest of the Texas City monitor. Of the six monitors used in this analysis, the Texas City monitor is the best example of the agreement between the locations of industrial formaldehyde sources and the variations in the  $R^2$  value.

The  $R^2$  values for the Deer Park monitor are overall the lowest values at any of the monitors. The location of the Deer Park monitor, which is shown on the map in **Figure 5**, seems to justify these low values. Throughout the northwest and the northeast of the Deer Park monitor is the Houston Ship Channel, which contains several large formaldehyde sources. The  $R^2$  values for octants seven, eight, one, and two, which correspond to the west to northeast directions, are the lowest, while the highest values occur for winds out of the southeast and southwest, where there are fewer large sources. Since the use of vector addition to assign a wind direction to a sample is only an approximation of the direction that the formaldehyde in the sample could have come from, it is highly likely that the formaldehyde emissions from the Ship Channel could affect the correlations for all of the wind octants, so the relationship between source location and  $R^2$  value shown at the Texas City monitor is much less clear at the Deer Park monitor.

**Figure 6** shows that the Clinton monitor is also located near the Houston Ship Channel, and three large formaldehyde sources are located directly to the south of the monitor, which is probably part of the reason that the Clinton monitor has the lowest  $R^2$  values after the Deer Park monitor. In spite of this, the variations in the  $R^2$  values also seem to correspond to source locations, with one notable exception. The  $R^2$  values are very low for winds from octant three in the east, where many of the Ship Channel formaldehyde sources are situated, and for winds from octant seven in the west, where the densest part of Houston is located. The exception is the correlation for wind from the southeast, octant four. This wind direction has the best correlation of any octant at the Clinton monitor in spite of the fact that there is a group of emitters located in this direction close to the monitor and that there are several large emitters to the south that would probably affect samples taken from wind from the southwest. A possible explanation is that the sources are located too close to the monitor and that the formaldehyde emitted from them is carried over the monitor in air too high for the monitor to capture, but determining whether that is the case is outside the scope of this analysis.

Both the Aldine and the Bayland Park monitors show some agreement between the variations in  $R^2$  and the locations of sources, but each also has some  $R^2$  values that don't fit. The Aldine monitor is located approximately 15 miles north and slightly west of the main Ship Channel area, as shown in **Figure 7**, and there are few other significant industrial formaldehyde sources

located near the monitor. Based on this information, the  $R^2$  value corresponding to wind from the southeast (octant four) should be low and the other correlations should be fairly strong. The  $R^2$  values for the Aldine monitor given in Table 6 do follow this expected pattern for all of the wind octants except for octant two, which has the lowest  $R^2$  value. According to the map for the Aldine monitor, there are no significant formaldehyde sources located to the northeast that are within 15 miles of this monitor, so the uncorrelated data for wind from the northeast should not be the result of industrial formaldehyde emissions. The Bayland Park monitor, shown in **Figure 8**, has only one large formaldehyde source located within 15 miles. This source is located to the northwest, so the low  $R^2$  values for octants eight and one could be the result of emissions from this source. All of the rest of the octants should show good correlations between ozone and formaldehyde since there are no other large sources, but the  $R^2$  value for octant five in the south has a much lower correlation than other octants in the south and east even though there are not any sources at all within octant five.

There are several characteristics of the data set used in this analysis that can make truly conclusive results difficult to obtain. One of these characteristics is the lack of a large quantity of data. Only two of the monitors used in this analysis, Clinton and Deer Park, have a substantial amount of data that spans several years. This can make it difficult to identify correlated data. If there are only three or four measurements for a given monitor in a given wind octant and they happen to be random, it does not necessarily mean that the data would be uncorrelated if there were fifty measurements for that monitor and wind octant. Another difficulty lies in the fact that most of the data and all of the recent data come from 24-hour cartridge samples. The problem with a sample this long in duration is that it is difficult to tie a single wind direction to the sample so that it can be assigned to a single wind bin. Using vector addition with the twenty-four individual wind directions weighted by wind speed can provide a loose estimate of the direction that the wind came from, but for samples with continuously varying wind directions, this estimate may not be very good.

## Summary

The purpose of the project was to examine the correlation between ozone and aldehydes, in particular formaldehyde, to determine whether the formaldehyde is secondary (strong correlation) or emitted (weak correlation). Formaldehyde data was collected at several monitors in the HGA area over both 24 hour and three hour intervals and all of the data collected at these monitors between 1995 and 2002 was used.

Overall, the ozone and aldehyde data separated by monitor and year only appeared to be well correlated at a few monitors during a few years, and these correlations did not appear to follow any particular pattern. There was very little improvement in the correlation between ozone and formaldehyde on days with high ozone or for samples with high or low aldehyde concentrations.

However, when the 24-hour samples were divided into wind bins based on resultant wind direction and compared to a map of formaldehyde sources, a pattern in the value of  $R^2$  did seem to appear for each monitor. The Texas City monitor gave the best example of changes in the value of  $R^2$  aligning with sources near the monitor. In directions where there were large sources located near the Texas City monitor, the value of  $R^2$  dropped, and for directions where there

were no significant formaldehyde sources, the correlations were much better. All of the other monitors showed a similar relationship between changes in the value of  $R^2$  and the location of formaldehyde sources, although there were a few exceptions to this pattern for several of the monitors. This relationship indicated that there was definitely some formaldehyde in the air that had been created as a secondary product during ozone formation, but that there was also formaldehyde in the air that had been emitted from sources in the HGA area.

It was difficult to attribute the low correlations seen at each monitor to specific sources because the resultant wind direction for the 24-hour samples was found by vector addition of the 24 hourly wind direction measurements, which gave only an approximation of the direction that the wind came from over the entire day. A more detailed analysis of wind directions and patterns would be needed for more specific formaldehyde source attribution, and could be especially useful in attributing high formaldehyde concentrations seen in the three-hour data.

### **Future work**

There are several different steps that could be taken to extend the analysis of the three-hour and 24-hour samples presented in this report. One step would be to develop back trajectories for several if not all of the hours during the 24-hour and three-hour sample intervals to get a better idea of where the wind was coming from during the collection of the sample. While it would require extensive time and effort to do this type of analysis for all the samples, creating back trajectories for some of the samples at each monitor could provide useful information. Also, part of the original purpose of this analysis was to identify outlying data, which consists of samples that have high formaldehyde concentrations and low ozone concentrations. Using vector addition to get a resultant wind direction makes it difficult to attribute these outlying samples to specific sources, but trajectories, especially for the three-hour outliers, could make it more obvious where the high formaldehyde concentrations are coming from. Another step could be to look at how collection time affects the three-hour samples. Well over half of these samples have start hours between 9 pm and 11 pm; at this time of the day, ozone formation would have slowed down and more of the formaldehyde in the air would be unlikely to be secondary formaldehyde, which would cause the data to be unreliable for attributing emissions to sources. If only the daytime three-hour samples were used, there might be better agreement between the three-hour correlations by octant and the 24-hour correlations by octant. One other step that could be taken in this analysis would be to create source maps for the industrial acetaldehyde emitters and see if the source locations relate to the ozone-formaldehyde wind octant correlations, similar to the analysis for the formaldehyde sources.

In addition to extending the analysis of the three-hour and 24-hour samples, further information on the relationship between the ozone and aldehyde concentrations measured in the HGA area could be obtained by examining the one-hour carbonyl samples in the 'Mo\_vocs' folder of the MOTHER database. Analyzing these samples would remove several of the problems encountered with the longer samples in that the one-hour samples can be directly connected to ozone and wind data. Also the one-hour samples are generally collected at several times in the same day, so the problem of having mostly nighttime data for the three-hour samples is not a problem for the one-hour samples.

## **Works Cited**

Berkowitz, Carl, Chester Spicer, Guangfeng Jiang. "Plume Characteristics Associated with Rapid O<sub>3</sub> Formation Events in Houston, Texas." Prepared for Submission to Atmospheric Environment, March 17, 2003.



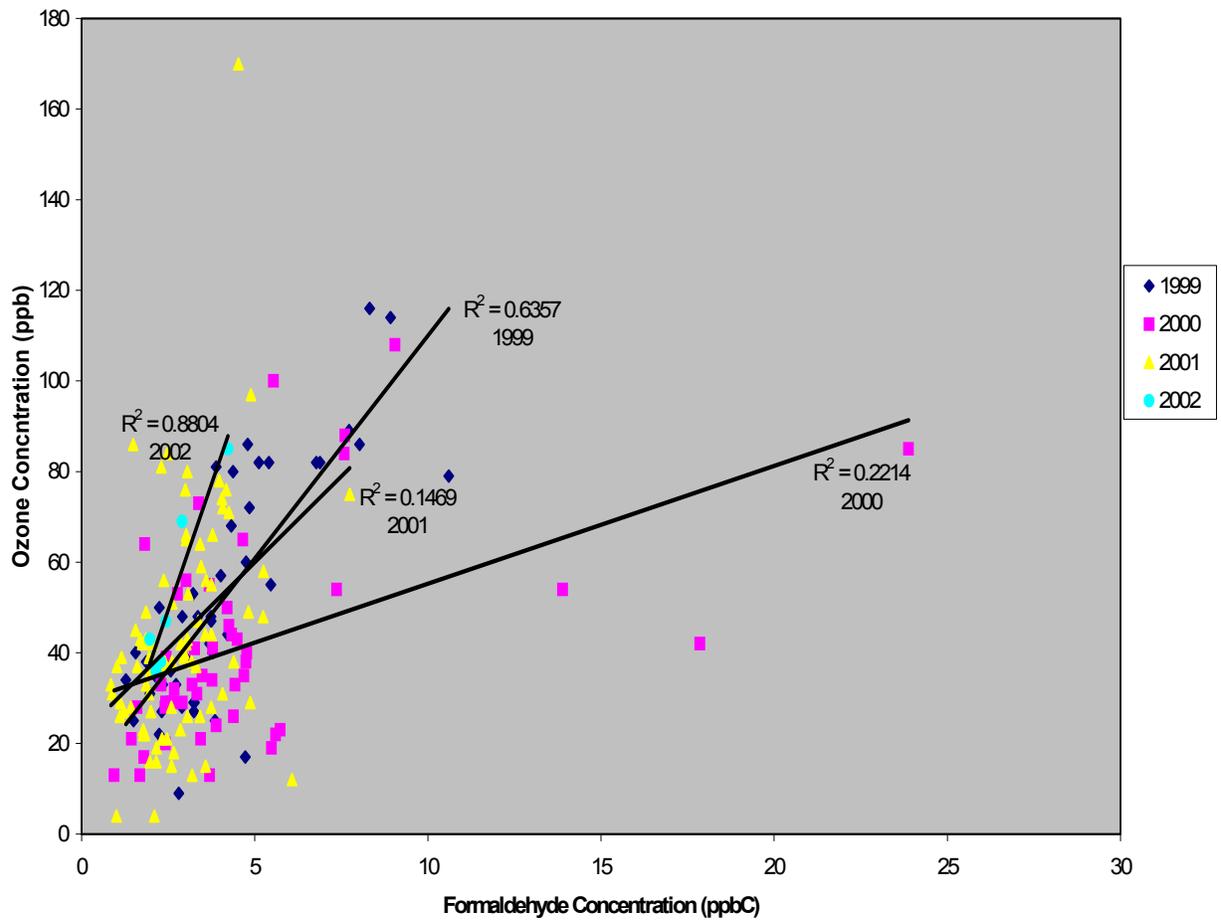


Figure 2. Ozone v. formaldehyde at the Clinton monitor for all years of data

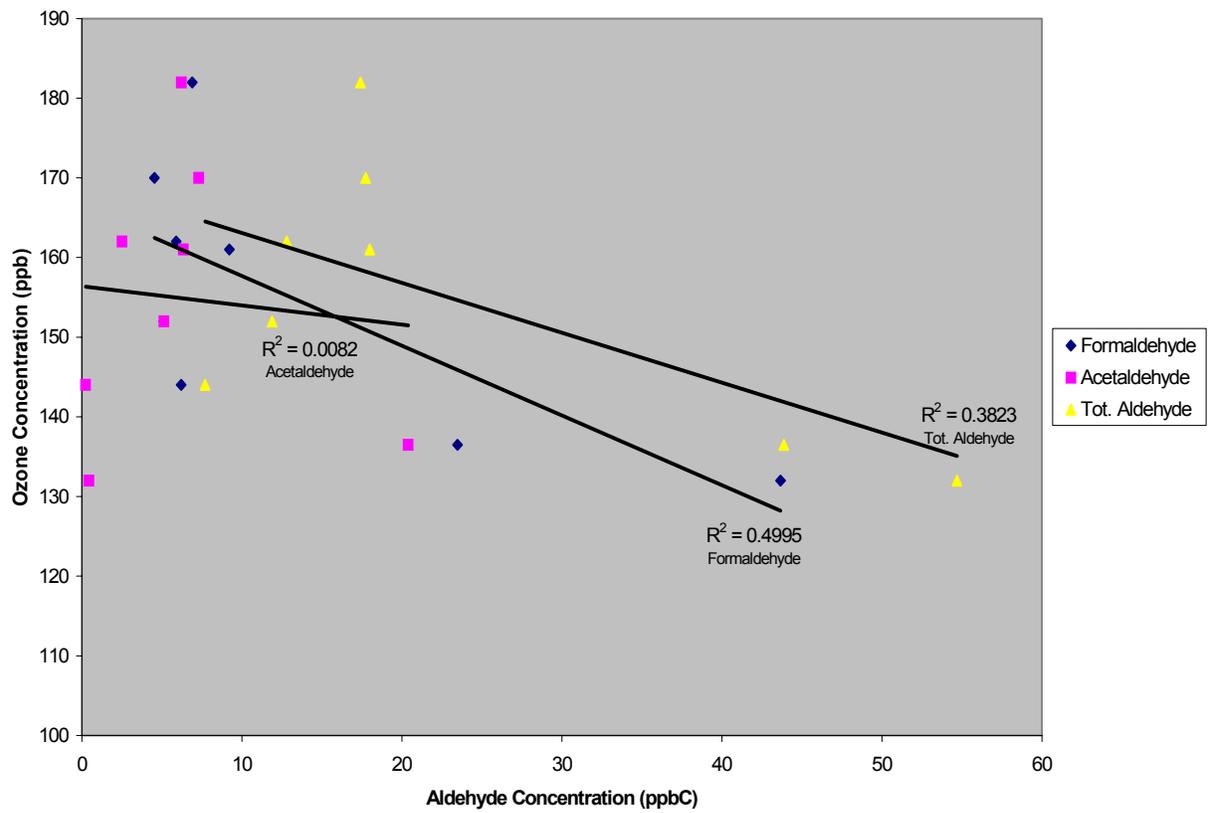


Figure 3. Ozone v. formaldehyde for 1-hr ozone exceedance days

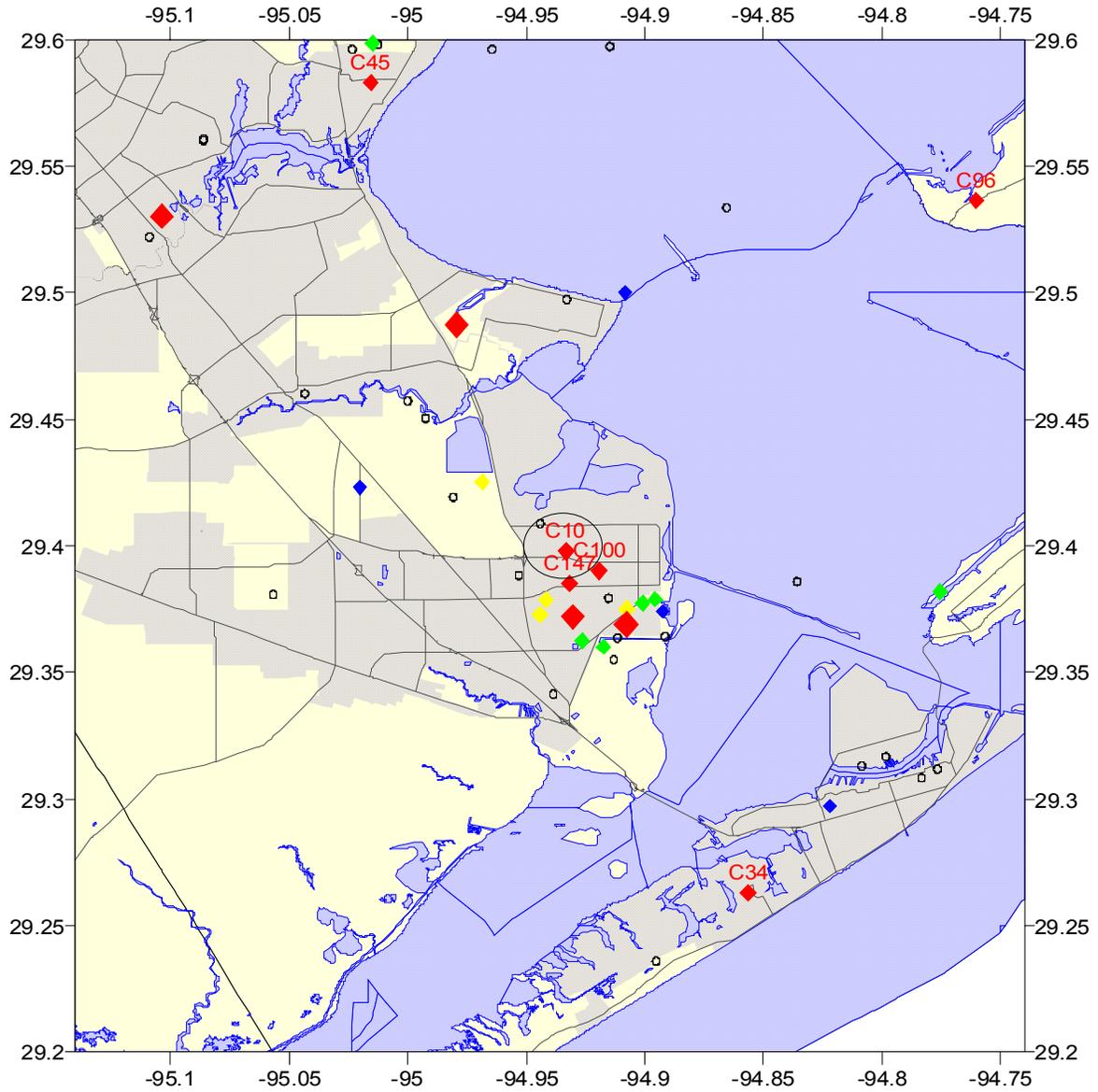


Figure 4. Source map for the Texas City monitor (C10)

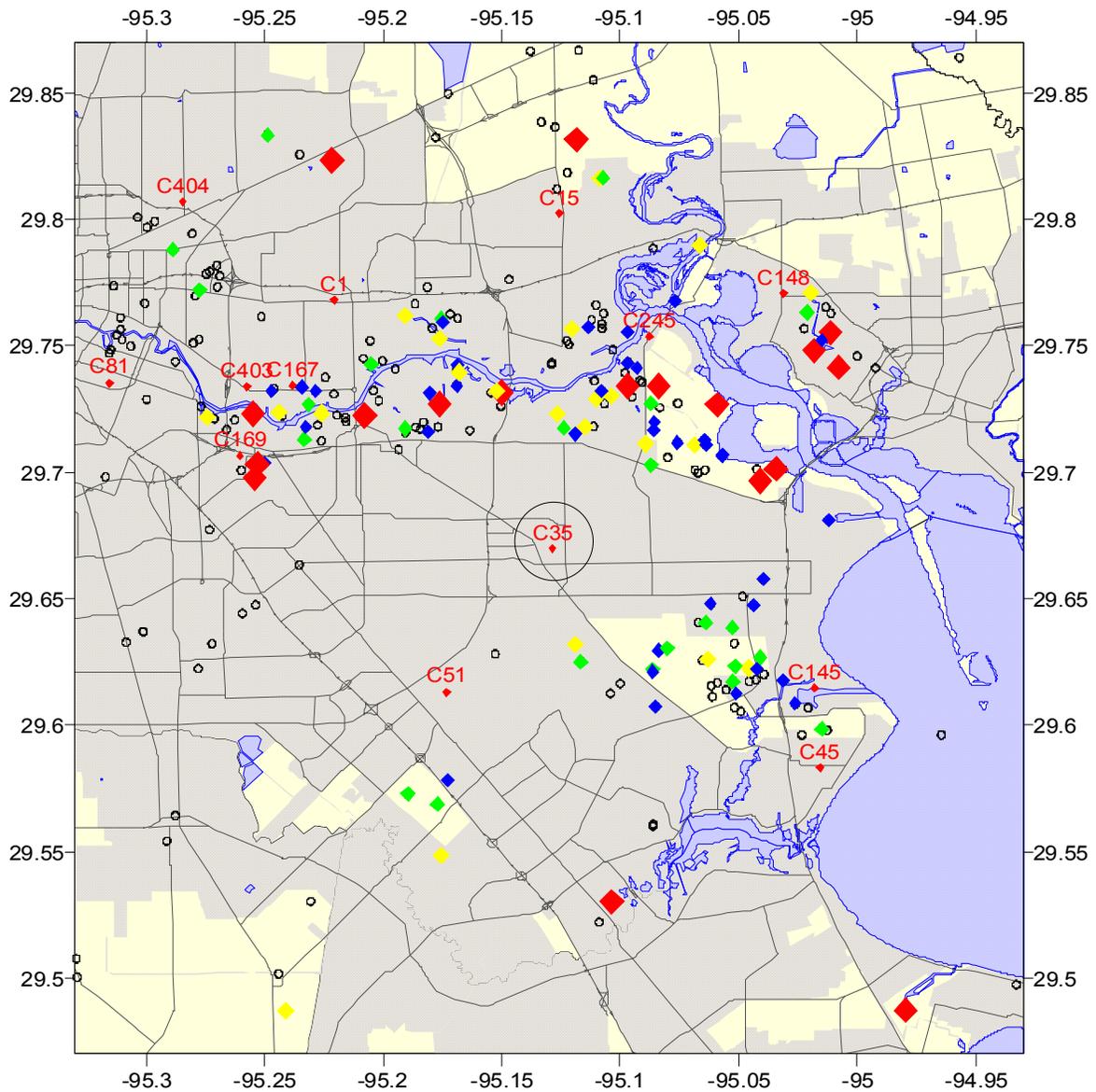


Figure 5. Source map for the Deer Park monitor (C35)

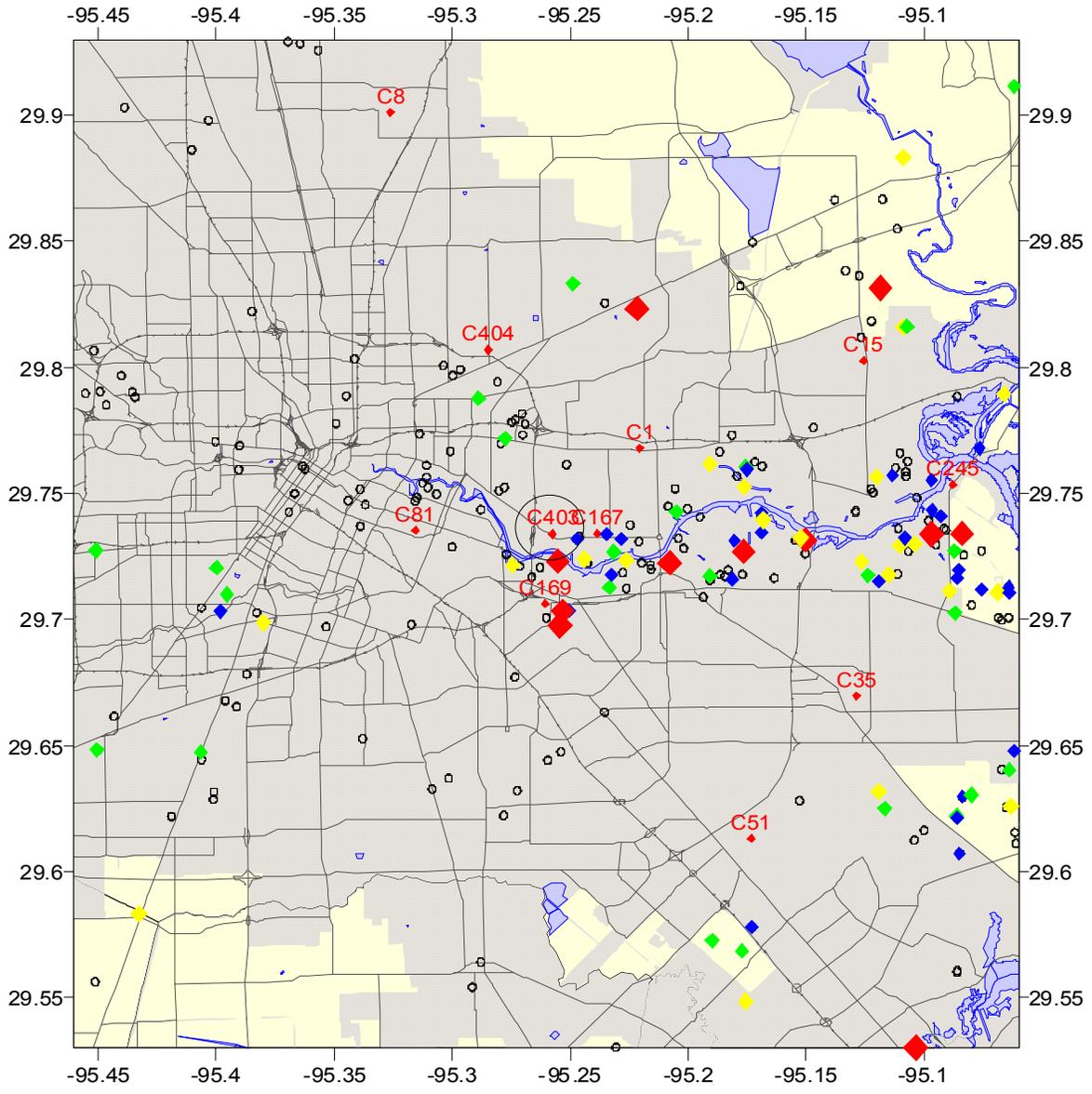


Figure 6. Source map for the Clinton monitor (C403)

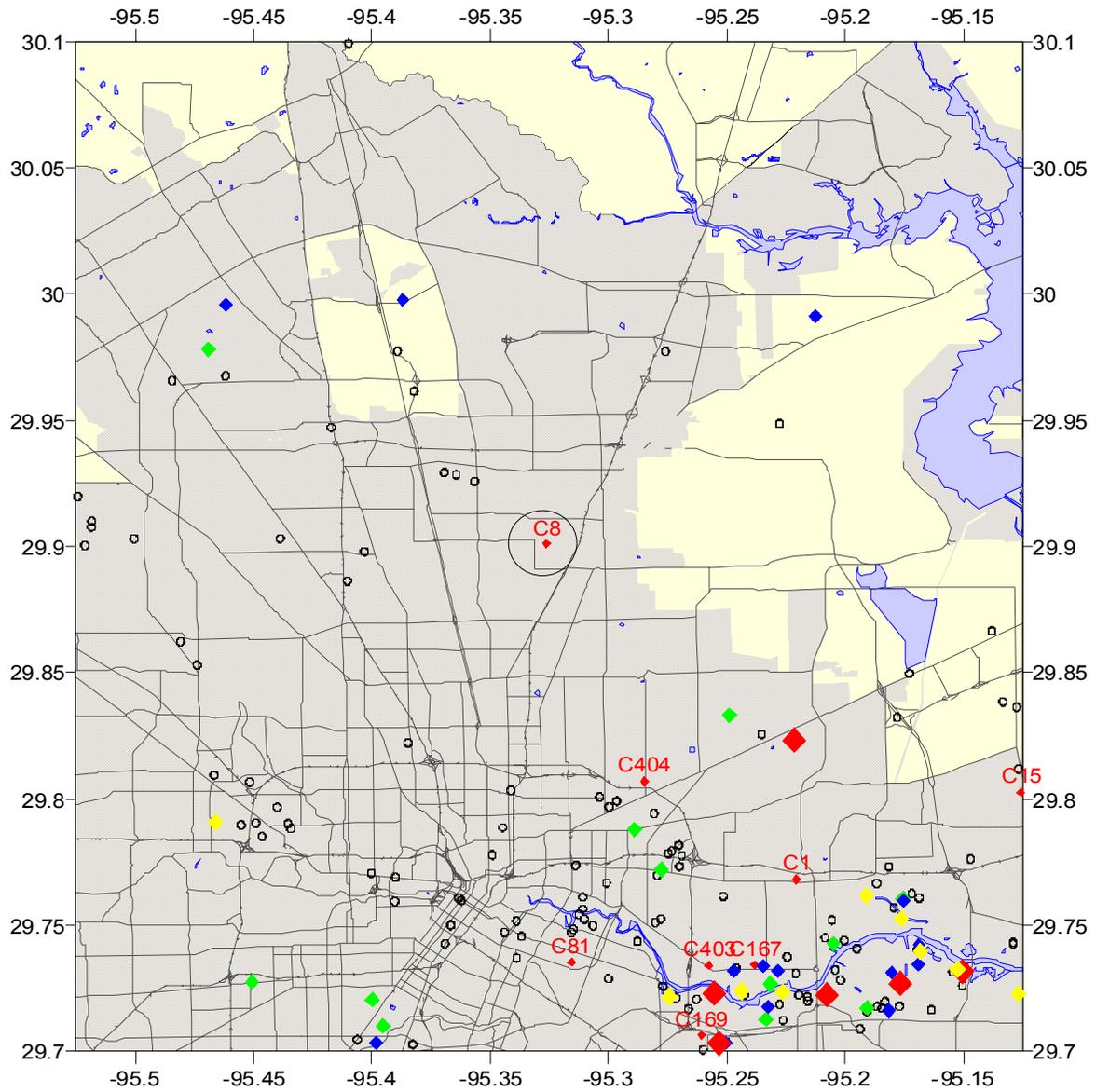


Figure 7. Source map for the Aldine monitor (C8)

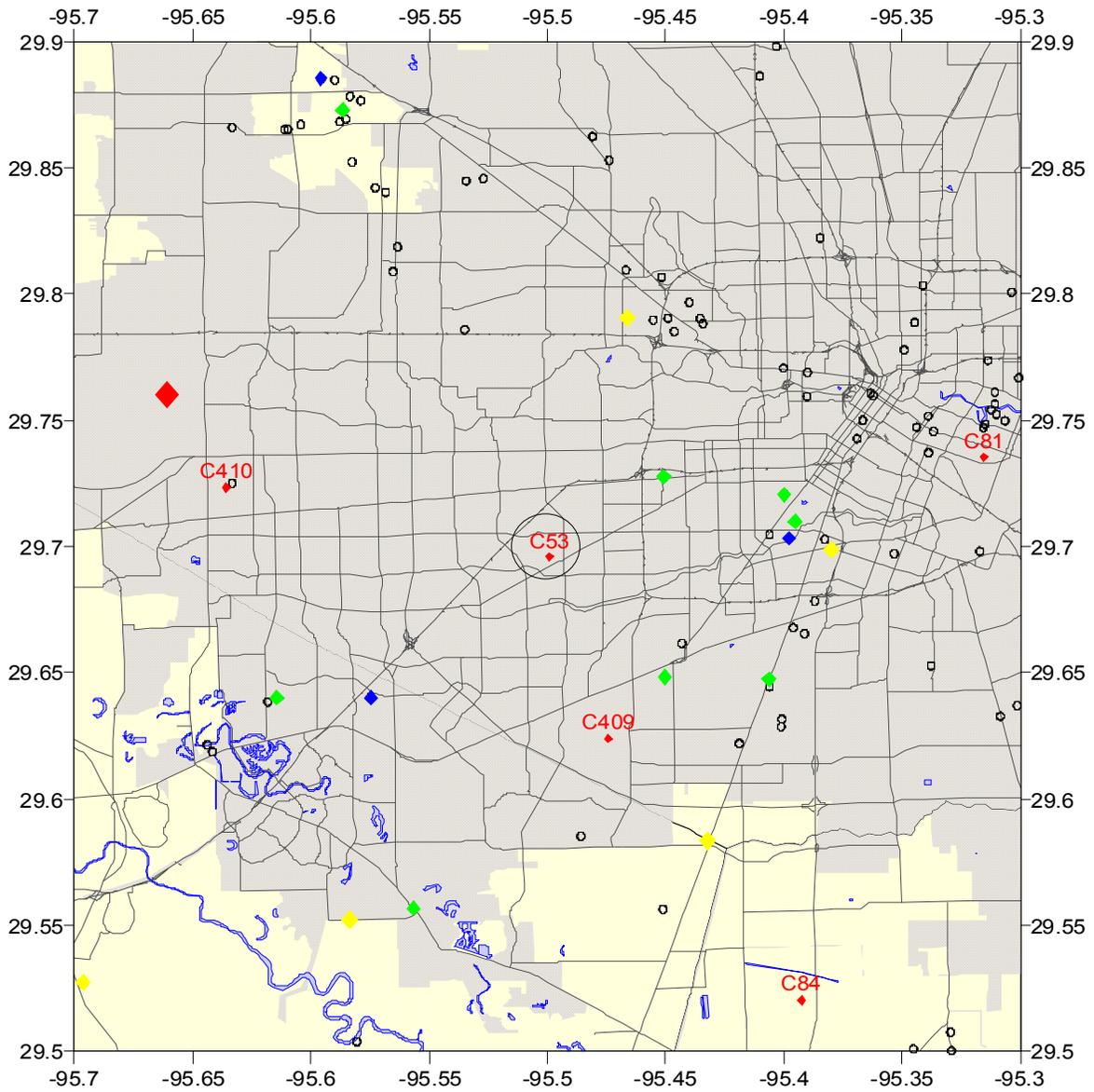


Figure 8. Source map for the Bayland Park monitor (C53)

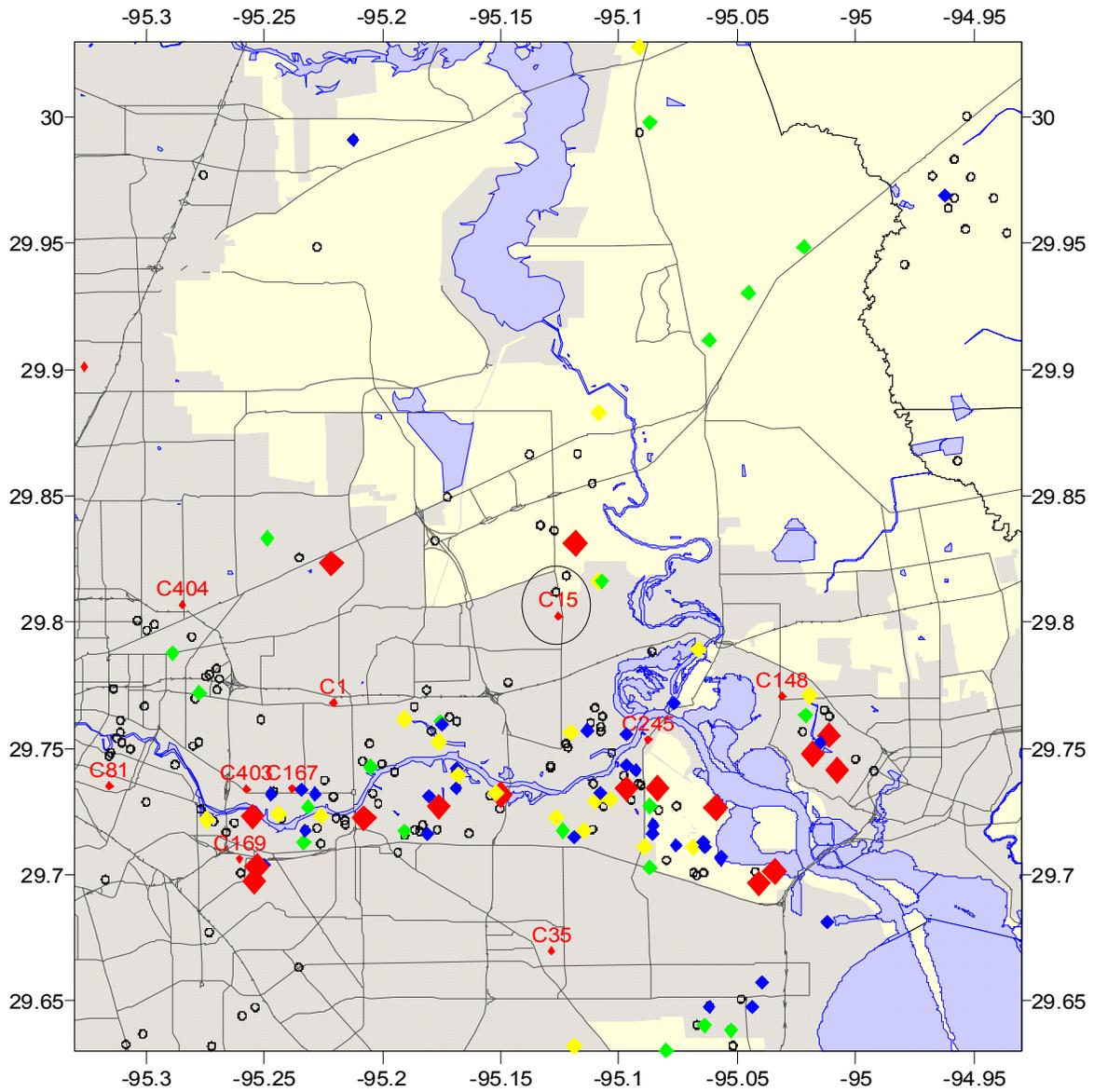


Figure 9. Source map for the Channelview monitor (C15)

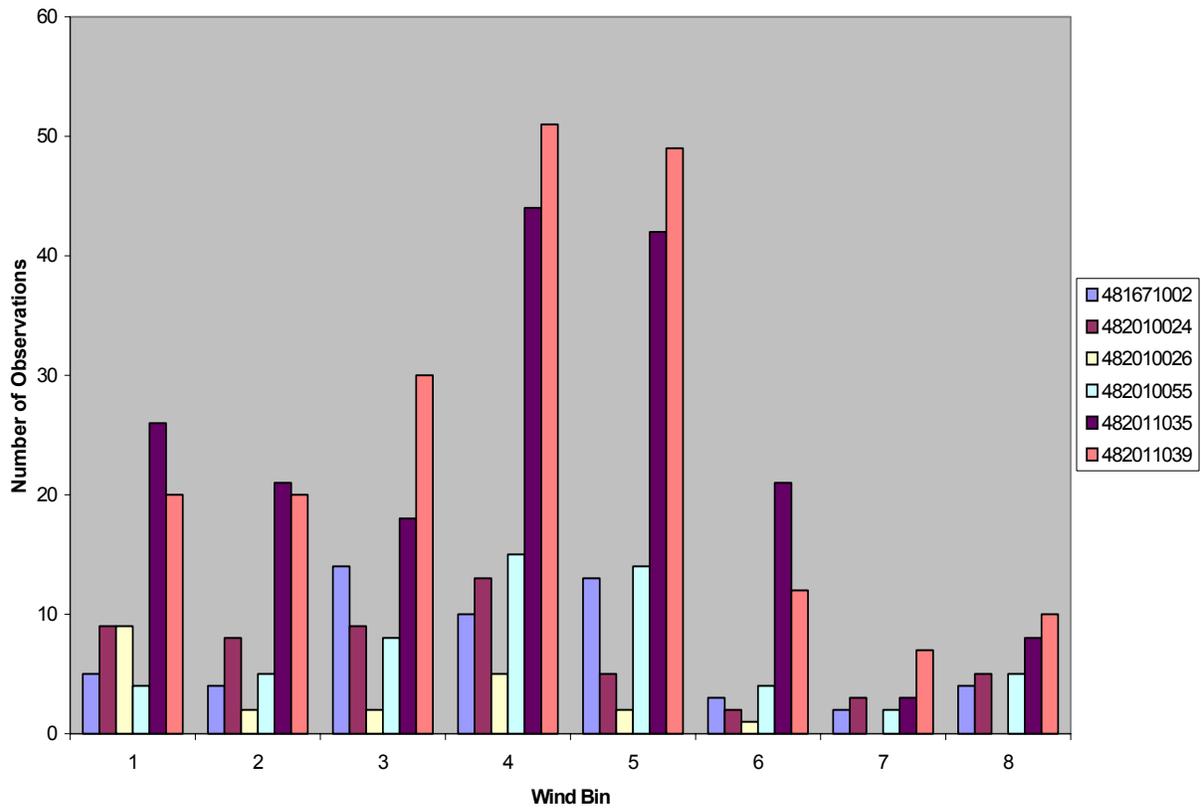


Figure 10. Number of samples for each monitor in each wind bin

