



Flint Hills Air Monitoring Data Analysis

**Summary Report
March 6, 2002**

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**FLINT HILLS AIR MONITORING DATA ANALYSIS
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1.0 INTRODUCTION

The Minnesota Pollution Control Agency (MPCA) currently conducts ambient air quality monitoring at four sites near the Flint Hills Rosemount petroleum refinery (facility). Table 1 summarizes which parameters are currently being monitored at each of these locations. In the past, several other monitors existed (e.g., Site 426) and other analytes, i.e., particulate matter (PM₁₀) and metals, had been monitored.

Table 1. Monitoring Site Summary

Parameter	Desig.	Site 420	Site 423	Site 441	Site 442
Carbon Monoxide ¹	CO	X	X		
Nitric Oxides ¹	NO _x	X	X		
Nitrogen Dioxide ¹	NO ₂	X	X		
Sulfur Dioxide ¹	SO ₂	X	X	X	X
Total Reduced Sulfur ¹	TRS			X	X
Hazardous Air Pollutants ²	HAPs	X	X	X	X
Wind Speed	WS	X	X		
Wind Direction	WD	X	X		
Temperature	Temp	X	X		

¹ Emitted from refinery in reportable quantities

² Only certain HAPs emitted from refinery in reportable quantities (see Table 4)

All of the parameters listed above are being measured in the field on a continuous basis, except for the hazardous air pollutants (HAPs). HAPs samples are taken as 24-hour composite samples, collected once every six days. HAPs samples are sent to the MPCA laboratory where they are analyzed for a variety of specific volatile compounds. Table 2 lists the specific chemicals currently being analyzed for in the HAP samples.

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Table 2. Analyzed HAP Species

Constituent
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)
Trichlorofluoromethane (Freon 11)
Dichlorodifluoromethane (Freon 12)
1,3-Butadiene
Formaldehyde
Acetaldehyde
Propionaldehyde
Acrolein
Butyraldehyde
t-Crotonaldehyde
Acetone
Methylene Chloride
Chloroform
Carbon Tetrachloride
1,1-Dichloroethane
1,1,1-Trichloroethane
1,2-Dichloroethane
Tetrachloroethylene
1,1,2,2-Tetrachloroethane
Bromomethane
1,1,2-Trichloroethane
Trichloroethylene
1,1-Dichloroethylene
1,2-Dichloropropane
t-1,3-Dichloropropylene
1,3-Dichloropropylene
c-1,2-Dichloroethylene
1,2-Dibromoethane
Hexachlorobutadiene
Vinyl Chloride
o-Xylene
m/p-Xylene
Benzene
Toluene
Ethylbenzene
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
Styrene
4-Ethyltoluene
Benzaldehyde
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene

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As discussed at a February 11, 2002 project meeting, the objective of this monitoring network was not specifically to determine the ambient air impacts of this facility on the surrounding neighborhoods. Rather, the system is primarily used to provide ambient air quality data to the MPCA from this area for comparison to other sites located throughout Minnesota. Thus, it is not surprising that our evaluation such as this of this monitoring network vis-à-vis its ability to determine the health impacts of the facility on its adjacent neighborhoods indicates a less than perfect system. Nevertheless, STS Consultants, Ltd. (STS) was requested by the Community Advisory Council to evaluate this monitoring network with respect to the neighbors' concerns, and to point out the specific strengths and weaknesses of the network. This evaluation is detailed in this report.

Our review of this monitoring network specifically involved answering a number of relevant and sequential questions. The remainder of this report has been formatted according to these questions. Other relevant questions, such as "Are the monitors located in the proper places to determine the maximum air impacts from the facility?" are beyond the charge to STS in this study.

2.0 REVIEW SUMMARY

2.1 Data Quality Analysis

Before any statements can be made regarding the health impacts of the monitoring data on the neighboring general public, the analytical data obtained from the monitoring network need to be reviewed with respect to its quality. Only quality data can be utilized to make risk statements of this nature.

To assess the quality of the monitoring data obtained near the facility, three groups of data acquisition questions were asked and answered:

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2.1.1 Data Collection Questions

- *Are the correct monitoring equipment being utilized?*

STS was provided copies of methods and procedures documents that are being used by MPCA to collect HAP samples from all of the ambient air monitoring stations throughout Minnesota, including these four Rosemount stations. This information contained a listing of the various HAP sampling equipment located at each station. The field equipment present at the locations within this network are the correct monitoring equipment needed to measure the analytes specified.

- *Are USEPA "reference" or equivalent collection methods being used?*

USEPA reference or equivalent collection methods are presumed to be used by MPCA personnel at all four of the monitoring stations in this network. The MPCA methods and procedures documents detail how the samples are to be collected, and MPCA staff stated to STS that these procedures are being followed. Verification of these collection procedures through field observations by STS was not conducted since this activity was beyond the scope of this project.

- *Are the sampling frequency and sampling duration appropriate?*

As mentioned in the Introduction to this report, all measurements are being recorded on a continuous basis at these monitors except for the HAPs. Continuous monitoring is USEPA's preferred sampling frequency/duration for the Criteria Pollutants (e.g., CO, NO_x, SO₂) and the meteorological parameters (WD, WS, Temp).

The HAPs are obtained as a 24-hour composite sample, taken once every six days. The data thus represent 24-hour average air concentrations of the chemicals for each day of collection at each monitoring location. As will be

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discussed in Section 2.2 (Table 3) of this report, the various HAP chemicals possess two types of health criteria -- acute and chronic. A health criterion represents an air concentration of a chemical that is considered to be "safe" for the public to be exposed to.

Acute health criteria are air concentrations of a chemical in air that the public can be exposed to over a short period of time and not experience any health consequences (from a regulatory standpoint, acute exposures are generally considered exposures lasting no more than one hour of continuous duration). Acute health criteria are established for chemicals, such as irritants, that induce adverse health consequences in a short period of time.

Chronic health criteria are ambient air concentrations of chemicals that the public can be exposed to without harm continuously (i.e., 24 hours/day; 365 days/year) throughout their entire lifetime. From a regulatory standpoint, annual-averaged air concentrations of chemicals are compared to chronic health criteria to show compliance and/or to make statements on air quality. This is a conservative (i.e., health protective) approach since if each year's concentration of a chemical is below the standard, the multi-year average concentration of the chemical must also be less than the standard.

The 24-hour averaged, one-out-of-every-six day HAP data from this monitoring network is not ideal for comparison to either type of criteria, but it is generally more acceptable for a chronic exposure evaluation due to the fact that annual and/or multi-year averages can be calculated and statistics can be generated from the data. For example, the measured data from an entire year's set of samples can be statistically evaluated to determine the annual average, and then the 95% confidence range of this average can be generated. The 95% confidence range accounts for the variability in the data that are obtained and recognizes the fact that continuous data are not being generated. The 95% confidence interval of the mean presents a concentration range that indicates the possibilities of the true average of the data with 95% probability (i.e., the calculated average from the data would

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fall within this range 95 out of 100 times that measurements are taken). Such an analysis was conducted in this project on the data (see Section 2.2.2).

Twenty-four hour-averaged data are not particularly useful for acute risk analyses since it is possible and quite likely that during specific sampling period(s) throughout the year, air emissions from the facility could be blown directly from their sources toward a specific monitor for a shorter period of time. Thus, during these “events” the air concentration of that chemical(s) at the monitor is likely to be much higher than what the 24-hour average concentration is. In the current analysis, these values have been adjusted using a factor of 2.5, reflective of the typical relationship between one- and twenty-four-hour averages.

Future options to address this issue include:

- Directional-specific monitors could be placed at one or more locations, which could monitor “events” as they occur. Decreasing the sample integration duration will reduce the analytical sensitivity, however.
- Air dispersion modeling analyses could be performed using the site-specific meteorological data to derive project-specific “extrapolation factors”, which are factors that are calculated as the ratio between the 24-hour average air concentration of a nominal pollutant and its maximum one-hour average air concentration at each monitoring station.
- *Are the sampler inlets and overall orientations such that representative “breathing zone” ambient air is collected?*

The sampling inlet ports for the criteria pollutants are set by USEPA at 3-15 meters for gaseous parameters. The monitors in this network that are measuring these pollutants are oriented accordingly. The monitors measuring the ambient air concentrations of the HAPs are set at 3 meters, which is somewhat higher than breathing zones for the public. Having these

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inlets higher than a breathing zone is preferred over ground-level monitors since the facility's primary sources are elevated above ground level. Elevated sources yield air plumes that are also elevated from the ground. However, whether the height at each monitoring location is ideal for measuring the maximum impact of the sources at this facility cannot be determined without a facility-specific air dispersion analysis being conducted. Such an analysis was beyond the scope of this project.

2.1.2 Sample Transportation Questions

- *Are the samples transported to the laboratory in a manner that preserves sample integrity?*

STS was provided copies of the methods and procedures that MPCA is utilizing to collect, preserve and transport samples from the air monitoring stations throughout Minnesota. These methods have been developed by USEPA to specifically preserve the integrity of air samples. MPCA staff have confirmed to STS that they are following these methods and procedures.

- *Is the chain of custody documented so as to minimize errors?*

The MPCA methods and procedures require chain-of-custody documents as part of the sample transport process. Provided MPCA staff are following these procedures, sample integrity should not be comprised. STS did not receive any specific chain-of-custody records from MPCA to examine, however.

2.1.3 Analytical Laboratory Questions

- *Are the laboratory methods appropriate for the parameters being analyzed?*

The MPCA methods and procedures documents which were supplied to STS contain the appropriate laboratory analytical methods for the chemicals being

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monitored. STS staff, however, did not witness first hand any analytical work being performed since that task was beyond the scope of this project.

- *Have maximum holding times been set and observed?*

The MPCA methods and procedures document maximum holding times of the samples before analyses must be conducted. MPCA staff confirmed to STS that they follow these guidelines. STS staff did not witness any laboratory activities as part of this study, however.

- *Are the detection limits adequate from a health risk perspective?*

The MPCA laboratory method developed by USEPA for all of the monitoring network chemicals contain adequate detection limits for each analyte. These detection limits are less than each chemical's acute and chronic health criteria. Thus, if the chemical is not detected, it is safe to say that its presence is less than the criteria. The MPCA analytical detection limits were reported in the analyses made available to STS. A review of this information confirmed that MPCA was meeting these values.

- *Is data recovery satisfactory?*

The MPCA laboratory methods which were developed by USEPA specify data recovery parameters. Review of the analytical data made available to STS revealed that these parameters are being met/exceeded.

- *Do the analytical procedures include mechanisms, such as periodic calibrations, to enable the accuracy of the data to be assessed?*

The MPCA's analytical methodologies contain mechanisms such as periodic calibrations to maintain data accuracy. STS did not receive any instrument read-outs from MPCA to verify that these mechanisms are being followed; however, verbal assurances were given to STS by MPCA staff that all

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laboratory procedures are being followed and that the results checked by laboratory QA/QC staff.

- *Do the analytical procedures include mechanisms, such as field and laboratory blanks, to enable the precision of the data to be assessed?*

The MPCA's analytical methodologies contain mechanisms such as inclusion of field and laboratory blanks in each data set to maintain data precision. STS did not receive any instrument read-outs from MPCA to verify that these mechanisms are being followed, however, verbal assurances were given to STS by MPCA staff that all laboratory procedures are being followed and the results checked by laboratory QA/QC staff.

The overall conclusion of this data quality analysis is that the monitoring results are acceptable for risk evaluation purposes.

2.2 Data Review/Findings

In order to put these ambient air monitoring data into perspective in regards to public health impacts, a toxicity assessment of each monitored chemical was first completed. This toxicity assessment involved a search of USEPA chemical toxicity databases (IRIS, 2002; HEAST, 1997) and the Minnesota Department of Health's proposed Health Risk Values (HRVs). Presented in Table 3 are the results of this search.

Listed in Table 3 are air concentrations of each chemical that are believed to be safe for the public to be exposed to. Acute criteria represent acceptable air concentrations of chemicals for exposure up to a one hour time period. Chronic criteria are air concentrations of chemicals that the public can be exposed to continuously throughout their entire lifetime.

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Table 3: Health Criteria

2000 Monitoring Chemical	Federal Standards/Criteria ^A	State Standards/Criteria ^B	
		Acute	Chronic
Carbon Monoxide	40,000 (1) ; 10,000 (8)		
Nitric Oxides			
Nitrogen Dioxide	100	470 (CAL EPA)	
Sulfur Dioxide	1300 (3); 365 (24); 80		
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	105,000		
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)			
Trichlorofluoromethane (Freon 11)	1050 ¹		
Dichlorodifluoromethane (Freon 12)	700 ¹		
1,3-Butadiene	0.04		0.04
Formaldehyde	0.8	94	0.8
Acetaldehyde	9		5
Propionaldehyde			
Acrolein	0.02		0.2 (s)
Butyraldehyde			
t-Crotonaldehyde			
Acetone	350 ¹		
Methylene Chloride	50	10,000	20
Chloroform	0.4		
Carbon Tetrachloride	0.7	1900 (CAL EPA)	
1,1-Dichloroethane			
1,1,1-Trichloroethane		137,000	
1,2-Dichloroethane	4		
Tetrachloroethylene	35 ¹	20,000	
1,1,2,2-Tetrachloroethane	0.2		
Bromomethane	5		5
1,1,2-Trichloroethane	0.6		
Trichloroethylene	5	2000	
1,1-Dichloroethylene	0.2		
1,2-Dichloropropane	4		10 (S)
t-1,3-Dichloropropylene	2		20
1,3-Dichloropropylene	2		20
c-1,2-Dichloroethylene			
1,2-Dibromoethane			0.05
Hexachlorobutadiene	0.5		
Vinyl Chloride	2.3	180,000 (CAL EPA)	1
o-Xylene	7000	44,000	
m/p-Xylene	7000	44,000	
Benzene	1.3	1000	1.3 – 4.5
Toluene	400	37,000	400
Ethylbenzene	1000	10,000	
1,3,5-Trimethylbenzene	180		
1,2,4-Trimethylbenzene			
Styrene	1000	21,000	1000
4-Ethyltoluene			
Benzaldehyde	350 ¹		
Chlorobenzene	70 ¹		
1,2-Dichlorobenzene	315 ¹		
1,3-Dichlorobenzene			
1,4-Dichlorobenzene	800		800 (S)

^A NAAQS or RfC ($\mu\text{g}/\text{m}^3$); carcinogens set at 10^{-5} risk level: (1) = 1-hour std. (8) = 8-hour standard; (3) = 3-hour standard, (24) = 24-hour standard; criteria not identified with an exposure period are chronic standards.

^B HRV ($\mu\text{g}/\text{m}^3$): (s) = subchronic health risk value

¹ Derived from oral RfD

CAL EPA = California Environmental Protection Agency

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2.2.1 Are the appropriate chemicals being monitored by the network to assess the facility's impact on public health in its surrounding neighborhoods?

2.2.1.1 Qualitative Analysis

To address this question, an initial qualitative investigation was conducted. As a first step, a comparison was made between the list of HAP chemicals currently being monitored by this network (Table 2) and the reported chemical emissions from the facility. The USEPA's Toxic Release Inventory (TRI) database was searched to obtain reportable emissions from this facility. Data from the last three reporting years were obtained. Table 4 provides this comparison.

As is evident from the data presented in this table, the monitoring network is evaluating many more chemical compounds than are reported emitted from this facility. This finding again points out that this network is not specifically designed by MPCA to monitor just this facility.

Table 5 provides another qualitative comparison. In this table, the facility's list of reportable chemical emissions (for the last three complete years) was compared to what is being currently monitored by the network. As can be seen in this table, the facility emits many more chemicals than what the monitoring network is set up to evaluate.

2.2.1.2 Quantitative Analysis

The toxicity data on these chemicals (Table 3) was then used to determine in a more quantitative manner whether or not the monitoring network is set up to evaluate the appropriate chemicals emitted from this facility. As shown in Table 5, this facility emits many more chemicals than what is currently being monitored by the network. In this quantitative analysis, it is determined if the chemicals being monitored are the highest risk chemicals emitted from the facility. A screening level, relative risk approach was used to address this question. This approach involved the following five steps:

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Table 4: Air Monitoring Analytes vs. Facility Emissions (TRI)

Monitored Chemical	TRI Reported Emissions		
	1998	1999	2000
Acetaldehyde			
Acetone			
Acrolein			
Benzaldehyde			
Benzene	✓	✓	✓
Bromomethane			
1,3-Butadiene			
Butyraldehyde			
Carbon Tetrachloride			
Chlorobenzene			
Chloroform			
t-Crotonaldehyde			
1,2-Dibromoethane	✓		
1,2-Dichloro-1,1,2,2-tetrafluoroethane (Freon 114)			
1,2-Dichlorobenzene			
1,3-Dichlorobenzene			
1,4-Dichlorobenzene			
Dichlorodifluoromethane (Freon 12)			
1,1-Dichloroethane			
1,2-Dichloroethane			
1,1-Dichloroethylene			
c-1,2-Dichloroethylene			
1,2-Dichloropropane			
1,3-Dichloropropylene			
Ethylbenzene	✓	✓	✓
4-Ethyltoluene			
Formaldehyde			
Hexachlorobutadiene			
Methylene Chloride			
Propionaldehyde			
Styrene	✓		
t-1,3-Dichloropropylene			
1,1,2,2-Tetrachloroethane			
Tetrachloroethylene	✓	✓	✓
Toluene	✓	✓	✓
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)			
1,1,1-Trichloroethane			
1,1,2-Trichloroethane			
Trichloroethylene			
Trichlorofluoromethane (Freon 11)			
1,2,4-Trimethylbenzene	✓	✓	✓
1,3,5-Trimethylbenzene			
m/p-Xylene	✓	✓	✓
o-Xylene	✓	✓	✓
Vinyl Chloride			

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Table 5: Reported Facility Air Emissions (TRI) vs. Air Monitoring Analytes

Emission Chemical	Reported Emissions (lbs./yr.) ^A			Monitored (?)
	1998	1999	2000	
<i>A. Organic Compounds</i>				
Anthracene (PAC)	60	60	500	
Benzene	10,400	10,400	10,500	✓
Benzo(g,h,i)perylene (PAC)	90	90	20	
Biphenyl	1,300	1,300	500	
Cumene	100	100	1,000	
t-Butyl alcohol	100	100	--	
Cyclohexane	3,200	3,200	--	
Ethylbenzene	17,000	17,000	6,300	✓
Ethylene	500	500	3,400	
Ethylene Glycol	23,000	23,000	26,000	
n-Hexane	104,000	104,000	28,000	
Methanol	46,200	46,200	98,000	
Naphthalene	10,500	10,500	5,700	
Phenanthrene (PAC)	90	90	500	
Phenol	500	500	1,000	
Propylene	22,100	22,100	24,000	
Tetrachloroethylene	4,200	4,200	4,200	✓
1,2,4-Trimethylbenzene	4,400	4,400	4,600	✓
Toluene	84,000	84,000	26,700	✓
Xylenes	106,000	106,000	38,800	✓
<i>B. Inorganics</i>				
Ammonia	15,000	15,000	16,500	
Barium compounds	220	220	500	
Carbon Disulfide/carbonyl Sulfide	640	640	1,500	
Chlorine	2,800	2,800	3,200	
Chromium compounds	1,000	1,000	500	
Cobalt compounds	16	16	1,000	
Copper compounds	1,000	1,000	--	
Hydrochloric Acid (Aerosol)	41,000	41,000	36,000	
Lead compounds	1,000	1,000	1,000	
Manganese compounds	180	180	1,000	
Mercury compounds	--	--	58	
Molybdenum trioxide	1,000	1,000	--	
Nickel compounds	2,800	2,800	1,500	
Selenium compounds	50	50	500	
Zinc compounds	2,200	2,200	37,100	

^A Total emissions: Fugitive + stack emissions

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- determine annual emission rate for each listed chemical emission from the facility;
- determine the lowest health criteria for those compounds possessing more than one value (Table 3);
- calculate a relative ranking of each chemical using the following equation:

$$\text{Relative Health Impact} = \frac{\text{Annual Emission Rate of Chemical}}{\text{Chemical's Toxicity Value}}$$
- list the chemical emissions by relative health impact, with the highest first;
- identify those emission chemicals that are currently being monitored by the network.

Tables 6 through 8 of this report present this quantitative analysis for the facility emissions that possess acute criteria. These three tables represent this analysis for the most current three facility reporting years (1998 - 2000). As can be seen in these tables, benzene is the highest ranking chemical being monitored, and this compound ranks fifth-seventh (depending on the year of evaluation) with less than 3% of the total relative risk. Nickel compounds are ranked first. These emissions singly account for approximately 80% of the total relative risk each year.

Tables 9 through 11 of this report present this relative risk analysis for those facility emissions that possess chronic criteria. These three tables also represent this analysis for the most current three facility reporting years (1998 - 2000). A similar finding can be seen in these tables as with the acute relative risk analysis. Benzene again is the highest ranking chemical being monitored currently and again represents only a small percentage of the total relative risk calculated for each year. In these three years, the highest ranked emissions from this facility are all inorganic substances -- nickel compounds, chromium compounds, cobalt compounds.

These data suggest therefore that if a monitoring network was to be established to specifically assess the health impacts of the facility emissions on regional public health, at least some of the monitors should evaluate metals.