Final Report: FY '04 Community-Scale Air Toxics Ambient Monitoring Project: Delray Community Monitoring Project

September 17, 2008

Michigan Department of Environmental Quality
Air Quality Division
P.O. Box 30260
Lansing MI 48909

Project Overview

The two main goals of the Delray Community Monitoring Project were to investigate the impact of the International border crossing on air quality and to collect background measurements before the Detroit Inter modal Freight Terminal (DIFT) is built. Both of these transportation-related projects impact the Delray community. This project established infrastructure and collected measurements. A detailed data analysis project was beyond the scope and budget of this study. Data will be analyzed in detail in a second community monitoring grant that was recently received by the MDEQ, called "Analysis of Air Toxics Data: Quality Assurance Implications, Source Apportionment Uncertainty Analysis and Updated Risk Assessment." The MDEQ is currently in the process of completing the work plan for the data analysis project.

The Delray project established monitoring stations downwind from the Ambassador Bridge on Lafayette Street (261630039) and downwind from the Kronk and Livernois DIFT site at Newberry School (261630038) on 28th Street. Supplemental measurements were leveraged from the MDEQ's $PM_{2.5}$ speciation and $PM_{2.5}$ FRM networks, the NATTS site at Dearborn and a speciated organic carbon study performed by LADCO. Instrumentation was acquired to allow the collection of trace CO and continuous formaldehyde measurements at two sites. Aethalometers were borrowed to increase the spatial coverage of carbon black measurements to four sites. Continuous measurements of fine particulate were collected at the same four sites. $PM_{2.5}$ FRM measurements were included at the new stations.

Another component of the project was field testing continuous formaldehyde units. If the samplers ran in a reliable fashion, the continuous data would have been compared to results generated using more conventional technology (Method TO-11a).

In summary, the goals of the project were to:

- generate actual ambient measurements of the air quality in the area;
- develop background levels in an area with expanding transportation activities;
- assess impact from delays at the Ambassador Bridge on air quality in the area;
- complement the Detroit Exposure Aerosol Research Study (DEARs);
- complement the Canadian bridge crossing monitoring project;
- investigate middle and micro variability in air toxics concentrations;
- field test continuous formaldehyde monitors, and trace carbon monoxide monitors;
- understand diurnal variations in CO and formaldehyde and how they relate to other mobile sources oriented pollutants such as carbon black, and continuous fine particulate;
- generate a database to support source apportionment estimates of the contributions from motor vehicle and diesel exhaust to air quality, and;
- identify other possible tracer compounds for diesel by comparing speciated organic carbon measurements from Del Ray, an area heavily impacted by diesel with Allen Park, a population-oriented mobile source dominated site, the St. Louis super site and with the Class 1 Seney Wildlife Refuge,

Description of Sources/Background Material

In previous monitoring projects, levels of formaldehyde as well as other mobile source signature compounds have been shown to be elevated in the Detroit area[1,2]. The observed concentrations are highly variable by site, and it is theorized that point sources are also contributing to the levels at some of the stations. Data analysis indicates that there is a large degree of heterogeneity in the ambient levels of other toxic air pollutants in the Detroit metropolitan area, as well.

In order to transport commodities to the market, trucks and trains are often used. Inter modal freight combines both methods of transportation by transferring large containers from various transportation vehicles, avoiding any unloading or repackaging. The enhanced efficacy and improved profit margins, plus the international port status of Detroit and proximity to Canada make expansion of existing inter-modal freight facilities very attractive. However, residents have expressed concerns about impacts from the increased freight on the air quality in their community and impacts on their health.

In addition, the Ambassador Bridge crossing is heavily used by trucking traffic as an international border crossing. As a result of increased traffic due to the North American Free Trade Agreement and because of enhanced security measures implemented by the U.S. Customs Service, delays at the border crossing have occurred. Recently, a second International bridge crossing has been proposed that could also impact the Delray Community. Also, the Ambassador Bridge may be expanded. These activities will bring even more traffic into this community. Residents have also expressed concern about impacts from the long delays and idling on the air quality in their community.

Heavy-duty diesel truck, container lifting equipment and train emissions consist of various toxic air contaminants including: benzene, 1,3-butadiene (and other VOCs), acetaldehyde, formaldehyde, acrolein and PAHs. These sources also emit components that could impact on the NAAQS, including nitrogen oxides, sulfur compounds and fine particulate.

In addition to a plethora of mobile source emissions, there is a diverse industrial base in Detroit, including automotive manufacturing, steel mills, coke batteries, oil refineries, chemical manufacturing plants and medical waste incinerators. Residential areas are well dispersed through the CMSA, with many neighborhoods and schools located close to these sources.

Measurements

This project investigated in more detail, the air quality in an area of Detroit containing a variety of industrial point sources as well as transportation–related activities. Transfer of products between rail and trucking operations (inter modal freight) is heavily concentrated in the Delray area and is expected to grow significantly in the future. Traffic backups and excessive idling that result from delays crossing the international border with Canada at the Ambassador Bridge impact air quality in this area. Previous ambient air monitoring activities, which include the Detroit Air Toxics Pilot Project and the Region 5 Air Toxics Project, have been conducted upwind of the location of the Delray area. The **upwind levels** of fine particulate and air toxics are the highest within the state, and dependent upon the parameter, are among some of the highest in the nation[3,4] This project supported the creation of a sites downwind of the International Border Crossing and the favored DIFT site. Fine particulate measurements were, and still are, collected using the Federal Reference Method (FRM) and using a Tapered Element Oscillating Microbalance (TEOM). Carbon black was collected at both sites using McGee

[1] " 2001 Urban Air Toxics Monitoring Program (UATMP) Final Report," October 2002, Eastern Research Group.
[2] Detroit Pilot Project Data, April 2001 to April 2002, unpublished data, MDEQ, February 2004.
[3] "2001 Urban Air Toxics Monitoring Program (UATMP) Final Report," October 2002, Eastern Research Group.
[4] "Phase II Air Toxics Monitoring data: Analysis and Network Design Recommendations" July 3, 2003, Battelle Memorial Institute.

Aethalometers that were borrowed from the EPA. The units were returned to the EPA in February 2008. Continuous EC/OC measurements using a Sunset monitor were, and still are collected at the Newberry site[5].

The chemical composition of organic carbon was investigated at the Newberry site (261630038) by deploying a URG 3000 B Hi-Volume $PM_{2.5}$ sampler to the site. Samples were collected on a once **every six day schedule** and sent to the University of Wisconsin for analysis. Some of the samples were combined in a batch before analysis. Dr Schauer's lab determined trace metals, organic carbon, elemental carbon and ions. The lab also speciated the organic carbon fraction to quantify marker compounds useful in source apportionment. The goal was to begin sampling at Newberry before a similar LADCO sponsored study at Allen Park ended, maximizing temporal overlap between the sites. The purchasing process delayed the start of the study so only two months of overlapping data sets were collected. This will support a comparison of the chemical profiles at the two sites.

Another facet of this project included various aspects of quality assurance. In this grant, the MDEQ purchased a continuous formaldehyde monitor and a trace level carbon monoxide monitor for the Delray site. Another continuous formaldehyde monitor was purchased using the FY04 NATTS program for Dearborn. A second trace level CO monitor was purchased through the reprogrammed PM.25 grant funds.

The original plan proposed a precision study of the formaldehyde samplers at a field station, either at Dearborn (261630033), or possibly at River Rouge (261630005), due to higher historical formaldehyde levels at the latter site. Other goals included investigation of inter method comparability and accuracy testing. Once the initial testing was completed the continuous formaldehyde samplers would be deployed to Dearborn (261630033) and Newberry School (261630038).

The MDEQ also planned to continue measurements at nearby sites to further enhance our knowledge of spatial variability. The leveraged measurements include: NATTS air toxics measurements at the Dearborn NATTS site, the $PM_{2.5}$ speciation sampling at Allen Park and the Michigan Toxics Air Monitoring Program (MITAMP) stations at Southwest High School and River Rouge. The locations of the monitoring sites are shown in **Figure 1**. The shaded area shows the proposed location for the consolidated inter-modal freight terminal. Two new monitoring locations for this study are located in the areas outlined by dark blue.

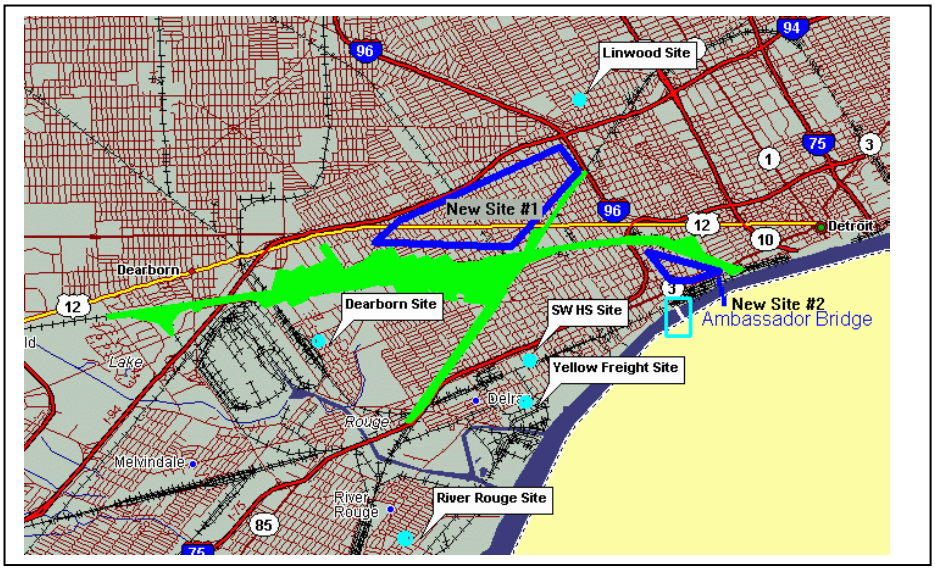


Figure 1: Detailed Map of Monitoring Area

[5] The continuous EC/OC sampler at Newberry has been temporarily deployed to a new site in Dearborn as part of a RARE grant. The MDEQ plans to redeploy the sampler back to Newberry School in December 2008.

The existing infrastructure, the resources available through the DEARS program and the reprogrammed $PM_{2.5}$ grant application were all leveraged to create a suite of measurements characterizing levels of air toxics and fine particulate in the area. Twenty-four hour VOC and trace level metals as TSP measurements are being collected at Dearborn and Allen Park on a once every six day sampling schedule. Trace level metals as PM_{10} are also collected at Dearborn. A summary of all proposed and leveraged measurements is shown in **Table 1.** The measurements covered by this grant are shown in *blue italics*.

Table 1: Measurements Made Near the Delray Area of Detroit

Site	**PM2.5 TEOM**	**PM2.5 FRM**	**PM2.5 Spec.**	**Carbon Black**	**Continuous EC/OC**	**Formal-dehyde and Carbonyls**	**Trace Level CO**	**Spec. Organic Carbon**	**PM10 TEOM**	**PM10 24-Hr.**
Delray (near Livernois)	Borrowed Monitor DEARS	1 in 3 leverage infra-structure	Reprog. PM2.5 Applic.	Borrowed Monitor DEARS	Reprog. PM2.5 Applic.	*Continuous & 24-Hr. TO-11A*	Reprog. PM2.5 Applic.	Reprog. PM2.5 Applic.	Leverage MDEQ	
Near Amb. Bridge		1 in 3 leverage MDEQ		Borrowed Monitor DEARS		*This grant*				
Dearborn	**E**	**E 1 in 3**	**E 1 in 6**	**E**		**Continuous NATTS, TO-11A 1 in 6**			**E**	**E 1 in 6**
SW HS		**E 1 in 3**				**TO-11A 1 in 12**				**E 1 in 6**
River Rouge						**TO-11A 1 in 6**				
Allen Park	**E**	**E 1 in 1**	**E 1 in 3**	**E**		**TO-11A 1 in 6, as regional site**	**E**	**E**		**E 1 in 6**

Key: E =Existing

What was Completed

Two new air monitoring stations were created. The Newberry site is located at 4045 29th Street in Detroit at the Newberry School. **Figure 2** shows a map of the location, a view of the station and a photograph of the DIFT. The site is located in a residential community downwind of the location favored for the DIFT. The site became active in December 2004. However, monitoring activities were curtailed in September 2005 when the site was repeatedly vandalized. Computers containing ambient air measurements, the EC/OC sampler, miscellaneous equipment in the station and the tower containing meteorological equipment were among the items lost. The site remained closed until April 2006, when enhanced security measures were completed at the site. An alarm system and cameras were added. Nonparametric linear regression analysis performed by Dr. Donna Kenski, LADCO, shows that this site is properly located to detect emissions from the rail yard near the intersection of Livernois and Kronk, as shown in **Figure 3**.

Figure 2: **The Newberry Site and a View of the DIFT**

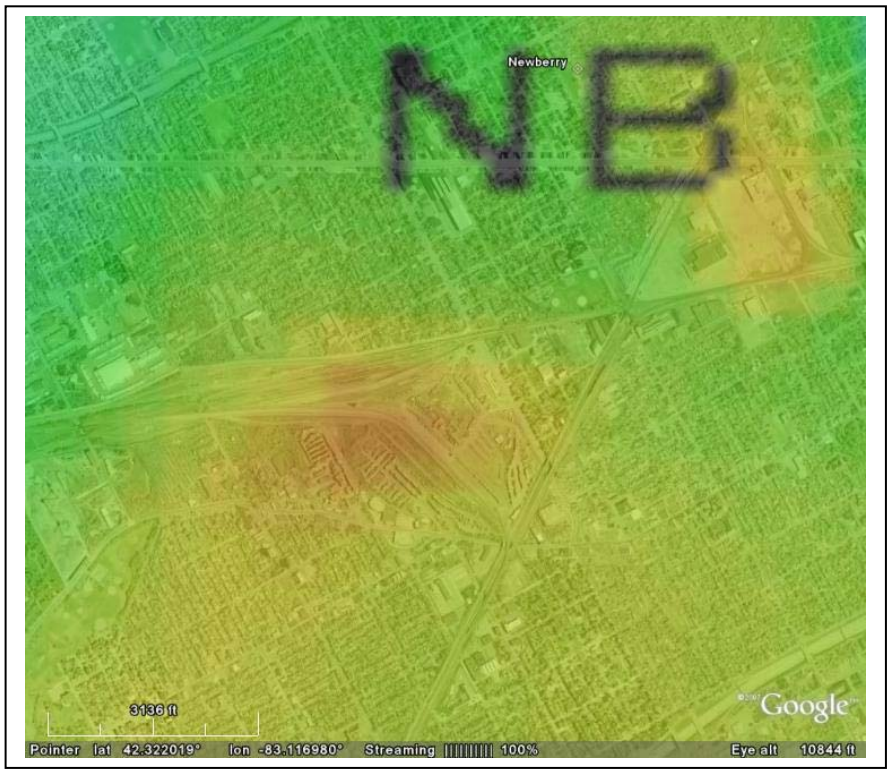


Figure 3: Nonparametric Linear Regression using Newberry BC Data

The FIA/Lafayette site is located at 2000 Lafayette Street in Detroit at the Michigan Family Independence Agency Building, now called the Michigan Department of Human Services. The site is located in a commercial area downwind of the Ambassador Bridge. **Figure 4** shows a map of the location, a photograph of the station and a view from the station roof looking toward the Ambassador Bridge. Nonparametric linear regression analysis performed by Dr. Kenski shows that this site is properly located to detect emissions from the bridge, as shown in **Figure 5**.

Figure 4: The FIA/Lafayette Site and a View of the Ambassador Bridge from the trailer

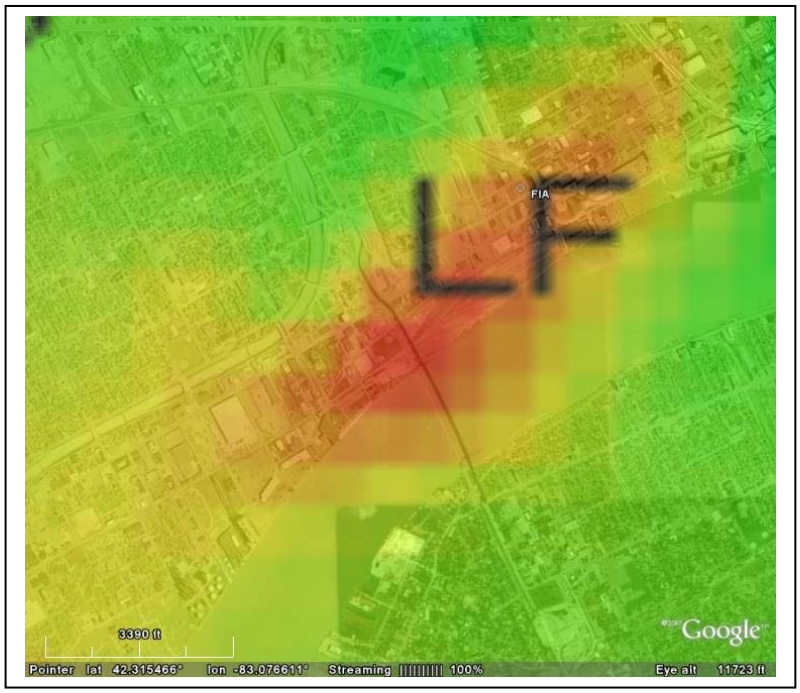


Figure 5: Nonparametric Linear Regression using FIA/Lafayette BC Data

The nonparametric linear regression was performed using BC as well as EC/OC data from each site. BC data from Dearborn (261630033) and Allen Park (261630001) was also used, but the results weren't as spectacular as shown above. This data was presented at the Air Toxics Monitoring Conference in Rosemont, IL on October 2 through 4, 2007. Details are available upon request. The analysis requires use of meteorological measurements collected on minute intervals. At the time this analysis was performed, only a few months of minute

meteorological data was available. Future work includes the use of a larger, more robust data set through February 2008. Other possible analysis include the use of EC/OC from multiple sites.

Carbon black measurements at Newberry School (261630038) and FIA (261630039) were discontinued on February 21, 2008 as the aethalometers needed to be returned to the EPA.

A total of three continuous $PM_{2.5}$ Tapered Element Oscillating Microbalance (TEOMs) samplers were deployed to the Newberry and FIA stations. As shown by the photograph of the Newberry station, it contains a concrete bunker. There are several issues hindering the deployment of a TEOM equipped with a FDMS inlet at the Newberry station. In the past, coring inlet holes through concrete roofs of bunkers has been problematic. MDEQ has traditionally installed roof decks near the inlets of TEOMs, to promote increased safety during the flow check and cleaning process. Staff felt that a roof deck at Newberry School may be too tempting a target for vandals. We had two old style TEOMs that were not compatible with a Filter Dynamic Measurement System (FDMS) inlet system. One of these was deployed at Newberry School in a climate controlled box on the deck.

To promote comparability with remaining portion of the MDEQ's continuous $PM_{2.5}$ network, which used FDMS inlets, a pair of TEOMs was deployed at the FIA station, which could accommodate roof access. One of the TEOMS was equipped with a FDMS inlet. The second unit was one of the non-FDMS compatible units. The unit without the FDMS inlet was directly comparable to the instrument at Newberry School, while the other instrument was comparable to the rest of the network. The co-located data set allowed extrapolation between the two different modes of operation. FIA was selected as the co location site because drilling a hole through the metal skin of the trailer was much easier than boring through concrete.

When these sites were first established, the MDEQ operated TEOMs in the rest of its network with FDMS inlets. However, maintenance issues with the FDMS inlets in hot, humid weather as well as the refurbishing costs of the Nafion driers on an annual basis, prompted the MDEQ to remove the FDMS inlets during the summer months. The performance of TEOMs was more similar to FRMs during the summer months anyway. Field staff determined that it was more efficient to remove the FDMS inlets and replace them at the end of ozone season than to constantly deal with maintenance issues and condensation in the lines during the summer. Staff selected the ozone season, which runs from April 1 through September 30, as the period when FDMS inlets would not be used. Then, in February 2007, the MDEQ could no longer obtain parts for the FDMS inlets and was reluctant to upgrade, yet again, to another version of the inlets, all FDMS inlets were removed. The MDEQ decided to operate the TEOM inlets at 30°C in the winter and 50°C in the summer so that the continuous data could be as similar to the FRM data as possible. The inlets of the pair of TEOMs at FIA were each operated with a different inlet temperature. So, over the previous three years, as MDEQ changed the way the TEOMs are operated, FIA served as a control site to compare performance differences.

Problems Encountered

Delays were encountered with the MDEQ's purchasing process. Although we started the process to purchase instrumentation and a contract for the laboratory analysis in May, the purchasing process wasn't completed until January. The goal was to have as much overlap with LADCO's speciated organic carbon study at Allen Park (2616630033) as possible. In actuality, there were only two months of overlap and that was only because elevated blank concentrations were found in LADCO's study and that study had to be extended two months.

Installing power and phone lines at FIA/Lafayette were also problematic. The owner of the property behind the parking lot housing the monitoring trailer would not grant an easement for the power lines. Eventually, power was obtained from a more distant location by running a feed along the fence line to the trailer. There were also communication difficulties obtaining phone access. Once the Michigan Family Independence Agency understood that our request to access their phone trunk line would not create any additional cost to them, we became operational.

During September 2005, the Newberry (261630038) site was repeatedly vandalized. The MDEQ lost the meteorological tower as well as computers and instrumentation inside the shelter including data contained on the hard drives. When staff discovered the break-in, all remaining equipment was removed and the site temporarily shut down. The MDEQ installed enhanced security that included an alarm system and video cameras. Data collection at the site resumed on April 1, 2006. However, the plan to collect a calendar year of speciated organic carbon data was ruined. The fourth quarter was forever gone.

Since we had successfully collected data from two consecutive years in June, July and August, and since the University of Wisconsin changed their price structure for speciated organic carbon measurements, we could afford to have more samples analyzed. This was a perfect opportunity to also analyze archived filters from Dearborn (261630033) and Allen Park (261630001) for speciated organic carbon to begin to assess temporal and spatial variability. Monthly composites were created as shown in **Table 2**. This turned out to be a wonderful opportunity because, previously, speciated organic carbon measurements have been conducted at only a few sites. Usually, at a single location for a finite time period. This work will allow users to assess the variability in the measurements and better understand the uncertainty in the source apportionment results.

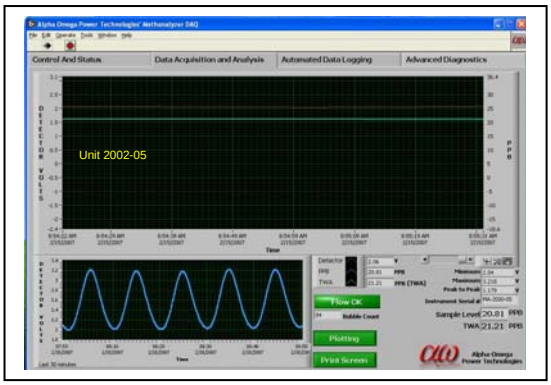
Table 2: Monthly Composites

Site	2005	2006
Newberry (261630038)	January, February, March, April, May, June, July, August	June, July, August
Allen Park (261630001)	June, July, August	June, July, August
Dearborn (261630033)	June, July, August	June, July, August

We received the formaldehyde samplers in November, 2004. According to the original purchase order, one year of consumables was to be provided for each unit. For most of the supplies, the parts we received were not the parts we consumed on a frequent basis. The units were quite prone to leaks near the many fittings involved with fluid transfer. Replacing the fittings to resolve leaks consumed an inordinate number of parts. Also, to minimize the introduction of air into the various lines, it would have helped with maintenance if more caps were supplied with the units. Contrary to what the manufacturer recommends, the filters used on the fluid intake lines are NOT reusable. Dirty filters contribute to a deterioration of the signal possibly through a reduction in flow rates of some reagents, increased bubble formation and possible cavitation. Calibration equipment to measure the flow more effectively would have helped with operation. The use of larger reagent reservoirs would have minimized the number of times the operator has to open the system, risking the introduction of more bubbles.

Initially both of the formaldehyde samplers were deployed to the Dearborn site (261630033) in January 2005. Staff from Alpha Omega Power Technologies arrived to set up the instruments and provide instruction in operation and maintenance. The shipping container that contained the permeation source was damaged during shipping. As shown by the photo at the left, the damage did not appear to be severe. However, on the training day, when the permeation source was plugged in, it delivered an electrical shock to the MDEQ's operator. Subsequently, the permeation source was shipped to Albuquerque for repair. Without the permeation source, calibrations of the units couldn't be performed. However, to become familiar with operation, staff attempted to operate the co-located units in the field. Staff had a difficult time overcoming bubble formation. Continued problems with broken tubing, leaks and other failures caused the units to be sent back to the manufacturer for repair. It took six months for the first set of repairs to be completed. The units were received by the MDEQ on September 20, 2005. More problems with operation occurred and the units were sent back repeatedly from January 23, 2006 to December 21, 2006. In May 2006, the site operator traveled to Albuquerque to receive training on the units. Finally, due to continued breakage during shipment, the units were driven from Albuquerque to the MDEQ's offices in December 2006.

In 2007, MDEQ beta tested software developed by Alpha Omega Power Technologies that was designed to simplify operation of the formaldehyde samplers. By observing the sinusoidal signal on a computer monitor, it was felt that this would provide an immediate confirmation about the operational status of the units. A good signal is shown to the right. Therefore, it would be easier to optimize all operational parameters of the instruments. Also, a team approach was taken to operation of the units. Since it appeared that almost daily attention was required, operation in the field was abandoned. Both units and the permeation source were installed in a trailer at the MDEQ's equipment support facility in Lansing.



A variety of problems continued including a damaged scrubber caused by a leak in one of the systems. The scrubber was returned for repair in June 2007. It was returned and the unit became operational July 26, 2007. Testing continued, investigating the reproducibility of the calibration using liquid injection. Preliminary data was presented at the Air Toxics Monitoring Conference in Rosemont, Illinois on October 2 through 4, 2007. It became apparent that the peristaltic tubing replacement schedule was too demanding and severely compromised the ability of the units to collect ambient measurements. Each time the peristaltic tubing is replaced, bubbles are introduced into the system. Bubbles severely compromise the unit's ability to collect data.

Another issue related to the peristaltic pump and bubble formation is a false positive reading by the detector when a bubble is introduced into the detector cell. This becomes especially evident when the units are operated in the liquid mode, similar to a HPLC. **Figure 6** shows the output when liquid injections of 40 ppb and five injections of 20 ppb formaldehyde are injected into the system.

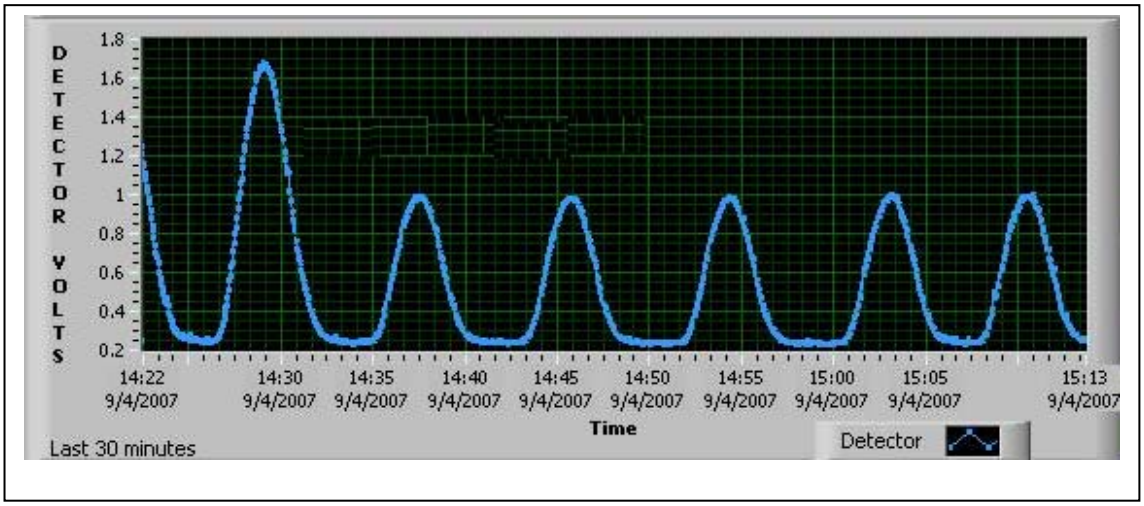


Figure 6: Liquid Injections of 40 ppb and 20 ppb Formaldehyde: Minimal Bubbles

The detector output when there are minimal bubbles is typically relatively precise ranging from: 37.41 ppb, 35.59 ppb and 35.58 ppb for a 40 ppb standard and 13.38 ppb, 13.37 ppb and 13.52 ppb for a 20 ppb standard. However, when a bubble co-elutes into the detector cell with an injected bolus of formaldehyde, the resulting signal may be more than 200 times as high as the response from other injections of the same standard, on the same day at approximately the same time of the day. A typical example of the bubble co-elution problem is shown in **Figure 7**, which was generated just prior to the results in **Figure 6**. In this case, the bubbles worked their way out of the system.

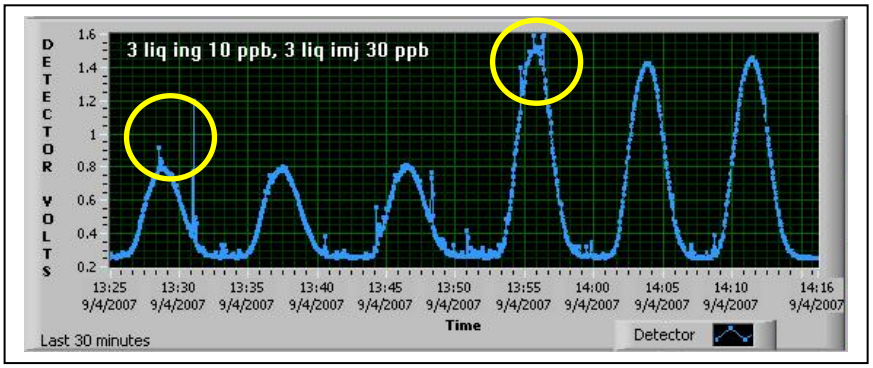


Figure 7: Co Elution of Bubbles with injections of a Standard Solution of Formaldehyde

Some bubbles can be much more recalcitrant. Many times, bubbles will become lodged in the detector cell and obstruct the collection of data as shown in **Figure 8**. The operator must flush the system with either acetone, methanol or isopropanol to remove the bubbles from the detector cell. We have found that alternating the use of various solvents is instrumental in breaking bubbles loose. For the 2000-02 unit, flushing the detector cell is very arduous possibly due to a smaller cell size. The MA 2000-05 is much easier to flush. The differences in cell size influence the response of each unit as well as the units susceptibility to bubble formation.

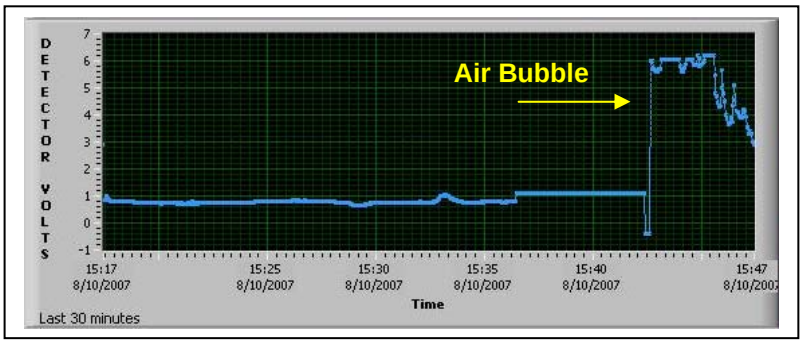


Figure 8: Detector Output Indicates a Bubble in Lodged inside the Cell

Clearly bubbles represent a huge issue in accurately quantifying formaldehyde. The current beta version software does not provide an output, that could be visualized akin to a strip chart recorder, that would make it easy for a reporting agency to identify bubbles misidentified as formaldehyde. The bubble issue must be resolved before any further development can take place. Replacing the peristaltic pumps with syringe pumps would be an excellent place to start to reduce the opportunities for bubble formation. The MDEQ is seeking funding to replace the peristaltic pumps with syringe pumps.

Initially, the MDEQ calibrated each unit using the permeation source. The calibration curves generated using the gaseous source are shown in **Figure 9**. The graph comparing two calibration curves illustrates the impact from changing the peristaltic pump tubing on the calibration. The curves were obtained from Unit 2000-02 on February 1, 2007 and February 8, 2007. Applying the calibration curve to a response near the middle of the curve results in a 4.5% difference in the final result after the two calibrations. If other variables could be controlled, this change in response could meet DQOs in an ambient monitoring program.

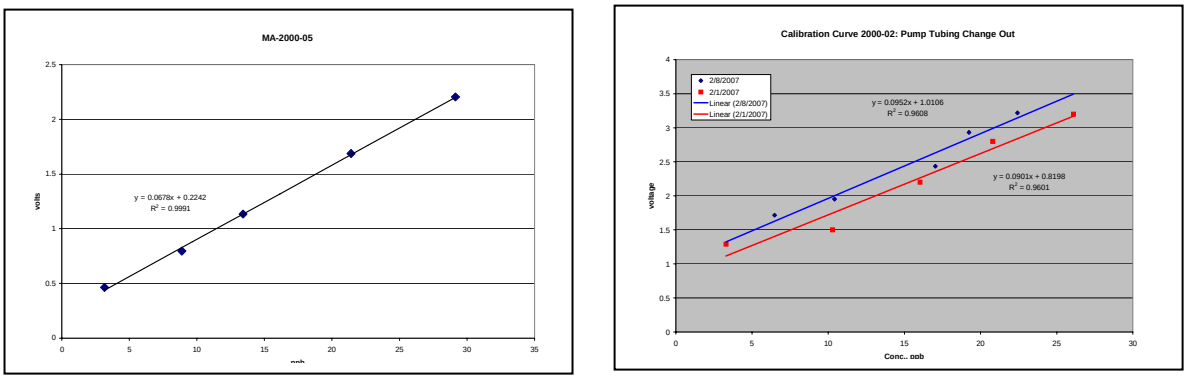


Figure 9: Calibration Curves using the Permeation Source and Gas Phase Formaldehyde

When the gas phase calibrations were repeated in September 2007, the results were less than satisfactory. In January 2007 a cylinder of zero air had been used to feed into the permeation source. However, due to budget problems, we attempted to use a zero air generator as the supply air source in September. The zero air source was not capable of generating a sufficient supply or perhaps, the permeation source needed to be regenerated.

Outputs from both units were compared to assess inter sampler precision as shown in **Figure 10**. As shown by the figure, the output is not congruent. The impact of a bubble lodged in the detector cell cam be seen by the very large spikes in the figure. As discussed in an earlier section, it is necessary to learn how to minimize bubble formation and optimize factors contributing to instrument performance.

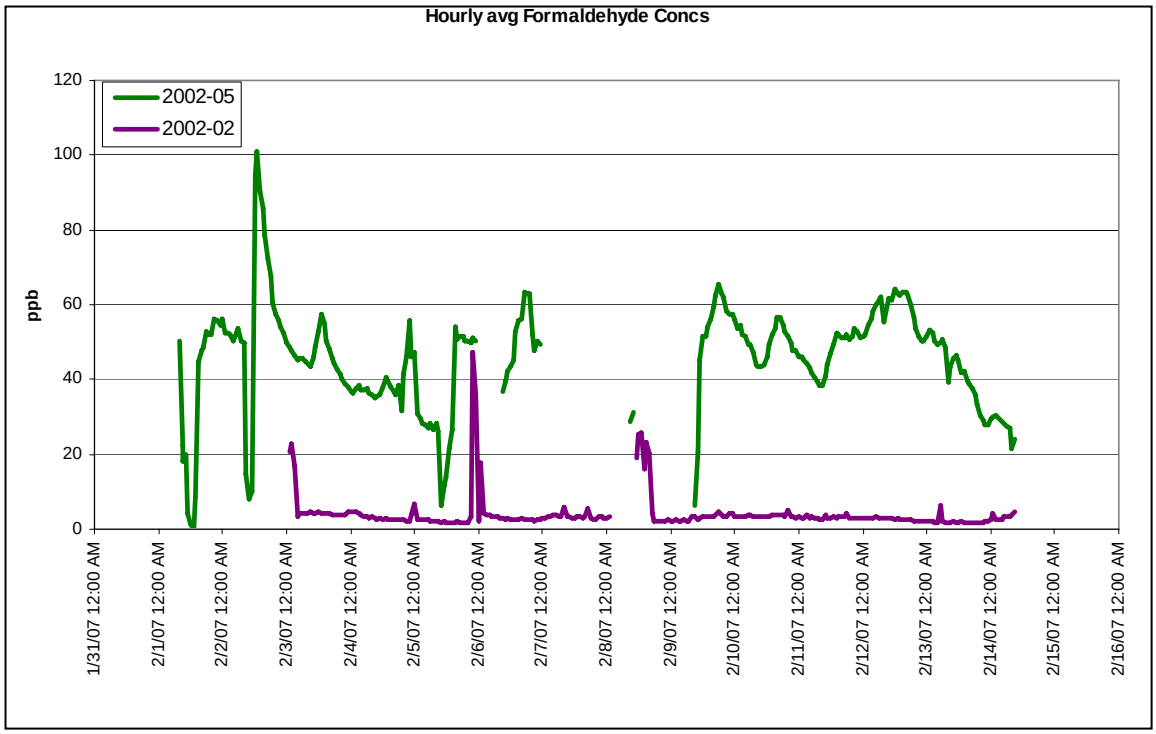


Figure 10: Output from both Continuous Formaldehyde Units February 2007

Because one unit was being repaired, comparability studies were put on hold until August 2007. The units were calibrated in the liquid mode using a liquid formaldehyde solution. **Figure 11** shows the disparity between the response rates for both units when calibrated in the liquid mode. The unit which did not suffer scrubber damage has a much smaller detector cell and is quite prone to bubble formation. **Figure 12** compares the response after bubbles were removed from the unit.

Figure 13 compares the hourly formaldehyde concentrations measured by each unit in September 2007. Both units appear to be tracking similar ambient concentrations and the responses are relatively comparable. The graph also shows that the time clock on one unit appears to be off by one hour. Unfortunately, on September 8 at approximately 9:30, unit 2 developed a leak. It was a Saturday, and fluid leaked all over the instrument and trailer until Monday, when staff arrived to check on the units. Given the effort that was involved in replacing peristaltic tubing, setting flow rates, leak checking, removing air bubbles and checking calibrations in order to get the units into proper operating condition to suffer a leak from the peristaltic pump tubing is unacceptable.

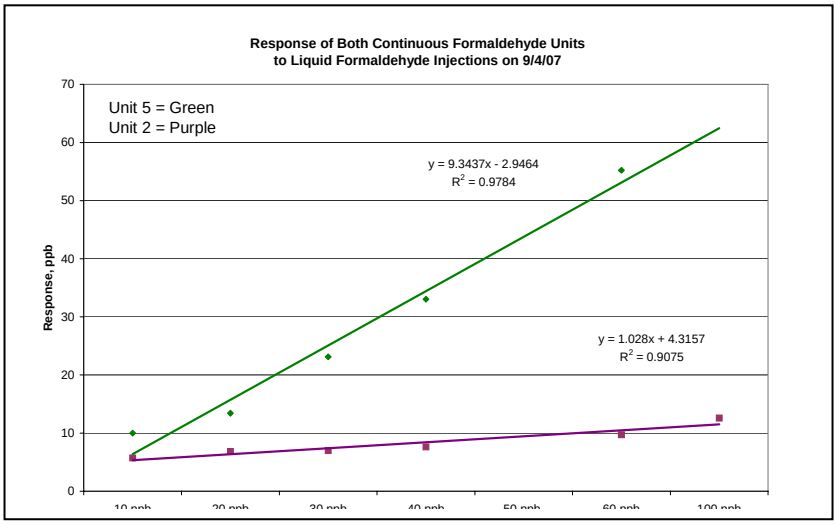


Figure 11: 9/4/07 Calibration Curves (Liquid Mode)

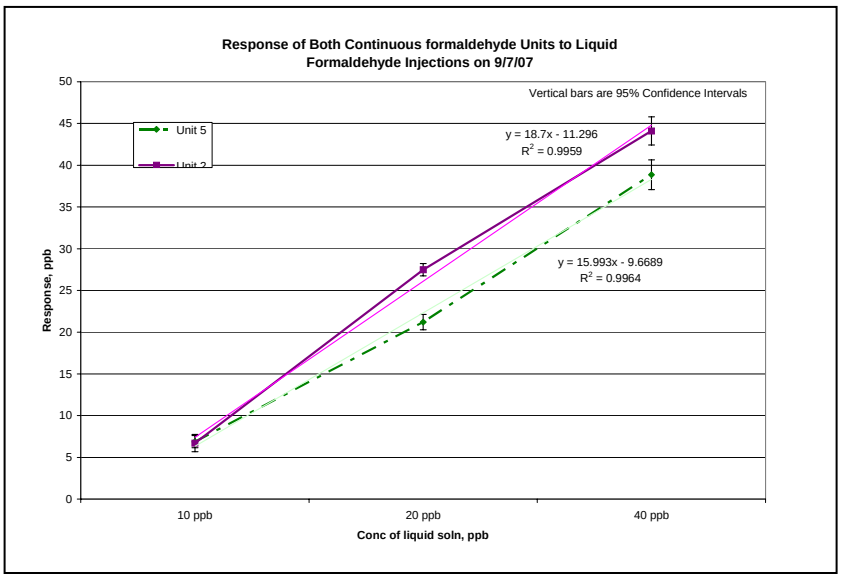


Figure 12: 9/7/07 Calibration Curves after Bubbles Removed (Liquid Mode)

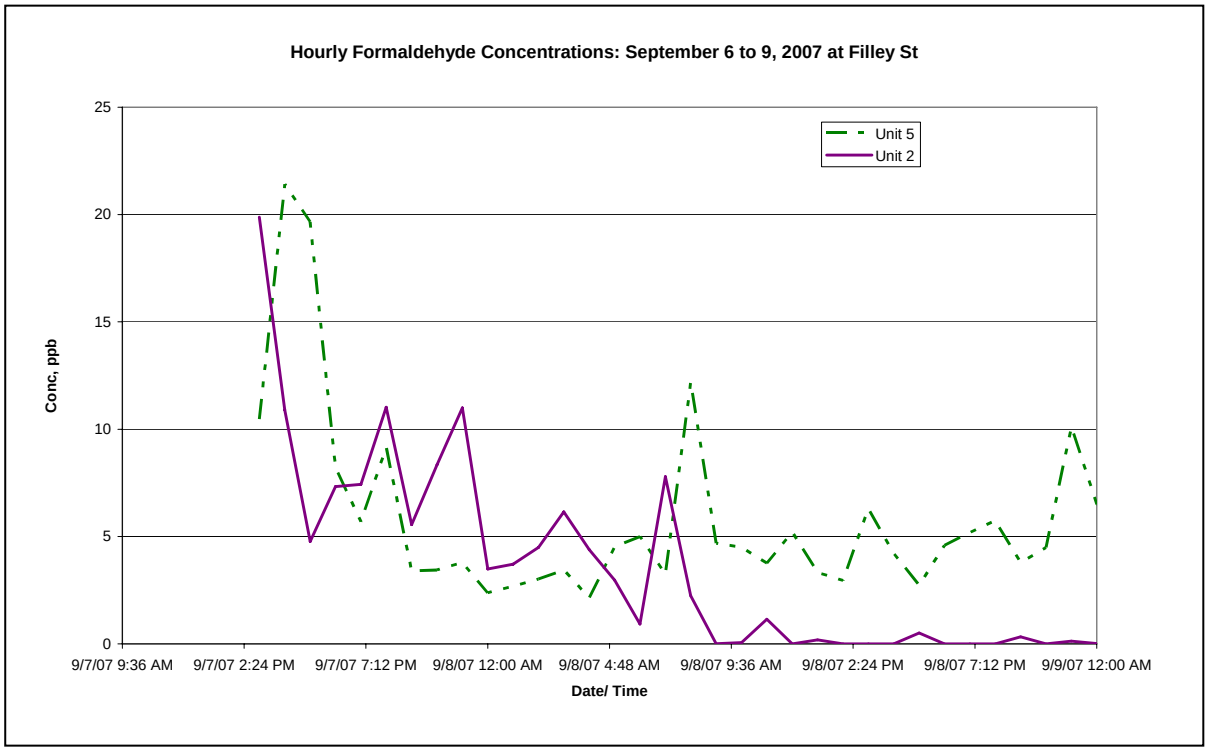


Figure 13: Hourly Ambient Concentrations Measured by Both Units: Filley St, September 2007

Data Capture

The percent data captured at sites established using this grant are shown in **Table 3**. The data completeness calculations were based on the start up dates of the stations as well as the date that operations resumed at Newberry School (261630038) with enhanced security measures. Since the FIA (261630039) site operated two TEOMs in different modes of operation at different time periods, all measurements from an individual unit were combined to generate the data completeness metric.

In addition to the measurements shown in **Table 3**, additional samples were collected to better understand the chemical composition of fine particulate material. Samples to be analyzed for speciated organic carbon content were collected on 90 mm quartz filters once every six days and composited into a monthly sample. Data completeness was 83% in 2005, and spanned January 1 through September 7. In order to compare the spatial and temporal changes in composition of organic carbon, archived filters from Dearborn and Allen Park were obtained from RTI and used to make monthly composites for June to August 2006. Samples collected every six days at the Newberry site were also used to form composites. **Table 4** shows the dates that were composited. Only one sampling event at Newberry School was missed making the data completeness of the samples to create composites equal to 100% and 93% for 2005 and 2006, respectively. The overall data completeness was 97%.

In addition to the data generated by analyzing archived filters, data collected at other sites including Dearborn (261630033), SW High School (261630015), River Rouge (261630005) and Allen Park (261630001) was available to supplement the analysis of the data collected through this grant, but isn't summarized here because collection was funded by other grants and programs. As discussed in earlier sections, the formaldehyde samplers were not reliable enough for unattended operation in the field. Therefore, large sets of hourly formaldehyde data are not available and not included in **Table 3**.

Table 3: Data Capture at Newberry and FIA Sites

		Newberry (2616300038)	FIA (261630039)
Parameter	**Year**	**% complete**	**% complete**
$PM_{2.5}$ FRM	2005	77 %	81 %
	2006	91 %	92 %
	2007	93 %	90 %
Continuous $PM_{2.5}$	2005	78 %	83 %
	2006	96 %	94 %
	2007	92 %	95 %
Continuous $PM_{2.5}$ (co-loc)	2005	Not collected	76 %
	2006	Not collected	87 %
	2007	Not collected	90 %
Carbon Black	2005	78 %	98 %
	2006	91 %	93 %
	2007	92 %	88 %
EC/OC	2005	81 %	Not collected
	2006	78 %	Not collected
	2007	58%	Not collected
CO	2005	76 %	89 %
	2006	discontinued	97 %
	2007	discontinued	discontinued

In 2007, the EC/OC sampler at Newberry (261630038) had two major problems. It was only sampling every other hour due to cool-down issues during the first quarter. The back oven coil needed replacement. When the coil was replaced, the oven was cracked and had to be returned to the manufacturer for repair.

After the break in, trace CO measurements were not resumed at Newberry School due to EPA cuts to the $PM_{2.5}$ grant as part of the Federal government's attempt to fund hurricane Katrina relief projects.

Table 4: Archived Filters Submitted to University of Wisconsin for Speciated Organic Carbon Analysis

X = Valid Sample

Composite	Date	Allen Park (261630001)	Dearborn (261630033)	Newberry (261630038)*
June 2006	June 3, 2005	X	X	X
	June 9, 2005	X	X	X
	June 15, 2005	X	X	X
	June 21, 2005	X	X	X
	June 27, 2005	X	X	X
July 2006	July 3, 2005	X	X	X
	July 9, 2005	X	X	X
	July 15, 2005	X	X	X
	July 21, 2005	X	X	X
	July 27, 2005	X	X	X
August 2006	August 2, 2005	X	X	X
	August 8, 2005	X	X	X
	August 14, 2005	X	X	X
	August 20, 2005	X	X	X
	August 26, 2005	X	X	X
June 2006	June 4, 2006	X	X	X
	June 10, 2006	X	X	X
	June 16, 2006	X	X	X
	June 22, 2006	X	X	X
	June 28, 2006	X	X	X
July 2006	July 4, 2006	X	X	X
	July 10, 2006	X	X	X
	July 16, 2006	X	X	X
	July 22, 2006	X	X	X
	July 28, 2006	X	X	X
August 2006	August 3, 2006	X	X	
	August 9, 2006	X	X	X
	August 15, 2006	X	X	X
	August 21, 2006	X	X	X
	August 27, 2006	X	X	X

* Not from STN archives, these filters were specially collected for this project.

Reporting

Quarterly updates were included in the Quarterly NATTS Reports. **Table 5** shows the reporting interval and the dates that the reports were sent to Region 5 EPA. This document serves as the close-out report and was delayed due to several factors. The seven-month delay created by the purchasing process was not anticipated. Also, significant delays were encountered with all of the shipping and repair issues associated with the continuous formaldehyde instruments. Furthermore, the break-in at Newberry School caused a delay in the analysis of speciated carbon samples by the University of Wisconsin. A strategy had to be developed and implemented to make up for the three months of samples that were forever lost due to the break-in. Then, the replacement samples had to be collected and shipped out for analysis.

Table 5: Summary of Quarterly Update Reports

NATTS Period of Performance	Reporting Date
April 2005 – June 2005 (purchasing delays)	July 22, 2005
July 2005 – September 2005 (purchasing delays)	April 4, 2006
October 2005 – December 2005 (purchasing delays)	May 12, 2006
January 2006 – March 2006	August 11, 2006
April 2006 – June 2006	October 2, 2006
July 2006 – September 2006	March 16, 2007
October 2006 – December 2006	May 8, 2007
January 2007 – March 2007	August 28, 2007
April 2007 – June 2007	October 31, 2007
July 2007 – September 2007	January 8, 2008
October 2007 – December 2007	May 7, 2008
January 2008 – March 2008	July 8, 2008
April 2008 – June 2008	pending

Results/Data Analysis

Detailed data analysis activities were beyond the scope of this grant. Preliminary analysis include an examination of diurnal profiles of various hourly pollutants at both Newberry School (261630038) and FIA (261630039). The continuous EC/OC data collected at Newberry School (2761630038) was examined by various seasons of the year and diurnal profiles compared, as discussed in greater detail below. Although precision calculations were planned, the lack of high quality continuous formaldehyde data makes this comparison impossible to do.

Diurnal Trends:

Figure 14 shows the diurnal trends at Newberry School (261630038). The concentrations of some pollutants have been multiplied by various factors so that trends could be compared on a single graph. The axis and legend to the graph explain which factor has been used for what pollutant. The trace CO, EC and BC all show a sharp increase from about 6:00 AM to 8:00 AM, during the morning rush hour. There is a small increase in CO at 3:00 PM that is not observed in the other pollutants. A second peak is observed late at night, presumably due to a reduced mixing height. In the graph, the CO reached 531 ppb during the morning rush hour. The continuous organic carbon measurements show a very slight increase during the morning rush hour and another increase near 8:00 PM. The $PM_{2.5}$ data shows an increase during the morning rush hour with small fluctuations over the rest of the day.

Figure 15 illustrates the diurnal trends for trace level CO, carbon black and $PM_{2.5}$ at FIA (261630039). The CO peak from the morning rush hour is quite evident but less concentrated than that at Newberry School, only reaching a maximum concentration 345 ppb. Elevated levels of BC were also shown during the morning rush hour. The graph also compares the performance of TEOMs when operated in two different manners.

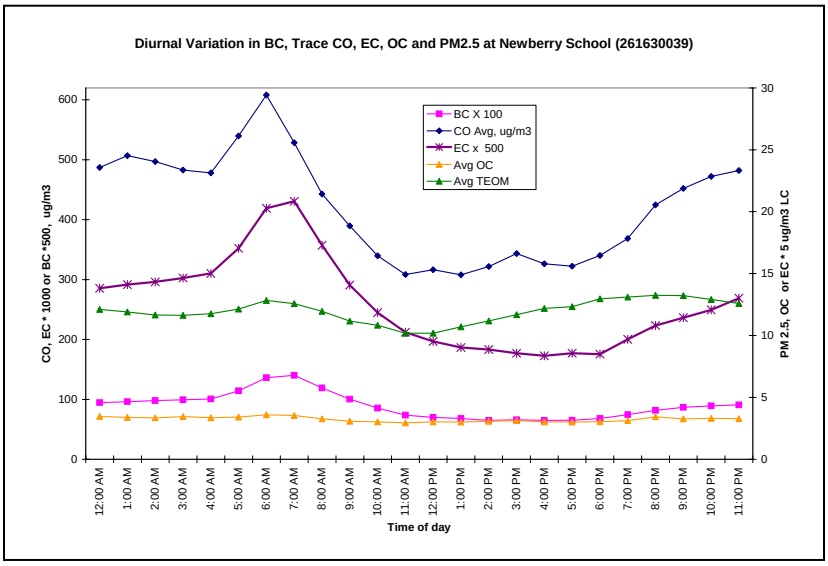


Figure 14: Diurnal Profiles of BC, trace CO, EC, OC, $PM_{2.5}$ and Carbon Black at Newberry School

As part of an ongoing project to better understand $PM_{2.5}$ in the residual nonattainment area in Detroit by the Southeast Michigan Ozone Study group (SEMOS), the EC/OC data collected at Newberry School (261630038) was compared with a smaller set of data collected at Dearborn (261630033). The measurements were analyzed by season and by wind direction.

The hourly data points were linked to wind speed and wind direction measurements. All hours with calm winds were removed from the data set. Calms were defined as wind speeds less than 2 mph. The data were classified into four seasons as defined in **Table 6**. **Figure 16** illustrates the variation in the diurnal profiles for EC, OC and the ratio of OC/EC for different seasons of the year.

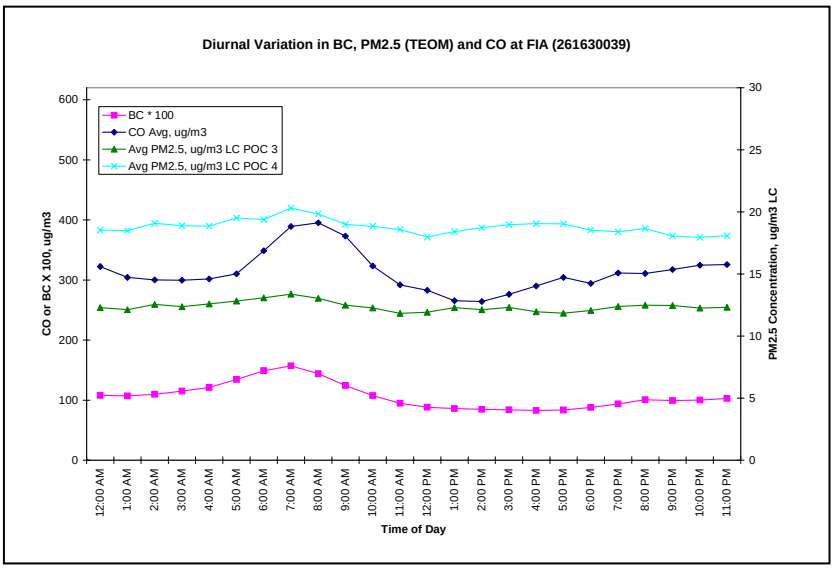


Figure 15 compares diurnal profiles of the two types of TEOMs, trace level CO and carbon black at FIA.
EC/OC: SEMOS Data Analysis

Table 6: Definition of Seasons

Season	Months
Winter	December, January, February
Spring	March, April, May
Summer	June, July, August
Fall	September, October, November

Figure 16 compares diurnal profiles of all the parameters measured hourly at Newberry School by season. Note the enhanced level of OC observed during daylight hours during the summer. The 0.7 ug/m^3 excess OC formed from 10:00 AM to approximately 7:00 PM could be secondary OC formed by exposure to sunlight.

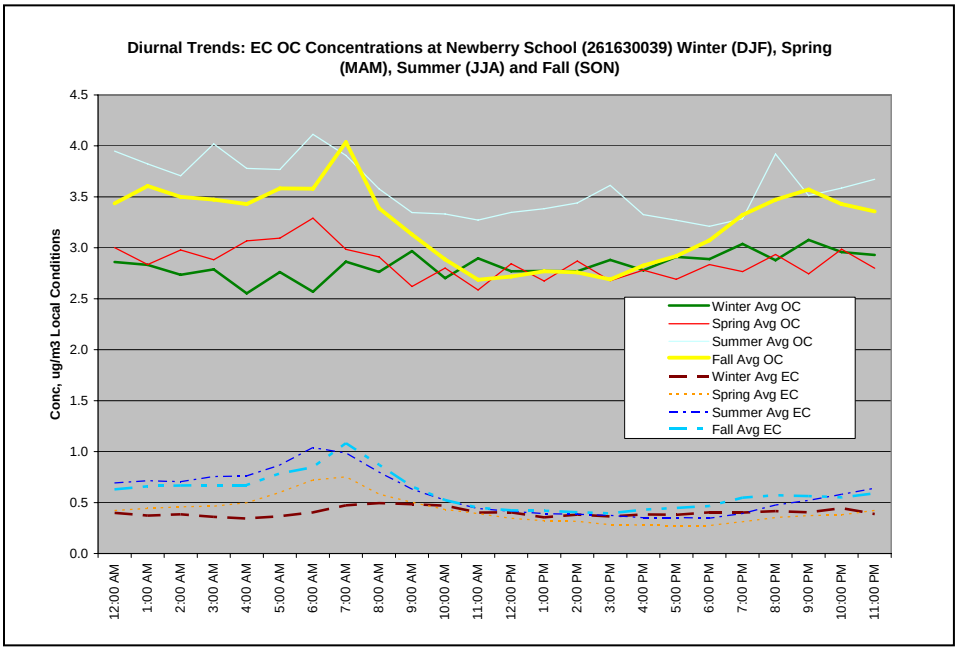


Figure 16 Diurnal profiles of various pollutants by season at Newberry School

Figure 17 plots the ratio of OC to EC by season and illustrates that there is a slight increase in the OC/EC ratio from about 5:00 to 7:00 PM in the spring, possibly due to more intense solar radiation triggering the formation of secondary OC. As the light intensity increases during the summer months, this trend is observed earlier in the day.

The analysis is taken one step further in **Figure 18**, where May through September hourly ozone data collected from New Haven, the design value site in SE Michigan is divided into three concentration ranges: low, medium and high. Each category had equal numbers of hours. This data was linked with the OC data collected at Newberry, and displayed in **Figure 18**. The hours with high ozone levels also showed high OC levels, adding more support to the possibility of secondary OC formation.

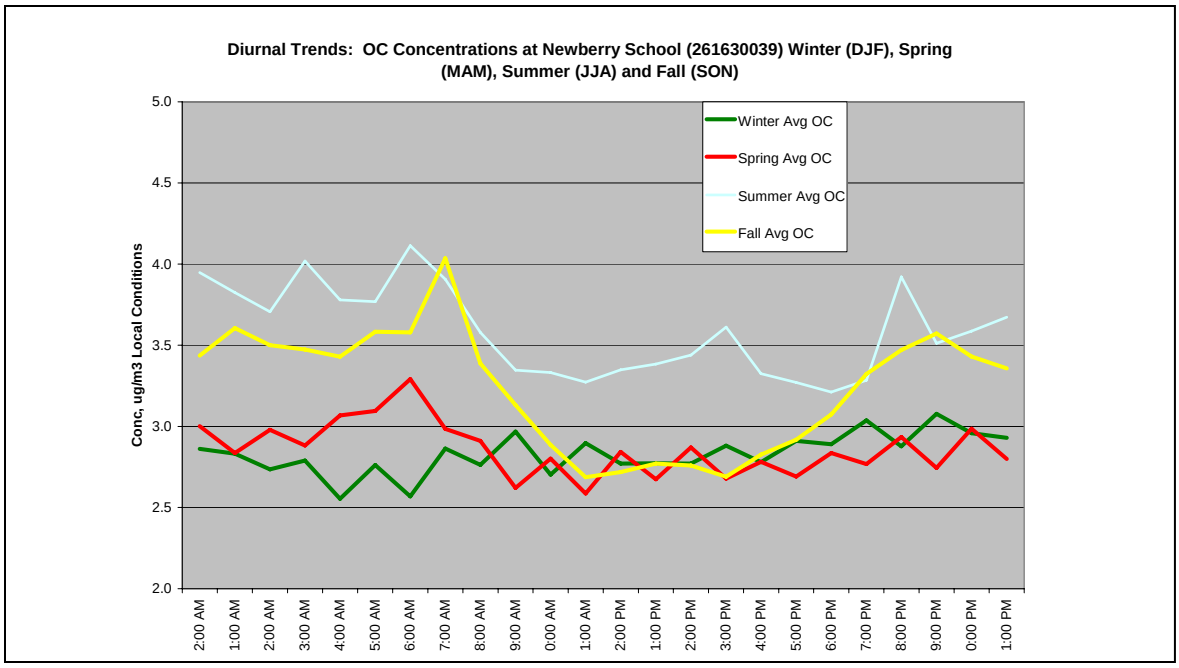


Figure 17 Diurnal profiles of OC/EC Ratio by season at Newberry School

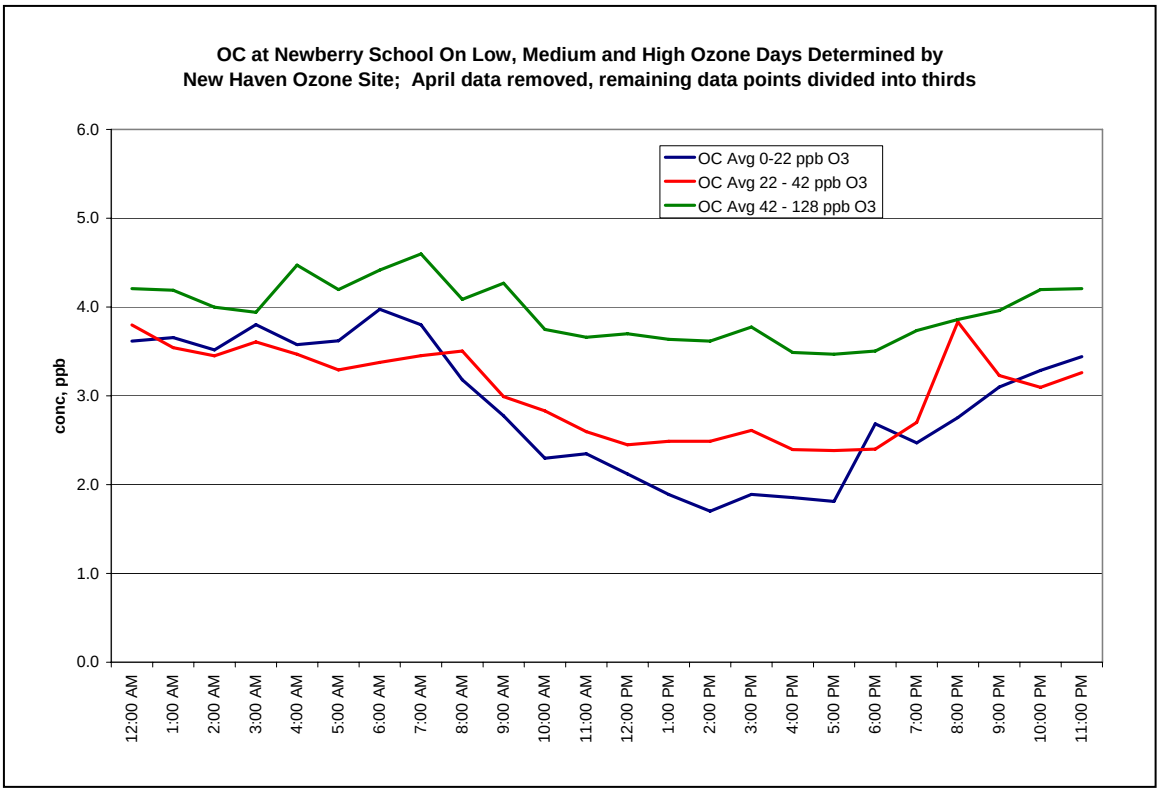


Figure 18 Diurnal profiles of OC for hours with low, medium and high ozone levels.

Spatial & Temporal Trends

The next series of graphs compares the annual and monthly average concentrations of pollutants at Newberry School and FIA. As shown in **Figure 19**, the levels of carbon black are slightly higher at FIA than at Newberry School. Average concentrations are about the same each year. Although some year-to-year variability is illustrated in the graphs, data capture in 2005 was not complete for either site and hence, the averages for 2005 could be skewed slightly. The graph also illustrates the differences in the concentrations of carbon black, which is determined using an absorption method, from elemental carbon (EC) which is determined using a pyrolytic method.

Figure 20 compares the fine particulate levels at Newberry School and FIA measured using a TEOM operated with an inlet temperature of 50°C. The measurements were matched by date and hour to minimize any temporal bias. The data shows that the fine particulate levels are decreasing at both sites. The levels at Newberry are consistently lower than those at FIA.

Figure 21 illustrates monthly average carbon black values at both Newberry School and FIA. The monthly average levels at FIA are higher than those measured at Newberry. The averages at FIA also show a consistent seasonal pattern, with elevated concentrations measured during June, July and August. Elevated concentrations were measured at Newberry School during June, July and August in 2007, but not during the summer months in 2006.

Figure 22 compares the differences in monthly averages of carbon black and elemental carbon at Newberry School. The absorption method produces consistently higher results than the pyrolytic method. Organic carbon is also shown for comparison. The vertical bars sown on the graph indicate data gaps that were caused by instrument breakdowns.

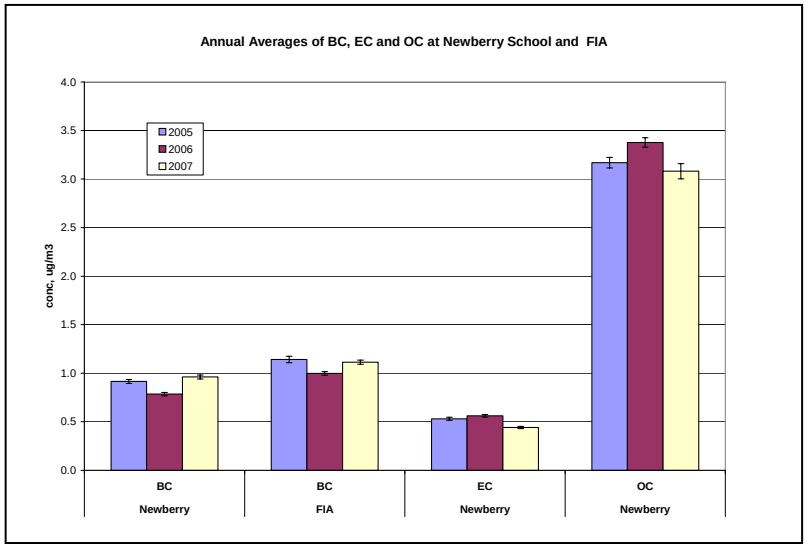


Figure 19: Comparison of annual average black carbon levels at FIA and Newberry School and comparison of carbon black, EC and OC at Newberry School.

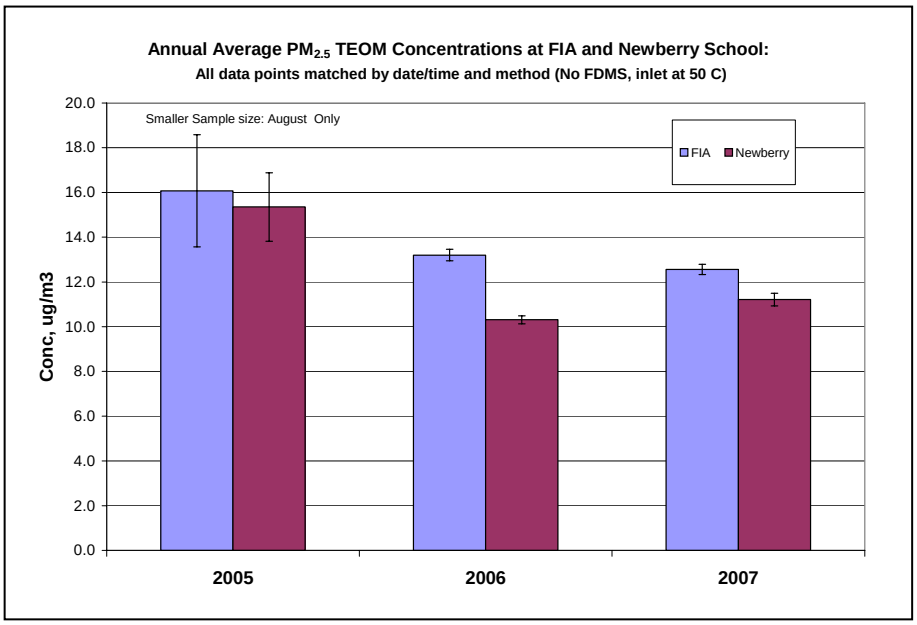


Figure 20: Comparison of Continuous $PM_{2.5}$ Levels at FIA and Newberry School.

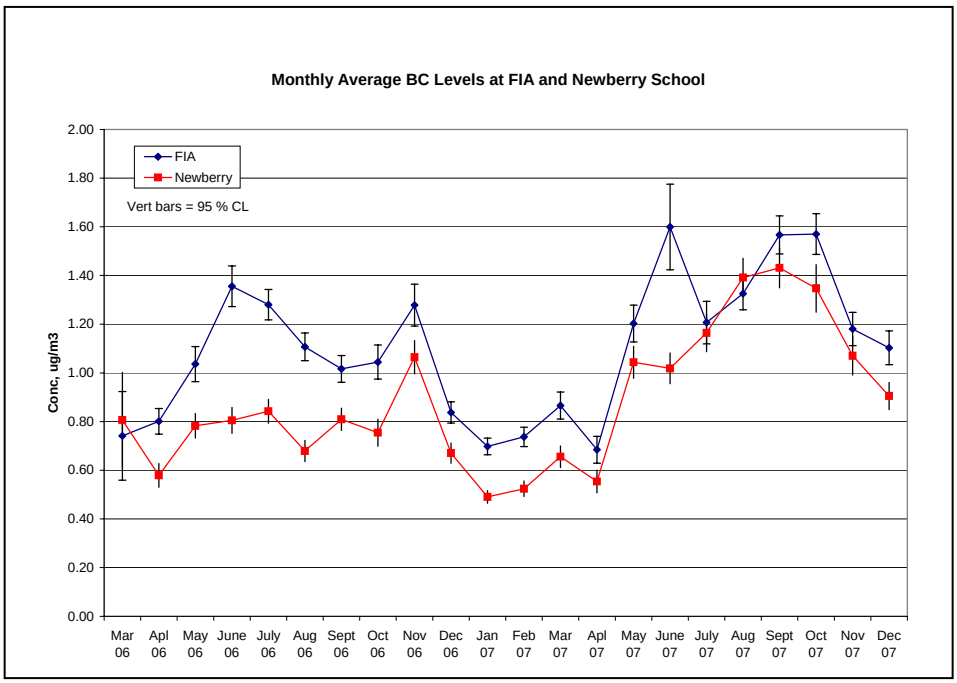


Figure 21: Monthly Average Carbon Black Levels at FIA and Newberry School

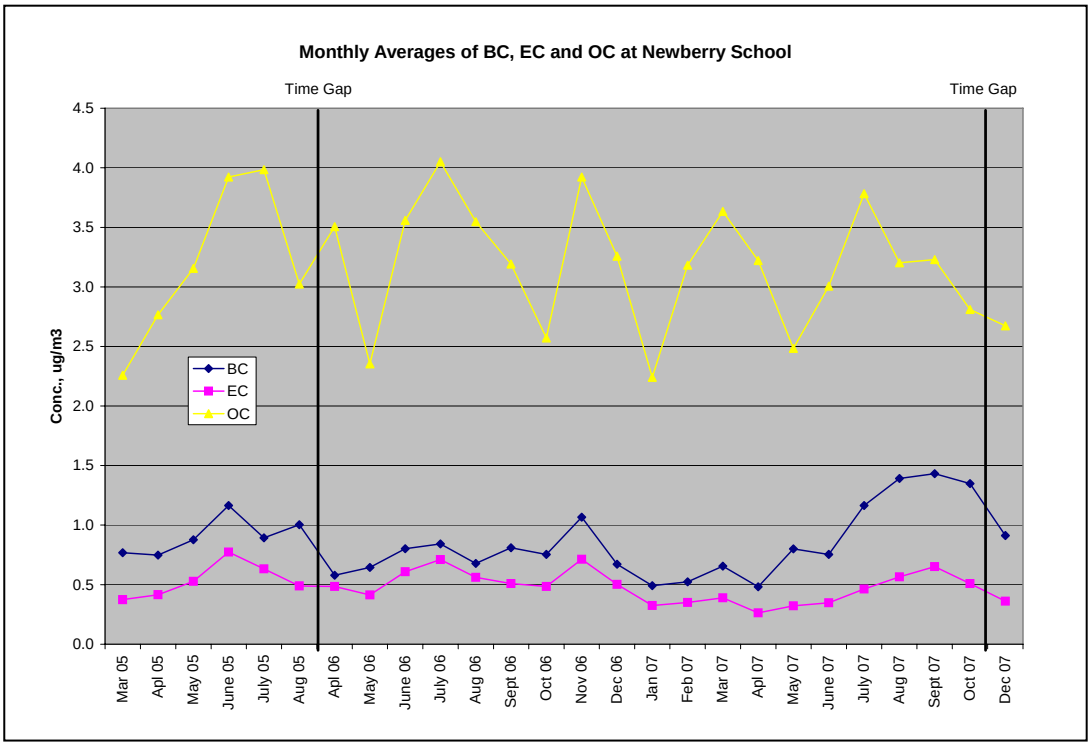


Figure 22: Comparison of Monthly Average Concentrations of Carbon Black, Elemental and Organic Carbon at Newberry School

Source Apportionment

Ultimately the data collected in this project will be used to estimate the relative proportion of mobile source contributions to the fine particulate loading in the area using source apportionment techniques. Also, the additional data that was collected during June, July and August 2005 and 2006 at Dearborn (261630033), Newberry School (261630038) and Allen Park (261630001) will help in characterizing the sensitivity of source apportionment techniques to spatial and temporal changes.

Although this grant didn't include funding to support source apportionment activities, the MDEQ recently received a community monitoring grant to analyze the air toxics data collected since the Detroit Pilot Project. Source apportionment makes up a significant portion of this project. The data collected by this grant will either be used in source apportionment activities in the grant or by MDEQ staff. A portion of the data analysis grant includes source apportionment training to build in house capacity.

Experiments Conducted with the Continuous Formaldehyde Samplers

The peristaltic pump requires constant maintenance and severely limits the utility of Alpha Omega Power Technologies MA-100 Methanalyzer unit in field applications. To assess how changes in peristaltic pump maintenance impacts performance of the continuous formaldehyde samplers over time, a series of liquid calibrations were performed at various intervals after the peristaltic pump tubing was changed. It was theorized that as the tubing ages, the efficiency of the pumping process declines and impacts the ability of the unit to effectively mix the reagents in a consistent fashion. This impacts accuracy over time. The efficiency of gas

transmission across the permeable membrane may be an issue and will be investigated at a later date. Only the liquid mode of operation was used in this study so that the impact from one variable at a time could be assessed.

A series of aqueous formaldehyde solutions was prepared using serial dilution that ranged from 10 ppb to 40 ppb. The continuous formaldehyde units received a series of injections of the standards while in liquid mode. Because the formaldehyde is so reactive at such dilute concentrations, standard solutions couldn't be retained and must be freshly made each day.

The data in **Figure 23** show the impact of changing the pre-filters in the reagent lines inside the bottles on performance.

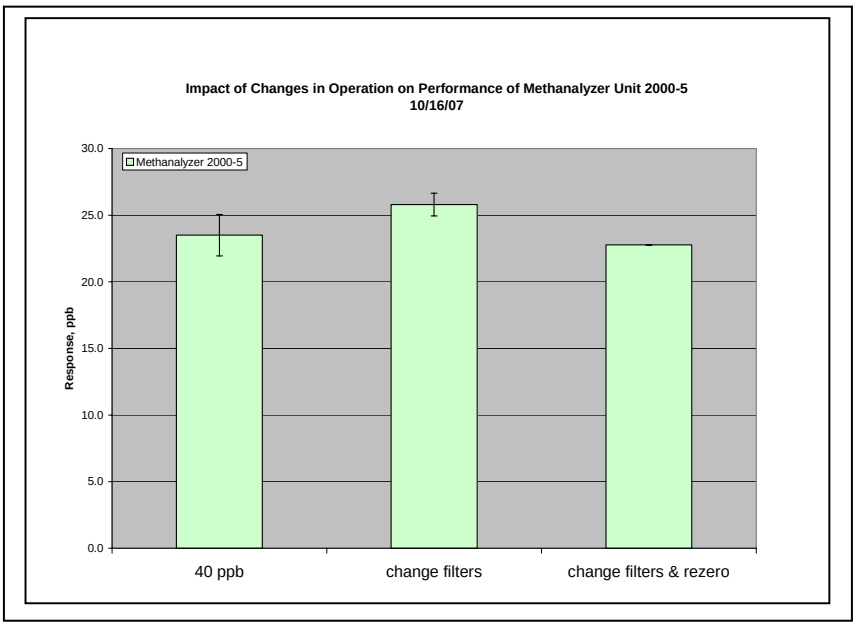


Figure 23 Impact of Changing Pre-filters on Performance

The vertical bars are 90% confidence intervals. The confidence interval on the last bar is quite small and is shown by a small dash below the surface of the bar. When flow rates were checked using a stop watch, the flow rate on the acetyl acetone line was 0.022 ml/min. After the new filters were installed, the flow rate was determined to be 0.020 ml/min. This indicates that a better method to determine flow rate needs to be developed. In order to fully understand and optimize the impact from flow rate on performance, an investment in better technology needs to be made. The method "supplied" with the unit is inadequate. It is recommended that a digital read out of the flows of all solvents at critical points be available.

Although the standard solutions were freshly made each day by using serial dilutions and volumetric glassware, Class A pipettes were not available. The imprecision created by using serological pipettes and syringes may have contributed to some of the variability in the responses. Therefore, all data presented here was generated from the same set of standard solutions, removing the standard accuracy variable from the analysis. The impact of tubing degradation over time on response rate couldn't be accurately determined due to consistency issues with creation of the standard solutions. A more detailed analysis needs to be performed when a full suite of Class A volumetric glassware is located. Perhaps this can be performed in conjunction with an investigation into the efficiency of the gas permeable membrane when a high volume zero air generator is located. The high volume zero air generator will help in the creation of gaseous formaldehyde standards.

The flow is difficult to measure given the very low flow and small volumes involved. To more accurately track changes in flow and optimize the flow rates of the various solvents and water, more precise flow is required as is the use of a direct read out device capable of measuring these low flows. However, if a better fluid handling system were to be employed that is capable of generating constant, reproducible flows, perhaps a flow read out device would be unnecessary.

The data shows that re-zeroing the instruments has a marked impact on response. A solution of 40 ppb was injected using the liquid mode of operation and the zero altered twice. The response changed from 14.2 to 20.9 to 25.2 ppb. Re-zeroing the units wouldn't be such an operational issue if the baselines remained stable

because the zero could be set and allowed to remain constant. Unfortunately, the units are also prone to baseline drift and require that the zero be reset. Often, the signals become negative over time. The units can be serviced and baselines set on one day. Then, when the station is revisited days later, baselines can be markedly different as shown by the screen capture in **Figure 24.** Factors that appear to impact the baseline stability include changes in flow rate and refreshing the solvents. The changes in flow rate impact the mixing ratios of the solvents required to generate the colorimetric response. The use of older deionized distilled water stored in the trailer may take up formaldehyde from the paneling. When this water is mixed with the fresher water contained within the instrument, a baseline adjustment occurs.

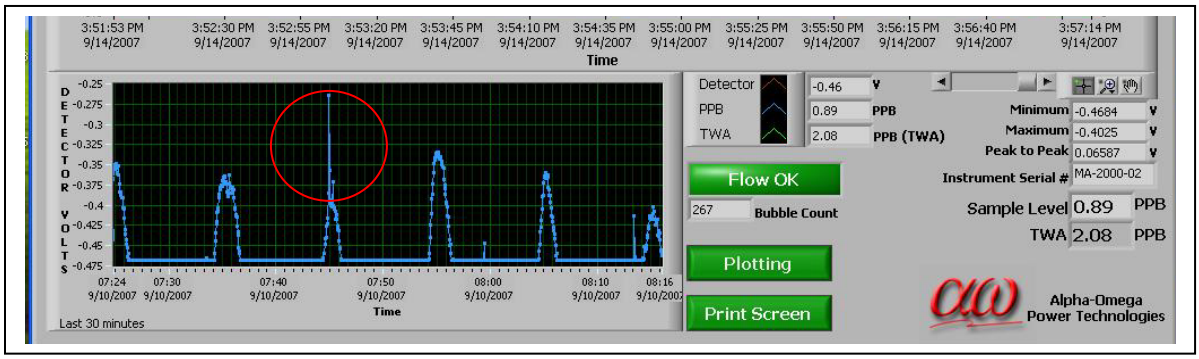


Figure 24: Impact of Base Line Drift and Bubble Formation on Sinusoidal Wave Integrity

Bubble formation also impacts the baseline as well as the response from the units. If a large bubble becomes stuck in the detector cell, the signal is pushed off scale and can impact the ability of the unit to regain the baseline. A large bubble is shown in **Figure 25**. Smaller bubbles that travel through the cell will impact the response. A bubble is shown in within the circle in **Figure 24** when the unit is operating in gas mode. Bubbles also impact the precision of liquid calibrations, without influencing the baseline as shown in **Figure 26**. On other days, when the units are operating bubble free good precision results can be obtained. The precision of liquid injections of a 40 ppb solution under both of these conditions are compared in **Table 7.** The introduction of bubbles into the system needs to be minimized. Changing the peristaltic pump tubing every two weeks causes too much bubble formation. Substitution of syringe pumps for the peristaltic pumps would create a much better mode of liquid handling.

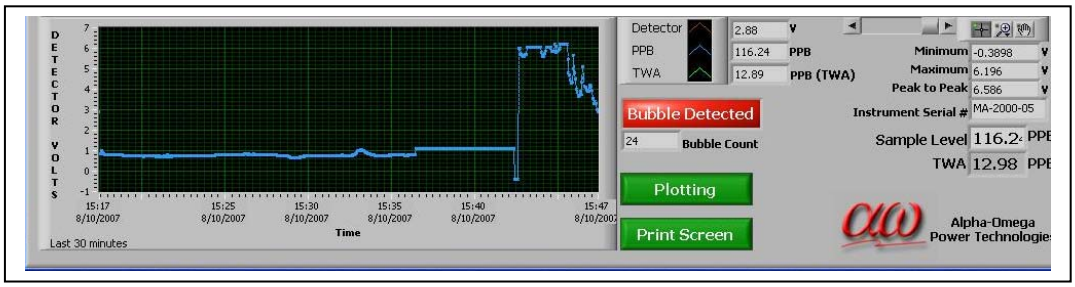


Figure 25: Illustration of a Large Bubble

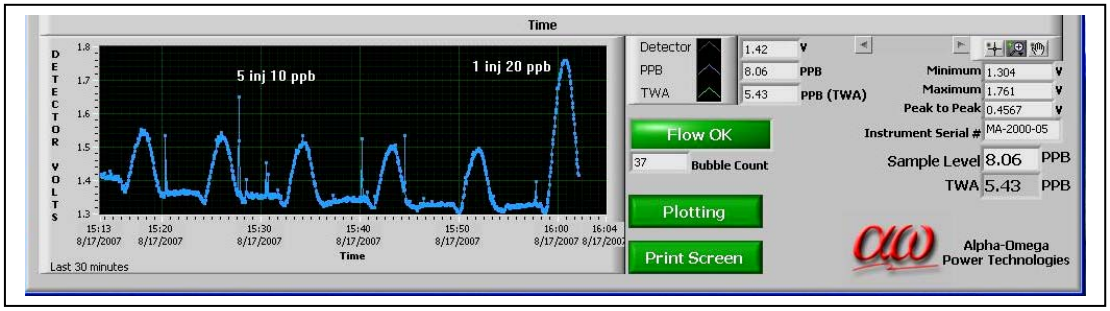


Figure 5: Bubbles Impacting Precision of Responses of Five Liquid Injections of 10 ppb and One Liquid Injection of 20 ppb Formaldehyde.

The peristaltic pump tubing was changed on 12/4/07, and is likely the cause in the change in the signal from 10/16/07 to 12/5/07, as illustrated in **Table 7**.

Another bubble related issue may be the design of the detector cell. It is much more difficult to remove bubbles from the detector cell of the Methanalyzer 2000-2 than the Methanalyzer 2000-5. The 2000-2 unit may have an inferior cell design that hinders the ability to efficiently remove the bubbles.

Table 7: Results from Repeated Injections of a 40 ppb Liquid Formaldehyde Solution Methanalyzer 2000-2

	Response on a Bubble Free Day, (10/16/07) ppb	Response on Day with Bubbles, (12/5/07) ppb
Injection # 1	22.76	14.51- Bubble Here ?
Injection # 2	22.79	8.17
Injection # 3	22.78	8.21

As the preceding discussion illustrates, trouble shooting and instrument optimization is a laborious process. It can take a week or more to stabilize the instruments, optimize the response and remove all bubbles. Then, the peristaltic pump tubing is almost ready for replacement. Typically, the peristaltic tubing is scheduled for replacement every 14 days to prevent a line rupture and leakage of solvent through out the units.

To improve operations of the units, the peristaltic pumps need to be replaced with syringe pumps capable of providing a continuous flow. In addition, laboratory supplies are needed to be able to more accurately make serial dilutions to test the units in liquid mode. Also, a zero air generator capable of delivering greater flows to dilute the permeation source is needed to perform a series of gas calibrations. The MDEQ has ordered some of these high flow calibrators to audit the trace gas monitors. Perhaps, we can borrow one of these units to test accuracy of the units in the gas phase.

Conclusions/ Future Work:

Formaldehyde Samplers

This work determined that there are several factors that impede the routine operation of the continuous formaldehyde samplers and impair sensitivity. They are:

- Bubbles impacted by fittings/leaks;
- Flow Rates impacted by peristaltic pump tubing age;
- Freshness of DI H20 (*and storage location – not in trailer!*);
- Zero/ baseline settings – impacted by solutions;
- Filters – impact flow rates, and;
- Integrity of tubing/ plumbing system/back pressure.

To make the operation of the formaldehyde units more reliable, the following modifications to the formaldehyde units are suggested:

- Replace peristaltic pumps with syringe pumps eliminating the need for tubing change-outs;
- Electronic controls of flow rates;
- Configure flush ports to the front of the unit so a single user can flush and see detector output;
- Larger fluid reservoirs should be housed AWAY from electronics, chilled if necessary;
- The scrubber should be located ABOVE & AWAY from solvents, and;
- Software should allow users more control over screen formatting.

Retrofitting the formaldehyde samplers with syringe pumps will eliminate the need for almost continual replacement of the peristaltic pump tubing and avoid the introduction of additional bubbles into the system. The instruments need a different mechanism, other than tracking the flow of air bubbles, to set flow rates in a reproducible manner. The output of the permeation source and zero air supply also need to be better characterized. If additional funding can be located, MDEQ is interested in pursuing these options.

EC/OC

As part of the SEMOS work group, and the process of creating a $PM_{2.5}$ SIP, a second continuous EC/OC sampler was purchased and deployed to the Dearborn (261630033) site. This data will be analyzed along with the Newberry EC/OC data to better understand spatial differences and diurnal patterns in EC/OC. In addition, a third EC/OC sampler was deployed in April 2008, upwind from the Detroit Metro area at Tecumseh (261090007). Once more measurements are collected, additional investigations will be undertaken examining the spatial and temporal differences of organic carbon across these three sites.

Will the Work Continue?

The research initiated in this grant will continue in a number of ways, contingent upon adequate staffing levels and future funding. It is anticipated that the Newberry School (261630038) and FIA (261630039) sites will continue operation. As the creation of the Detroit Inter-Modal Freight Terminal progresses, the background data collected at Newberry School will be invaluable to characterize the impact of such a major source on the air quality in the Delray area. Also, Detroit's Ambassador Bridge crossing may be modified in the future. A second, state owned bridge may be built that will connect Windsor with the Delray area of Detroit and may have an exit ramp near the SW High School (261630015) monitoring station. The existing Ambassador Bridge may be expanded to handle more traffic. The MDEQ will continue to track the International border crossing issue and operate the FIA site.

The MDEQ was recently awarded an Air Toxics Community Monitoring grant to support data analysis activities. This Project called "Analysis of Air Toxics Data: Quality Assurance Implications, Source Apportionment

Uncertainty Analysis and Updated Risk Assessment" will analyze data collected in this project.

Region 5 EPA has received a RARE grant to study the impact of locomotives on air quality in the Dearborn, Michigan area. The MDEQ operates two sites impacted by locomotives: Dearborn (261630033) and Newbery School (261630038). The MDEQ will be assisting Region 5 EPA in the collection of EC/OC and BC data at several locations near the Rougemere rail yard. Two temporary stations will be created, a far upwind site and a site located upwind and adjacent to the Rougemere tracks. The data collected in this grant will be used to supplement the Rougemere project database, providing information about spatial distributions and possible sources.

Acknowledgements

The MDEQ would like to thank Mr. Alan Vette, EPA/ORD for the loan of aethalometers; Ms. Donna Kenski, LADCO for consultation and non parametric linear regression analysis; Ms. Loretta Lehrman, Ms. Motria Caudill and US EPA Region 5 for providing additional funding and support for this project and especially for providing travel funds to support training at Alpha Omega Power Technologies, Inc. in Albuquerque, New Mexico. Most of all, the MDEQ would like to thank EPA OAQPS for providing funding.