

**Flint Hills Air Monitoring
Network Data Analysis**

Flint Hills Community
Advisory Council

STS Project 30012

October 8, 2007

Flint Hills Air Monitoring Network Data Analysis

**Summary Report
October 8, 2007**

**STS Consultants, Ltd.
Maple Grove, MN
Project No. 30012**

Table of Contents

1.0 INTRODUCTION	1
2.0 REVIEW SUMMARY	3
2.1 Data Review/Findings	3
2.1.1 Health Standards and Comparison.....	3
2.1.2 Data Comparison to Air Quality Standards	4
3.0 CONCLUSIONS	13



Flint Hills
 STS Project 30012
 October 8, 2007

1.0 INTRODUCTION

The Minnesota Pollution Control Agency (MPCA), as part of their state-wide air quality assessment network, currently conducts ambient air quality monitoring at five sites near the Flint Hills Rosemount petroleum refinery (facility). Table 1 summarizes which parameters are currently being monitored at each of these locations.

Table 1. Monitoring Site Summary

Parameter	Desig.	Site 420	Site 421	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
Total Suspended Particulates	TSPs	X	X	X		X
Metals	--	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

Each of the parameters listed above are being measured in the field on a continuous basis, except for the hazardous air pollutants (HAPs), the total suspended particulates (TSPs), and metals. HAPs, TSPs, and metals samples are taken as 24-hour composite samples, collected once every six days. HAPs and TSPs samples are sent to the MPCA laboratory where, for HAPs samples, they are analyzed for a variety of specific volatile compounds, for TSPs samples, they are analyzed for a variety of inorganic elements, and for metal samples, they are analyzed for sixteen specific metals.

STS Consultants, Ltd. (STS) was requested by the Flint Hills Community Advisory Council (Council) in 2002 to evaluate the data being generated by this local monitoring network with respect to facility impacts. An initial analysis of the data was performed in 2002 and presented to the Council on March 6, 2002. The first quarter of the calendar year 2007 is the most recently evaluated dataset by STS. This report integrates the new

Flint Hills
STS Project 30012
October 8, 2007

data (calendar year 2006 plus first quarter 2007) with these past data. The newly acquired data includes data collected for the criteria pollutants: CO, NO_x, and SO₂, for the HAPs samples, and for the TSPs samples (metal data).

The following five chemicals have been included in each of these criteria pollutant/HAP evaluations: sulfur dioxide, nitrogen dioxide, formaldehyde, carbon tetrachloride and benzene. Ethylbenzene has typically been included in this evaluation. However, since the levels detected are very low and no changes have been observed in the level of this chemical over the past several years, no evaluation was performed on these data in this report.

The following sixteen metals were included in the dataset: aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, and zinc. Measurements were taken for all sixteen metals at four of the five monitored sites. Only seven of the sixteen metals have a health risk value. These seven are included in this evaluation: antimony, arsenic, beryllium, cadmium, chromium (total), manganese, and nickel. Based on our initial air quality evaluation (March 2002) for the Council, five metals were designated as target analytes: chromium (total), cobalt, manganese, nickel, and zinc. There are no longer any state/federal standards/criterion that exist for these metals, however.

The TSP data reported by the MPCA did not contain a particle size distribution. The only air quality standards that exist for particulate matter are the PM₁₀, particles that are less than 10 microns in diameter, and the PM_{2.5}, particles that are less than 2.5 microns in diameter. Since no total particulate standard exists and a particle size distribution was not performed on the TSP data by the MPCA, no health analysis could be performed related to total suspended particulates. Also, since the ambient air quality standards for these metals assume respirable particulates, i.e. PM₁₀, comparison of the TSP metals data to these standards is a highly conservative procedure.

Flint Hills
STS Project 30012
October 8, 2007

2.0 REVIEW SUMMARY

2.1 Data Review/Findings

2.1.1 Health Standards and Comparison

In order to put these ambient air monitoring data into perspective in regards to public health impacts, a toxicity assessment for each requested, monitored chemical was first completed. This toxicity assessment involved a search of USEPA chemical toxicity databases (IRIS, 2005; HEAST, 1997), the Minnesota Department of Health's Health Risk Values (HRVs), and California EPA's Air Toxics Standards. Presented in Table 2 are the results of this search. The results in Table 2 have been recently updated since the last report submittal in October 2006.

Listed in Table 2 are air concentrations of each chemical of concern in this study 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.

Flint Hills
 STS Project 30012
 October 8, 2007

Table 2: Health Criteria

Chemical	Units	Federal Standards/Criteria	State Standards/Criteria ^D	
			Acute	Chronic
Criteria Pollutants^A				
Nitrogen Dioxide	ppb	250 (1), 53 (A)	250 (CAL EPA)	
Sulfur Dioxide	ppb	500 (3); 140 (24); 31 (A)		
HAPs^B				
Formaldehyde	ppb	0.65	77	1.5
Carbon Tetrachloride	ppb	0.11	300 (CAL EPA)	
Benzene	ppb	0.41	314	0.41 – 1.42
TSPs^C				
Antimony	ug/m ³	0.2		0.2
Arsenic	ug/m ³	0.002		0.002
Beryllium	ug/m ³	0.004		0.004
Cadmium	ug/m ³	0.006		0.006
Chromium (VI)	ug/m ³	0.0008		0.0008
Manganese	ug/m ³	0.05		0.2
Nickel	ug/m ³	0.04	6	0.04

^A NAAQS (National Ambient Air Quality Standard): (1) = 1-hour standard, (3) = 3-hour standard, (24) = 24-hour, (A) = annual

^B RfC; carcinogens set at 10⁻⁵ risk level

^C Total Suspended Particulates

^D Minnesota HRV (ug/m³); acute standard = 1-hour exposure; chronic standard = annual exposure. CAL EPA = California Environmental Protection Agency

2.1.2 Data Comparison to Air Quality Standards

The latest data from calendar year 2006-2007 for the HAPs samples were evaluated by STS in the same manner as was performed in the previous submittals to the Council. The TSPs samples were evaluated in the same manner as the HAPs samples in the past. Each monitored parameter at each of the monitoring sites for this quarter was analyzed to compute standard descriptive statistics: maxima and means for annual and 1-hour averaging times (also 3-hour for SO₂), as well as the 95% confidence limits of the mean values. Also calculated was the probability (chance) that the true average of the data would exceed the health criteria for a chemical. Since the HAPs and TSPs analyses were obtained with 24-hour integrated samples, a numerical adjustment was made to adjust the data to the shorter averaging period, when applicable. [Note: as discussed in the report submitted to the Council on May 10, 2004, this adjustment could not completely account for the “worst” one hour-averaged concentration of each acute toxic

Flint Hills
STS Project 30012
October 8, 2007

chemical as is desirable for the acute risk analysis. Only continuous monitoring could accurately provide that data.]

The results of this descriptive analysis are presented in Figures 1 through 5 for the two criteria pollutants, SO₂ and NO₂, and Figures 6 through 9 for the other HAP chemicals. Figures 10 through 17 present the descriptive analysis for the seven metals which possess health criteria. Each figure has been formatted in a similar manner. Data for the seven metals lacking health criteria have been summarized in Table 3.

For the criteria pollutants, HAPs, and metals with a health risk value, the X-axis designates the latest quarter from which the data are taken. On the Y-axis is the air concentration range chosen to encompass both the chemical's health criterion and the maximum or calculated average of the monitoring data. Data specific to each monitor location is designated by a different symbol. The "criterion line" does not contain any symbols. The smaller graph is an expanded image of the latest 2007 first quarter data. The small graph has the data points affiliated with each monitoring site, as well as the monitored concentration ranges (for maximum values) or the standard deviation (for averaged values).

Reading each figure is performed in an identical manner. If the monitoring data for any given reporting period at any given monitor is less than the criterion concentration, then with respect to that chemical at that location, no risk to public health is present. For example, Figure 1 shows the three-hour averaged data for sulfur dioxide. The health criterion is 500 ppb. All of the most recent monitoring data are at or below 20 ppb. Thus, it can be concluded from these data that acute exposure to sulfur dioxide in the areas of the monitors does not present a health risk to the public. Statistical analyses of these data were performed, but not shown on this figure because the confidence interval is so small. In a separate analysis, it was determined that there is less than 0.01% chance that the true three hour-averaged sulfur dioxide concentration at these monitoring locations would actually exceed this air quality standard.

The following sections detail the analysis for each of the 17 figures.

Flint Hills
STS Project 30012
October 8, 2007

Sulfur Dioxide 3-hour Average

Figure 1 displays the maximum three-hour averages for sulfur dioxide at each of the four monitored sites for each quarter and compares these concentrations to the 500 ppb criterion. The maximum three-hour average was calculated from the hourly data available in each quarter. Each monitoring site has a maximum well below the criterion. The monitoring data are all less than 20 ppb, considerably below the USEPA standard of 500 ppb. Statistical analysis of the data indicates that there is less than 0.01% chance probability that the concentration of this chemical would exceed this standard.

Sulfur Dioxide 24-hour Average

Figure 2 displays the maximum 24-hour average for sulfur dioxide at each of the four monitored sites for each quarter and compares the concentrations to the 140 ppb criterion. The maximum 24-hour average was calculated from the hourly data available. Each monitoring site has a maximum well below the criterion. The monitoring data are all less than 10 ppb, considerably below the USEPA standard of 140 ppb. Statistical analysis of the data indicates that there is less than 0.01% chance probability that the concentration of this chemical would exceed this standard.

Sulfur Dioxide Annual Average

Figure 3 displays the average annual concentration for sulfur dioxide at each of the four monitored sites and compares these concentrations to the 31 ppb criterion. The data presented are rolling annual averages with the latest quarterly data in each dataset denoted on the X-axis. The annual averages for each monitoring site and 95% confidence level are well below the criterion. The expanded view also illustrates that the means are less than 5% of the criteria. The monitoring data all have averages at or less than 1 ppb, considerably below the USEPA standard of 31 ppb. Statistical analysis of the data indicates that there is less than 0.1% chance probability that the concentration of this chemical would exceed this standard. The use of rolling averages allows discernment of time trends in the data. As shown in this figure, the sulfur dioxide levels have remained low and relatively flat as compared to the standard over the latest thirteen quarters.

Flint Hills
STS Project 30012
October 8, 2007

Nitrogen Dioxide 1-hour Average

Figure 4 displays the maximum one-hour average for nitrogen dioxide at each of the two monitored sites for each quarter that addresses this pollutant and compares these concentrations to the 250 ppb criterion. The maximum one-hour average was calculated from the hourly data available. Each monitoring site has a maximum well below the criterion. The monitoring data are less than 50 ppb, considerably below the USEPA standard of 250 ppb. Statistical analysis of the data indicates that there is less than 0.01% chance probability that the concentration of this chemical would exceed this standard. As shown in this figure, the nitrogen dioxide concentrations have been relatively low and stable over the past thirteen quarters.

Nitrogen Dioxide Annual Average

Figure 5 displays the annual average for nitrogen dioxide at each of the two monitored sites that address this pollutant and compares these concentrations to the 53 ppb criterion. Rolling annual averages are again shown on this figure. The annual averages for each monitoring site and 95% confidence level are well below the criterion. The expanded view illustrates that the means are 20% or less of the criteria. The monitoring data have averages less than 11 ppb, considerably below the USEPA standard of 53 ppb. Statistical analysis of the data indicates that there is less than 0.2% chance probability that the concentration of this chemical would exceed this standard. As with sulfur dioxide, the nitrogen dioxide data indicate that its concentration has remained relatively constant over these thirteen quarters.

Formaldehyde 1-hour Average

Figure 6 displays the maximum one-hour average for formaldehyde at each of the four monitored sites for each quarter and compares these concentrations to the 77 ppb criterion. The maximum one-hour average was scaled from the 24-hour averaged data available with a factor of 2.5. Each monitoring site has a maximum well below the criterion. The monitoring data are all at or less than 1.0 ppb, well below the Minnesota Department of Health standard of 77 ppb. Statistical analysis of the data indicates that there is less than 0.1% chance probability that the concentration of this chemical would exceed this standard. As shown in this figure, the formaldehyde concentration has

Flint Hills
STS Project 30012
October 8, 2007

remained low and relatively flat over the past year; no “bump” was seen in the air concentration this past spring/summer.

Formaldehyde Annual Average

Figure 7 displays the annual average concentrations for formaldehyde at each of the four monitored sites and compares these concentrations to 1.5 ppb criterion. These data are again rolling annual averages. No data were collected from site 420 in the first quarter of the calendar year 2004. As shown in this figure, the calculated annual averaged mean concentrations of formaldehyde, at all four stations, have been steadily decreasing over this past year. The data from the latest four quarters were all below the MDH health criterion.

Carbon Tetrachloride Annual Average

Figure 8 displays the annual average for carbon tetrachloride at each of the four monitored sites and compares these concentrations with the 0.11 ppb criterion. These data are also rolling averages. The scaled annual average for each monitoring site and its 95% confidence level are below the criterion. The expanded view illustrates that the averages are all less than 0.10 ppb. Statistical analysis of the data indicates that there is less than 0.1% chance probability that the concentration of this chemical would exceed this standard. The trend in the data as a function of time over the last two years is slightly downward.

Benzene Annual Average

Figure 9 displays the rolling annual average for benzene at each of the four monitored sites and compares these concentrations to the 0.41 ppb criterion. The annual average for each monitoring site and its 95% confidence level are below the criterion. The monitoring data all have averages less than 0.2 ppb, below the Minnesota Department of Health standard of 0.41 ppb. Statistical analysis of the data indicates that there is less than 0.1% chance probability that the concentration of this chemical would exceed this standard. The time trend in the data is relatively flat over the last thirteen quarters.

Flint Hills
STS Project 30012
October 8, 2007

Antimony Annual Average

Figure 10 displays the rolling annual average for antimony as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.2 \mu\text{g}/\text{m}^3$ criterion. The annual average for each monitoring site and its 95% confidence level are below the criterion. The monitoring data all have averages at or less than $0.005 \mu\text{g}/\text{m}^3$, considerably below the Minnesota Department of Health standard of $0.2 \mu\text{g}/\text{m}^3$. Statistical analysis of the data indicates that there is less than 0.01% chance probability that the concentration of this chemical would exceed this standard. The data indicate that the antimony concentration has remained low and relatively constant over the past thirteen quarters.

Arsenic Annual Average

Figure 11 displays the rolling annual average for arsenic as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.002 \mu\text{g}/\text{m}^3$ criterion. The annual average for each monitoring site is less than $0.0015 \mu\text{g}/\text{m}^3$, which is below the Minnesota Department of Health standard. Statistical analysis of the data indicates that there is less than 10% chance probability that the concentration of this chemical would exceed this standard. Since these site data are based on TSP and not PM_{10} , this comparison to the standard is highly conservative. The data indicate consistent air concentrations of arsenic over the past two years.

Beryllium Annual Average

Figure 12 displays the rolling annual averages for beryllium as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.004 \mu\text{g}/\text{m}^3$ criterion. The annual average for this monitoring site and its 95% confidence level are below the criterion. The monitoring data have an average less than $0.0001 \mu\text{g}/\text{m}^3$, considerably below the Minnesota Department of Health standard of $0.004 \mu\text{g}/\text{m}^3$. Statistical analysis of the data indicates that there is less than 0.01% chance probability that the concentration of this chemical would exceed this standard. The data indicate that the beryllium concentrations are low and relatively flat as compared to the health criterion over the past thirteen quarters.

Flint Hills
STS Project 30012
October 8, 2007

Cadmium Annual Average

Figure 13 displays the rolling annual average for cadmium as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.006 \mu\text{g}/\text{m}^3$ criterion. The annual average for this monitoring site and its 95% confidence level are below the criterion. The monitoring data have an average less than or equal to $0.0002 \mu\text{g}/\text{m}^3$, considerably below the Minnesota Department of Health standard of $0.006 \mu\text{g}/\text{m}^3$. Statistical analysis of the data indicates that there is less than 0.2% chance probability that the concentration of this chemical would exceed this standard. The data indicate that the cadmium concentrations are low and relatively flat for the past thirteen quarters as compared to the health criterion.

Chromium Annual Average

Figure 14 displays the rolling annual average for total chromium as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.0008 \mu\text{g}/\text{m}^3$ chromium VI criterion. Two of the four annual averages and their 95% confidence interval for the latest annual averages are above this criterion. The time trend in these data has been upward over the past year.

Since these data are total chromium and not chromium VI and were generated from TSP data, not PM_{10} data, no definitive conclusion can be drawn from the long-term exposure to this element.

Chromium VI is the most toxic form of chromium. California, which monitors both total chromium and chromium VI, shows statewide averages of total chromium to be thirty to fifty times higher than chromium VI. Data from ten other Pilot Cities sites where air monitoring is being funded by EPA have shown nearly identical results. Thus, chromium VI likely contributes only two to three percent to the total chromium concentration shown in this figure. Assuming three percent, all of these monitoring data would fall below the health standard, even with the total particulate measurement.

Manganese Annual Average

Figure 15 displays the rolling annual average for manganese as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.05 \mu\text{g}/\text{m}^3$

Flint Hills
STS Project 30012
October 8, 2007

criterion. Three of the four annual averages and their 95% confidence levels are below the criterion. Statistical analysis of the data indicates that there is less than 0.1% chance probability that these concentrations would exceed this standard. Station 421 has shown a steady increasing trend in manganese concentration over the past six quarters. The data from the latest two quarters exceed the health standard. As mentioned earlier, these are TSP data and not PM_{10} data, so without knowing the particulate size distribution, no definitive statement can be made regarding the health significance of these data.

Nickel 1-hour Average

Figure 16 displays the maximum one-hour average for nickel as calculated from TSP data at each of the four monitored sites. These data are compared to the $6 \mu\text{g}/\text{m}^3$ criterion. The maximum one-hour averages were scaled from the 24-hour averaged data available with a factor of 2.5. Each monitoring site has a maximum and 95% upper confidence limit well below the criterion. The monitoring data are all less than $0.002 \mu\text{g}/\text{m}^3$, considerably below the Minnesota Department of Health standard of $6 \mu\text{g}/\text{m}^3$. Statistical analysis of the data indicates that there is less than 0.01% chance probability that the concentration of this chemical would exceed this standard. These data indicate that the nickel concentrations have been very low and relatively flat as compared to the health criterion over the past thirteen quarters.

Nickel Annual Average

Figure 17 displays the rolling annual average for nickel as calculated from the TSP data at each of the four monitored sites. These data are compared to the $0.04 \mu\text{g}/\text{m}^3$ criterion. The annual average for each monitoring site and its 95% confidence level are below the criterion. The monitoring data all have averages less than $0.002 \mu\text{g}/\text{m}^3$, considerably below the Minnesota Department of Health standard of $0.04 \mu\text{g}/\text{m}^3$. Statistical analysis of the data indicates that there is less than 0.1% chance probability that the concentration of this chemical would exceed this standard. These data indicate that the nickel concentrations have been very low and relatively flat as compared to the health criterion over the past thirteen quarters.

Flint Hills
STS Project 30012
October 8, 2007

Table 3

Table 3 displays the annual averages and standard deviations for aluminum, barium, cobalt, copper, iron, lead, mercury, selenium, and zinc at the four monitored sites, as calculated from the most recent datasets. The aforementioned metals do not have a health risk criteria so no further evaluation was performed.

Summary of Results

As requested, a summary of the results from the latest monitoring dataset have also been included. Table 4 displays the chemical, time increment, criterion, and the corresponding result for this latest quarter.

Flint Hills
STS Project 30012
October 8, 2007

3.0 CONCLUSIONS

None of the criteria pollutants or HAPs exceeded its standard at any of the monitoring stations during this past year. The concentrations in this local monitoring network are all within the range of data reported throughout the Twin Cities.

The data for total chromium was shown to exceed the chromium VI air quality standard at two stations over the past two quarters. These two stations are 420 and 421. These datasets were generated from total suspended particulates. Total suspended particulates can contain a wide range of particle sizes. However, only particles less than ten microns in diameter (PM_{10}) are respirable and therefore of concern for exposure to any metal constituents. Since the PM_{10} fraction could constitute a small percentage of the TSP measurements, these data could grossly over-estimate the potential risk present. Chromium impacts are additionally likely over-estimated because only chromium VI is considered toxic from the inhalation route of exposure. Most of the chromium in the environment is in the more stable chromium III state. No speciation of the chromium in the ambient air near these stations has been conducted to date. In California, air monitoring data have indicated that only 2-4% of the total chromium measured in air samples is chromium VI.

The monitoring data from the last two quarters at site 421 also indicated a slight exceedance of the manganese air criterion. The time trend at this monitor was upward over the past year, as compared to the data from the other three monitors. The rationale for this upward trend is unknown at this time. The health significance of this finding is undeterminable at this time also because these data are TSP data, not PM_{10} . It is very likely that the PM_{10} fraction of TSP is small, but this would have to be confirmed through particle size testing.