

4.4 Formaldehyde

4.4.1 Method: The method employed for collection and analysis of formaldehyde was based on TO-11 of EPA's Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air.⁽¹⁴⁾ This method uses DNPH cartridges (2,4-dinitrophenylhydrazine) to collect the formaldehyde via a chemical derivitization reaction. The cartridges are subsequently extracted and the extract analyzed by high performance liquid chromatography (HPLC) for the derivatized formadehyde compound. The sample collection was conducted by the NC DAQ. A contract lab conducted the extractions and analyses.

4.4.2 Time Frame: Two 8-hour samples were collected at the 3 sampling sites on 3 consecutive days. The sampling times were from 8:00 to 16:00 hrs and again from 20:00 to 04:00 hrs. The sampling tubes were collected from the sampling sites and new tubes placed in the sampling assembly within 1 hour of the start of the sampling period. The total number of field samples was 21 (18 samples and 3 trip blanks).

4.4.3 Agency / Team Size: This team consisted of personnel from the NC DAQ who were responsible for site set up, operation, and data collection. A contract lab in Raleigh, NC, Enthalpy Analytical, Inc. conducted the analysis of the samples.

4.4.4 Equipment / Supplies:

Xontech™ 911

Plastic building

Supply lines and fittings, ¼" stainless steel

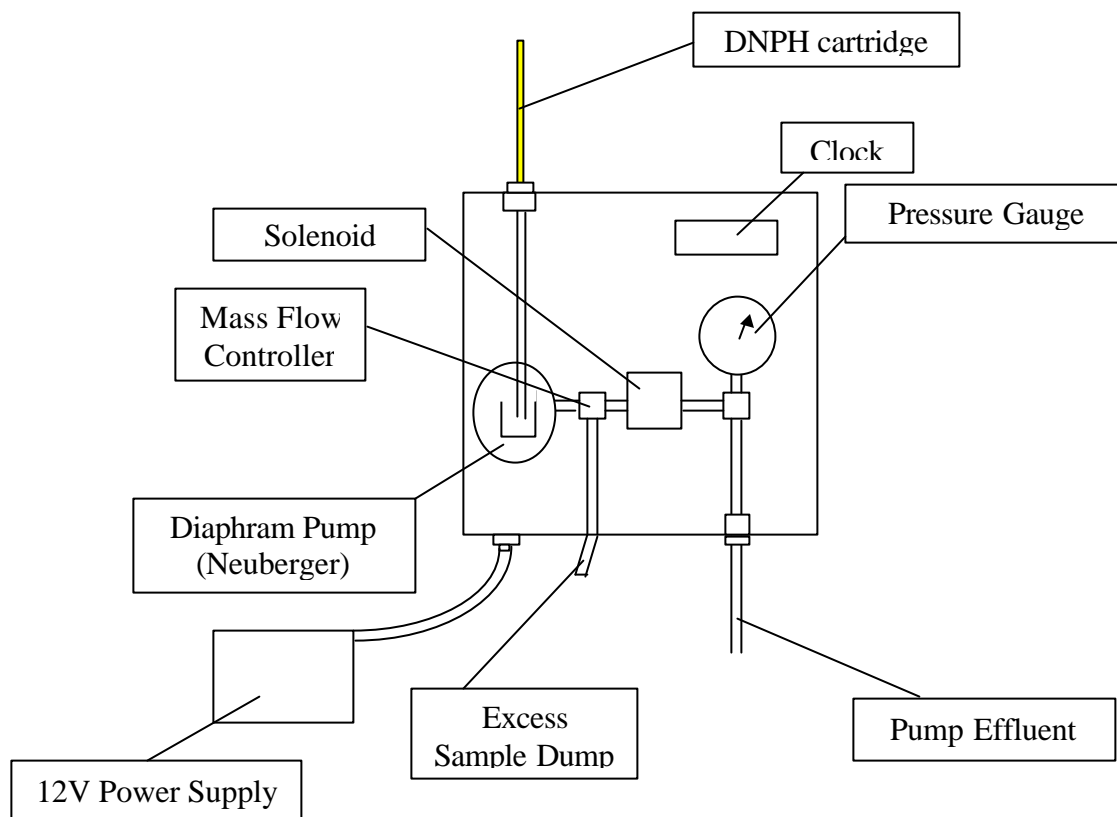
Flowmeter

DNPH tubes

4.4.5 Sampling Procedure: The sampling assembly (see Diagram 4.4.1) consisted of a Xontech™ 911, a length of stainless steel tubing and one DNPH tube and was used in the following manner. Air first enters the assembly through an inlet funnel that is 3 meters above the ground. The air then travels through a 15micron filter and then through ¼" GC-grade stainless steel tubing to the upstream end of the DNPH-coated silica gel tube. The downstream end of the tube is connected to the Xontech™ 911 pump with Tygon tubing. The sampling flow rate was set at approximately 200 ml/min for a total sample volume of approximately 96 liters for an 8-hr sample period.

Before field deployment, the sampling equipment was assembled and certified operational and clean by the following procedure. A volume of 96 liters of zero air (the approximately the amount of air to be sampled in the field) was drawn through each sampling assembly to determine the background level of formaldehyde in that system. This tube was then sent to the contract lab for analysis and the results indicated that the system was free of quantifiable amounts of formaldehyde.

Figure 4.4.5 XonTech 911A configured for formaldehyde sampling



Once in the field, the assembly was operated as described above. Within one hour of the start of next 8-hr sampling period, the exposed tubes were removed from the assembly and replaced with a new tube. At this time the flow rate was checked and recorded. Exposed tubes were placed in a refrigerated container for transport back to the TPB lab and subsequently to the contract lab.

4.4.6 Sample Analysis and Data Reduction: The samples were collected at the end of each 8-hr sampling period and refrigerated until time of analysis. All sample tubes were prepared and analyzed according to the procedures outlined in EPA Method TO-11 by a contract lab. The analysis was performed using a Hewlett-Packard HPLC with ultraviolet (UV) detection. Results from the analyses were submitted by the contract lab to the NC DAQ lab and reported below.

The concentrations observed for the 18 field samples and 3 trip blanks are given in Table 4.4.1. The ambient air concentration of formaldehyde was calculated by dividing the catch weight by the sample volume of air (Ex.: $0.633\mu\text{g} \div 0.096\text{m}^3 = 6.59\mu\text{g}/\text{m}^3$) The result represents an average formaldehyde concentration over the 8-hr sampling period.

Table 4.4.1 Results of Formaldehyde Analyses

Sample ID Number	Catch Weight (mg)	Sample volume (m ³)	Ambient Air Conc. (mg/m ³)
1MC041499B	0.633	0.096	6.59
1MC041599A	0.559	0.096	5.82
1MC041599B	~ 0.330	0.096	~ 3.43
1MC041699A	~ 0.467	0.096	~ 4.86
1MC041699B	~ 0.362	0.096	~ 3.77
1MC041799A	~ 0.265	0.096	~ 2.76
1MC Trip Blank	< 0.250	0.0	< 2.60*
2MC041499B	0.886	0.096	9.23
2MC041599A	0.661	0.096	6.88
2MC041599B	< 0.250	0.096	< 2.60
2MC041699A	< 0.250	0.096	< 2.60
2MC041699B	0.715	0.096	7.45
2MC041799A	0.888	0.096	9.25
2MC Trip Blank	< 0.250	0.0	< 2.60*
3MC041499B	~ 0.443	0.096	~ 4.61
3MC041599A	0.593	0.096	6.18
3MC041599B	~ 0.348	0.096	~ 3.62
3MC041699A	0.963	0.096	10.03
3MC041699B	0.517	0.096	5.38
3MC041799A	0.744	0.096	7.75
3MC Trip Blank	< 0.250	0.0	< 2.60*
Limit of Quantitation (LOQ) ⁺⁺	0.517	0.0	5.38*
Min. Detectable Limit (MDL) [∞]	0.250	0.0	2.60*

* These values were obtained by dividing the catch weight by 0.096 m³ to use as a comparison value to the actual samples. These concentrations represent values that would have been obtained if 0.096 m³ of zero air had been drawn through the tubes.

++ LOQ refers to the amount (concentration) of analyte below which the analytical method cannot accurately determine the amount but detection is still possible.

∞ MDL refers to the amount (concentration) of analyte below which the analytical method cannot distinguish between the analyte signal and the baseline signal.

In Table 4.4.1, the catch weight refers to the total amount of formaldehyde collected on the tube. The Minimum Detection Limit (MDL) for the analysis was 0.250 µg catch weight and the Limit of Quantification (LOQ) was 0.517 µg catch weight. This means that catch weights that lie between the two values are approximations (~) and the formaldehyde derivative can be detected but not precisely quantified. The values that have < 0.250 µg catch weights are below the MDL. The trip blanks are considered to be indicative of any possible pre-existing formaldehyde in the DNPH-tubes since they are

unused and unopened. Sample concentrations that are $< 0.250 \mu\text{g}$ indicate that no additional detectable formaldehyde was collected on the tube over the 8-hr period.

Direct correlation of the formaldehyde concentrations with the meteorological data is possible for only two of the sites, MC1 and MC3. The meteorological data from MC2 for the period of time that the formaldehyde samplers were in operation was lost due to a data logger malfunction. However, the data from the MC1 site can be used to give a good approximation of the wind direction at MC2 because of their proximity. These are the wind direction data that were used to plot the pollution rose for the MC2 site.

Figures 4.4.1A/B, 4.4.2A/B, and 4.4.3A/B present the pollution roses that correlate the average wind directions and the average air concentration of formaldehyde sampled in each of the 8-hr sampling periods at each of the three sites (Table 4.4.1). In order to simplify the presentation of the tabulated data, the tabulated data points were assigned “absolute” values without the $<$ or \sim symbols. These symbols and their meanings are explained above. In the six figures there are four color-coded concentric rings that represent four “levels of interest”. The innermost ring (red) represents the MDL for the analysis ($2.60 \mu\text{g}/\text{m}^3$) and is the level below which formaldehyde concentrations cannot be detected. The sample results that are within this value are tabulated with a “ $<$ ” to denote that no formaldehyde was detected in these particular samples above the MDL.

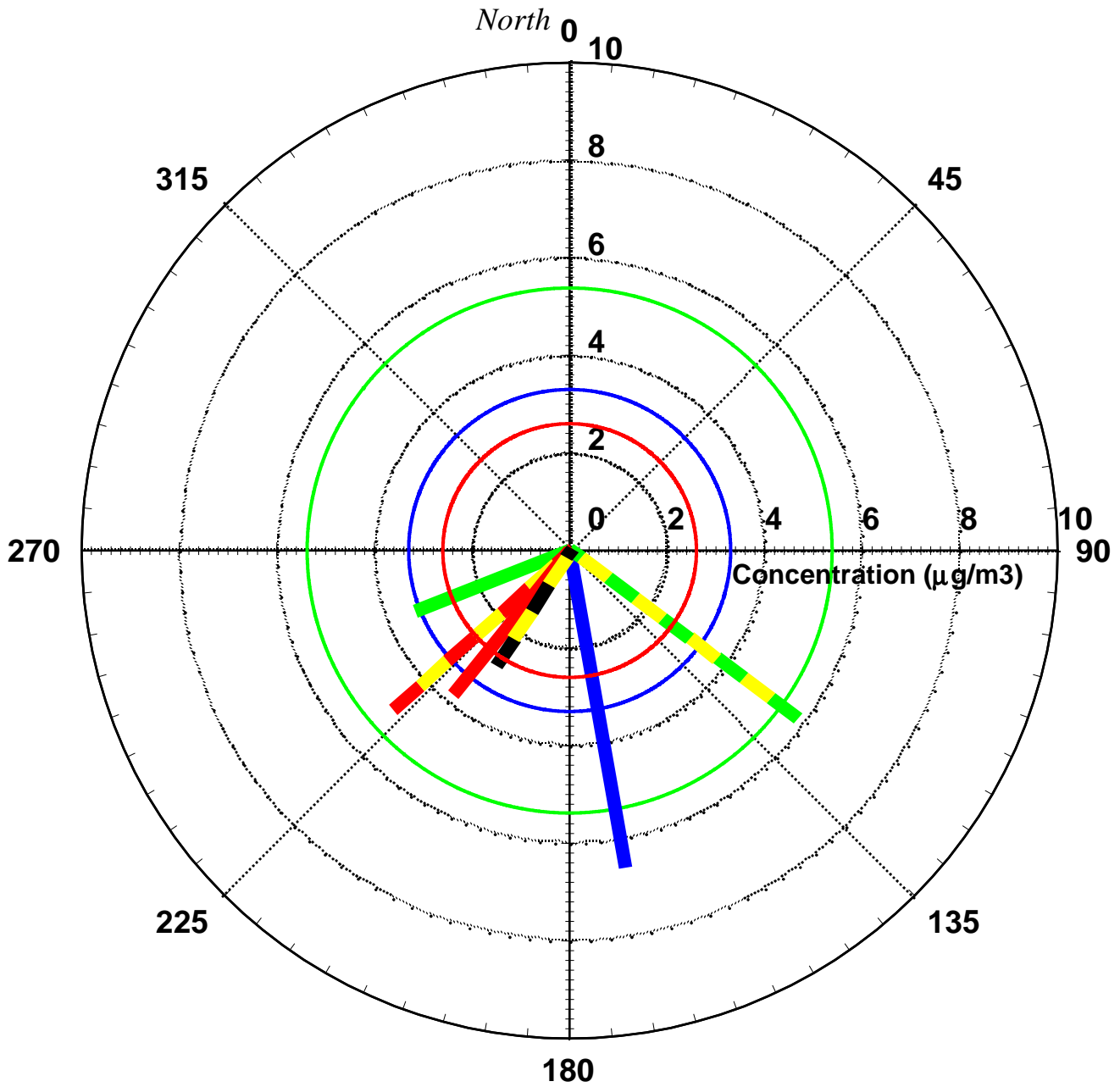
The next ring (blue) is an average ambient air concentration ($3.3 \mu\text{g}/\text{m}^3$) taken from Reference 4 and it represents an *average ambient air concentration* in populated areas. The reference states that “the focus of this survey was on ambient data in populated areas of the United States. Data from remote sites and data indicating direct source impacts were excluded.” It is important to note that the average ambient air concentration is above the MDL, which means that the ambient air contribution to the sample concentration can be detected. The exception would be that if the ambient air concentration were lower than the MDL (for whatever reason), then of course the sample would be analyzed and return the result of a non-detect. There were only two of the 18 samples that had values denoted as “ $<$ ” the MDL and those values (2MC041599B & 2MC041699A) are shown in Figures 4.4.2A&B as inside the MDL ring.

The green ring depicts the LOQ and as stated above any values that lie within this ring are approximations of the sampled concentration and are represented as such by using a “ \sim ” before the tabulated value. This is observed in six of the 18 samples. The remaining 10 values lie above the LOQ. Lastly, the outermost circle (aqua) at $61.5 \mu\text{g}/\text{m}^3$ in the “B” figures represents the ATSDR Minimal Risk Level for formaldehyde and represents the acute exposure concentration via inhalation.¹ This level is considered an appropriate concentration for comparison purposes because the NC regulatory level for formaldehyde is based on formaldehyde being classified as a 1-hr acute exposure irritant. It is important to note from these data that although there are a few concentrations higher than an average ambient air concentration of $3.3 \mu\text{g}/\text{m}^3$, all of the samples are significantly lower than the ATSDR acute exposure concentration of $61.5 \mu\text{g}/\text{m}^3$. This is clearly depicted by the histogram in Figure 4.4.4. (Again, levels depicted at the MDL of $2.60 \mu\text{g}/\text{m}^3$ represent a level at which formaldehyde could not be detected, as stated above.)

Given this conclusion, there are two other interesting trends that can be noted. The first is the observation that although there are sample concentrations above the average ambient air concentration at site MC1 when the average wind direction was from the southwest quadrant there are higher concentrations from the same general quadrant at site MC3 during the same time period. This indicates that the air mass had a higher formaldehyde concentration than the average ambient concentration before it moved into the area. This is seen by comparing samples 041599B, 0141699A, 041699B, and 041799A between sites. This conclusion can be reached because site MC3 is located southwest of site MC1 and the site locations are within 1 mile of each other. Second, there are concentrations that are above the average ambient concentration but the samples were collected when the average wind direction was from the southeast quadrant. This is the case when comparing samples 041499B and 041599A between sites.

These observations may be indicative of one or more of the following influences on the air concentration of formaldehyde in the survey area: 1) the formaldehyde concentration in the air varied due to the influx of an air mass carrying higher levels of formaldehyde from other areas, 2) the influence of mobile sources such as cars, trains, or other vehicles, and/or 3) natural variation in the ambient air concentration of formaldehyde from all sources of formaldehyde.

**Figure 4.4.1A - Matthews Survey
Formaldehyde Monitoring
Site MC1 - 8 hr Sampling Periods
April 14-17, 1999**

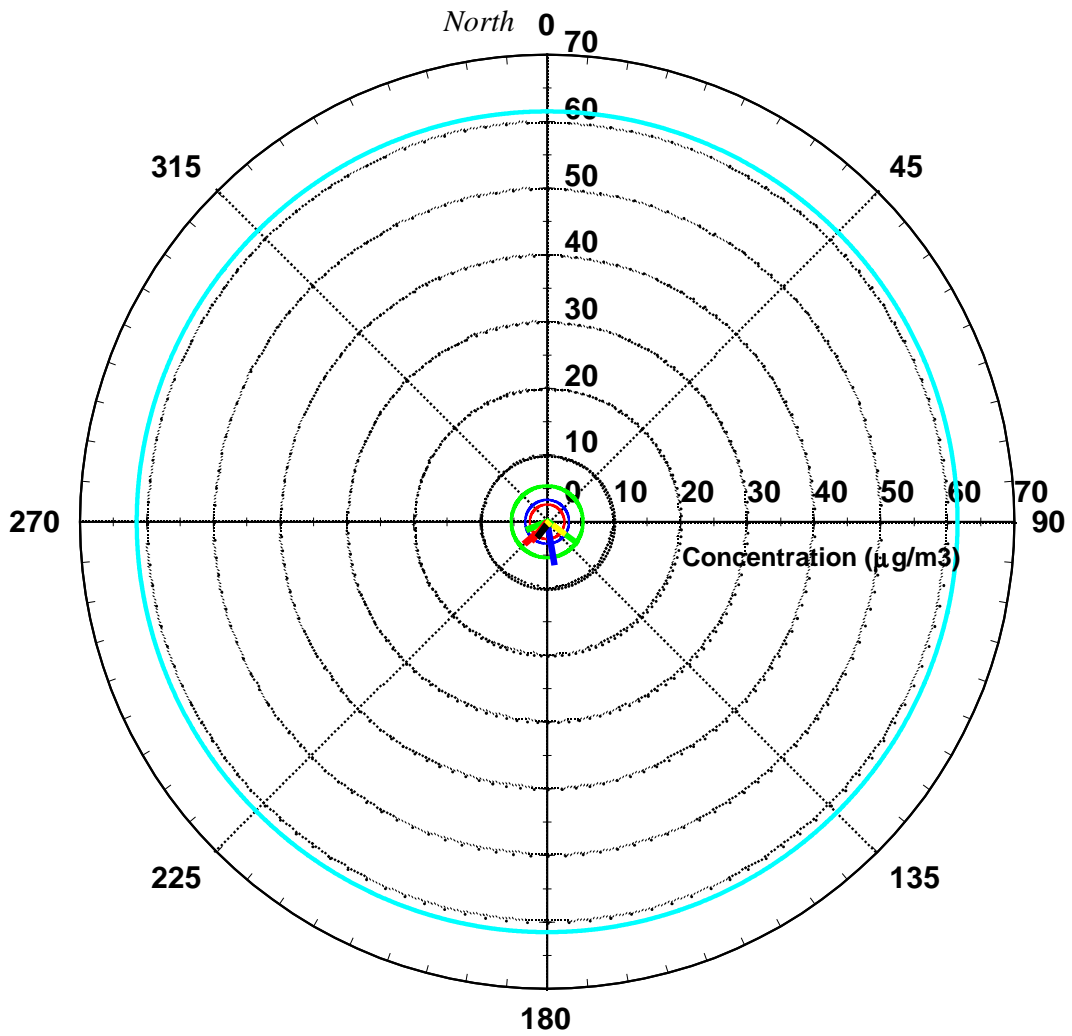


	Limit of Quantitation = 5.38 $\mu\text{g}/\text{m}^3$
	Ref. 4 Amb. Conc. = 3.30 $\mu\text{g}/\text{m}^3$
	Min. Detection Limit = 2.60 $\mu\text{g}/\text{m}^3$

	1MC041499B		1MC041699A
	1MC041599A		1MC041699B
	1MC041599B		1MC041799A

"A" samples taken 08:00 - 16:00 hrs
"B" samples taken 20:00 - 04:00 hrs

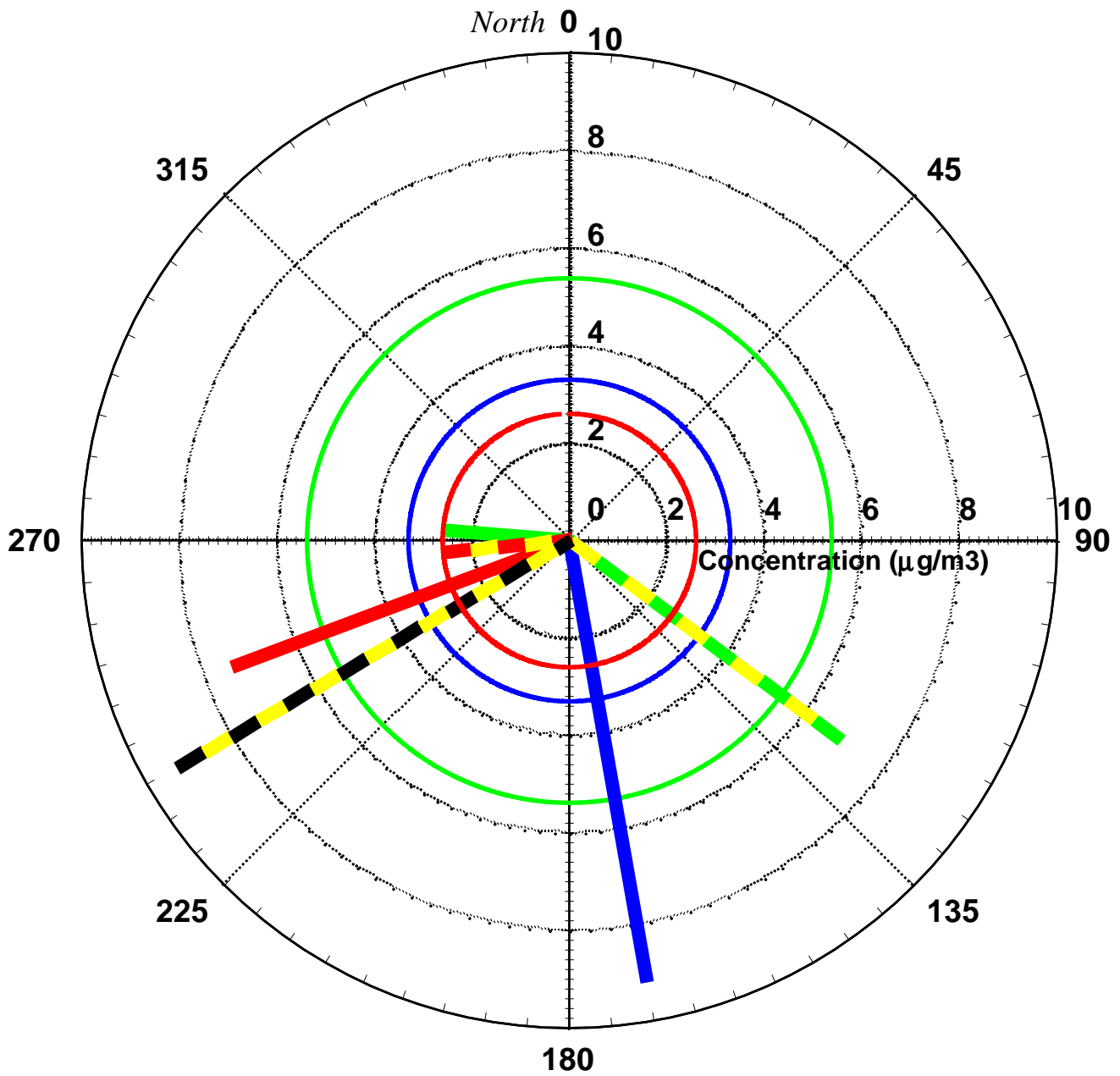
**Figure 4.4.1B - Matthews Survey
Formaldehyde Monitoring
Site MC1 - 8 hr Sampling Periods
April 14-17, 1999**



"A" samples taken 08:00 - 16:00 hrs
 "B" samples taken 20:00 - 04:00 hrs

Minimal Risk Level (MRL) = 61.5
 Limit of Quantitation (LOQ) = 5.38
 Ref. Ambient Concentration = 3.30
 Min. Detection Limit (MDL) = 2.60

Figure 4.4.2A - Matthews Survey
Formaldehyde Monitoring
Site MC2 - 8 hr Sampling Periods
April 14-17, 1999

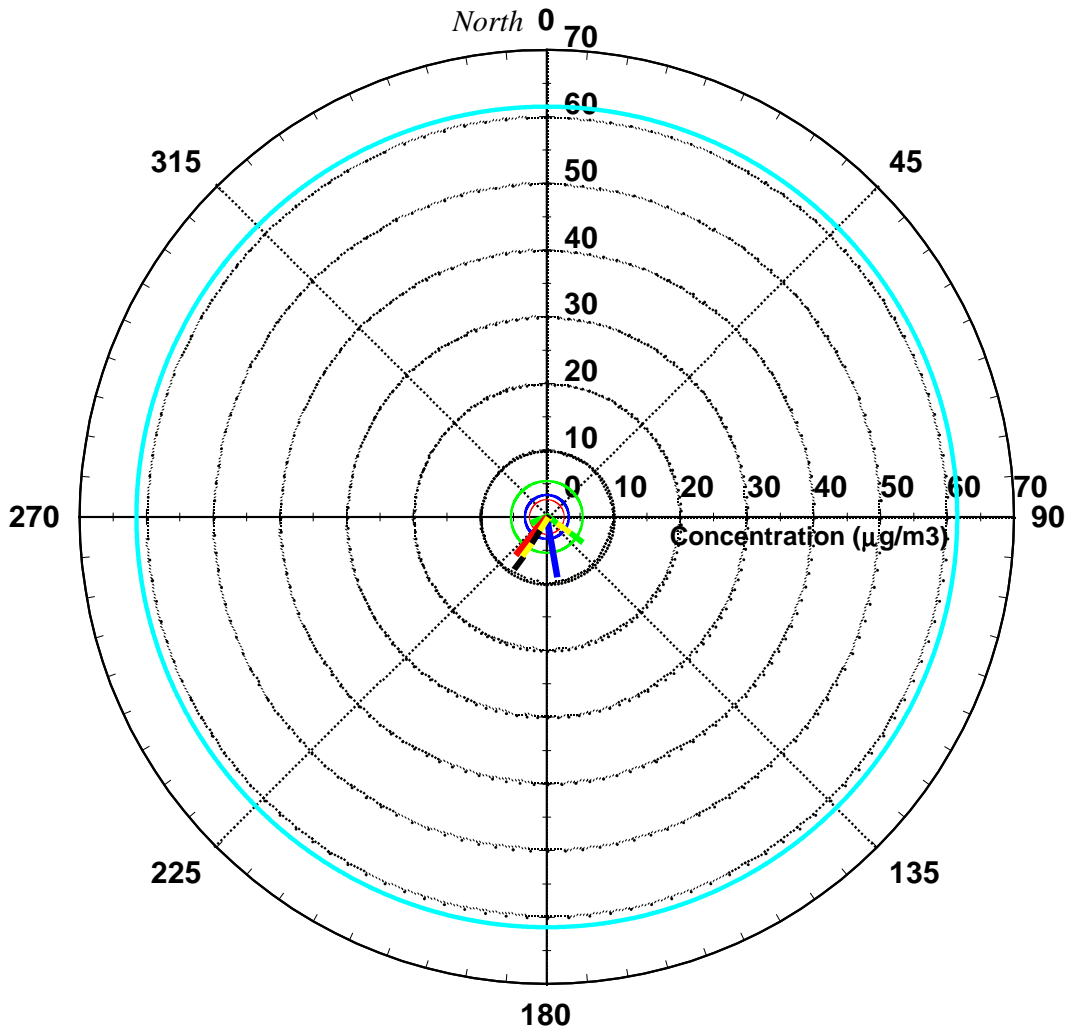


	Limit of Quantitation = 5.38 $\mu\text{g}/\text{m}^3$
	Ref. 4 Amb. Conc. = 3.30 $\mu\text{g}/\text{m}^3$
	Min. Detection Limit = 2.60 $\mu\text{g}/\text{m}^3$

	2MC041499B		2MC041699A
	2MC041599A		2MC041699B
	2MC041599B		2MC041799A

"A" samples taken 08:00 - 16:00 hrs
 "B" samples taken 20:00 - 04:00 hrs

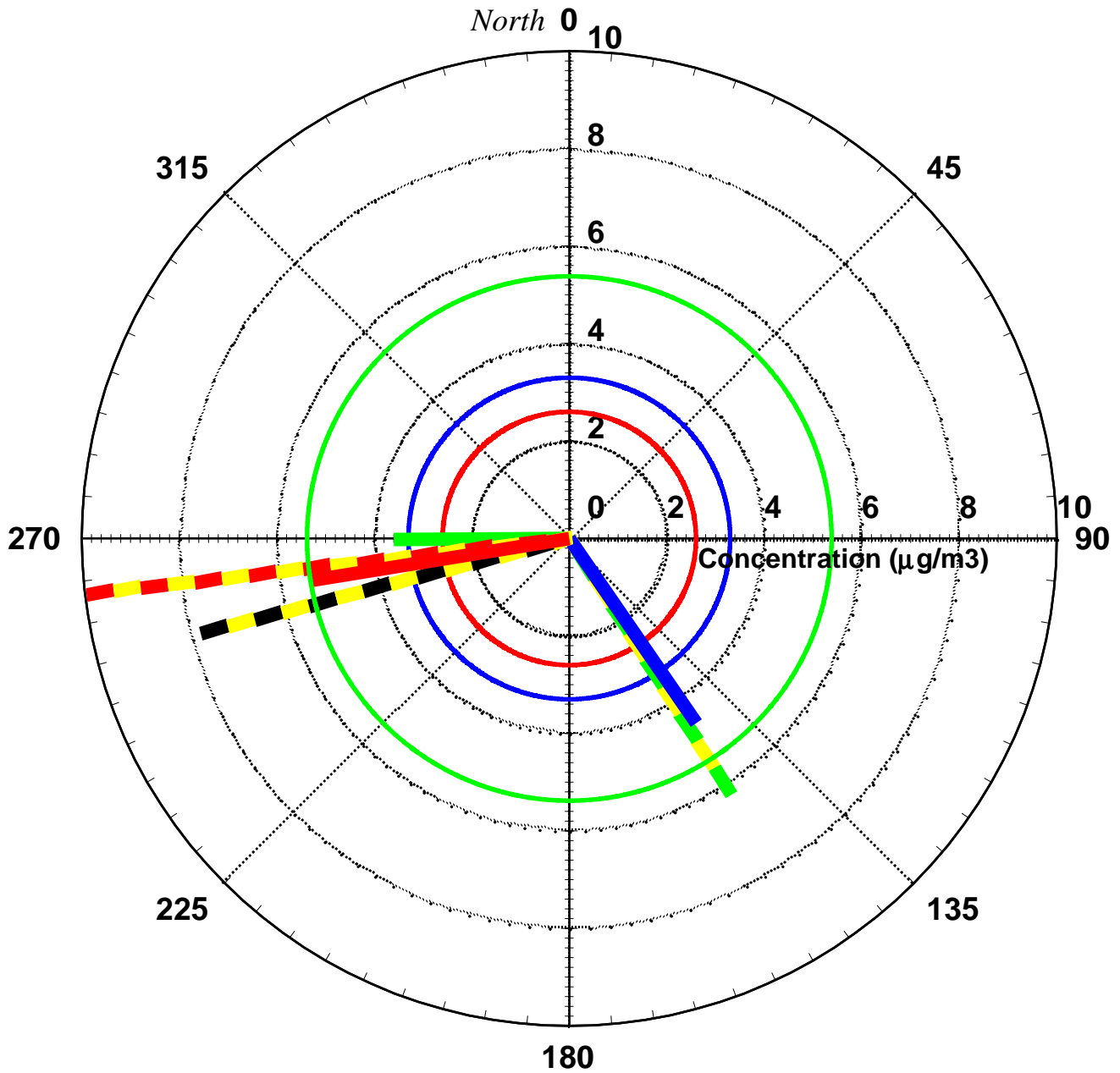
**Figure 4.4.2B - Matthews Survey
Formaldehyde Monitoring
Site MC2 - 8 hr Sampling Periods
April 14-17, 1999**



"A" samples taken 08:00 - 16:00 hrs
"B" samples taken 20:00 - 04:00 hrs

Minimal Risk Level (MRL) = 61.5
Limit of Quantitation (LOQ) = 5.38
Ref. Ambient Concentration = 3.30
Min. Detection Limit (MDL) = 2.60

Figure 4.4.3A - Matthews Survey
Formaldehyde Monitoring
Site MC3 - 8 hr Sampling Periods
April 14-17, 1999

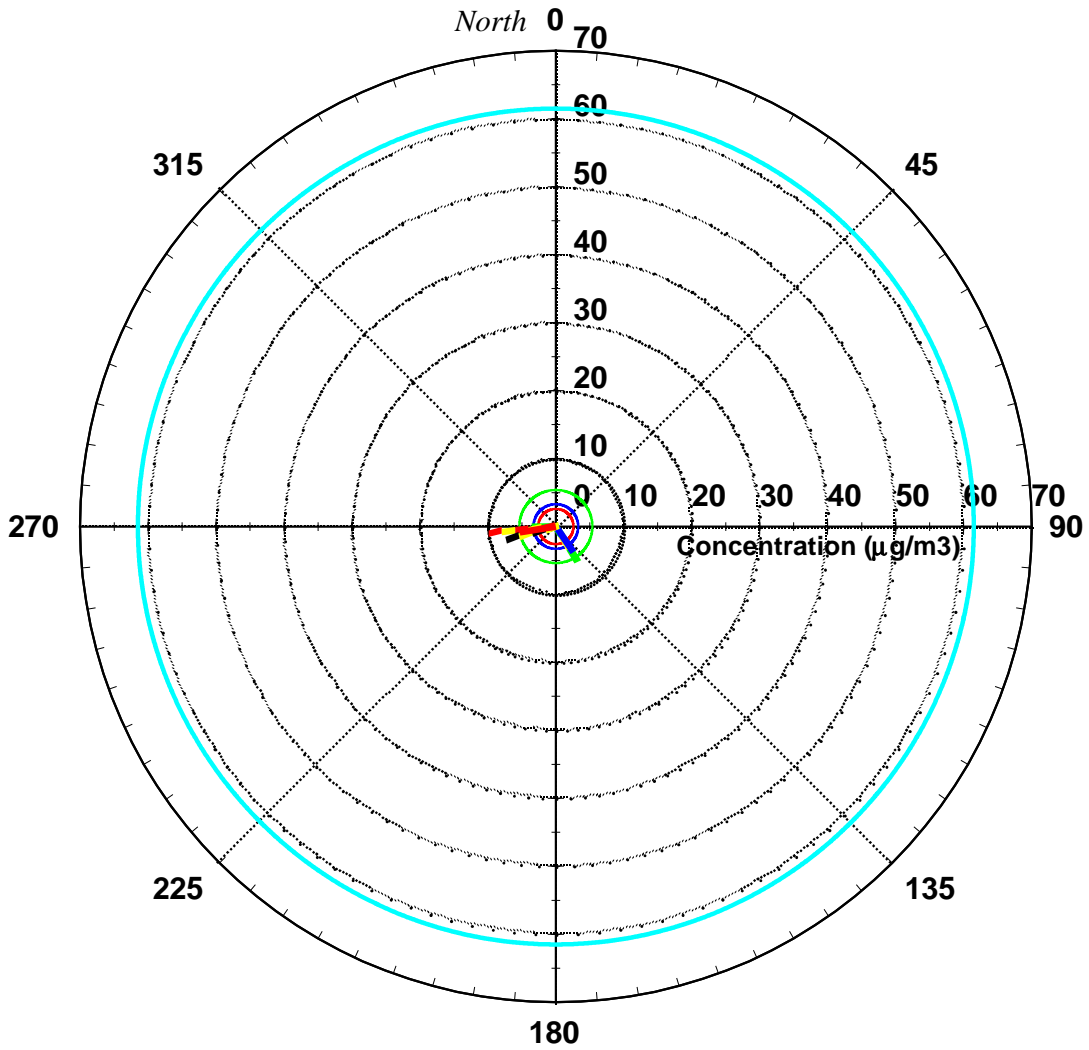


	Limit of Quantitation = 5.38 $\mu\text{g}/\text{m}^3$
	Ref. 4 Amb. Conc. = 3.30 $\mu\text{g}/\text{m}^3$
	Min. Detection Limit = 2.60 $\mu\text{g}/\text{m}^3$

	3MC041499B		3MC041699A
	3MC041599A		3MC041699B
	3MC041599B		3MC041799A

"A" samples taken 08:00 - 16:00 hrs
"B" samples taken 20:00 - 04:00 hrs

**Figure 4.4.3B - Matthews Survey
Formaldehyde Monitoring
Site MC3 - 8 hr Sampling Periods
April 14-17, 1999**



"A" samples taken 08:00 - 16:00 hrs
"B" samples taken 20:00 - 04:00 hrs

Minimal Risk Level (MRL) = 61.5
Limit of Quantitation (LOQ) = 5.38
Ref. Ambient Concentration = 3.30
Min. Detection Limit (MDL) = 2.60

Figure 4.4.4 - Matthews Survey - Formaldehyde Monitoring

