

Grand Rapids Air Toxics Initiative:

*A Comparison of Risks between
Grand Rapids & Detroit*

July 22, 2011



Cover picture courtesy of Thurston Devos

Executive Summary

The Michigan Department of Environmental Quality (MDEQ) received a Community-scale Air Toxics Ambient Monitoring grant that supported a number of data analysis activities which included updating an analysis of risk for Southeast Michigan. This analysis compares the levels of risk in Grand Rapids with the investigation performed for Southeast Michigan, also called the Detroit Air Toxics Initiative: Risk Assessment Update (DATI-2). This paper is meant to be used as a companion to the main DATI-2 document and the reader is encouraged to consult the main report for details about how the analysis was performed. DATI-1 (DEQ, 2005) did not include Grand Rapids data, however, the data was collected and is included in this report.

Comparison of Grand Rapids to Other Areas: The monitoring data from Grand Rapids were compared to levels at other locations in Michigan, primarily Southeast Michigan. Risk levels were estimated and two time periods for Grand Rapids were compared using the techniques described in the DATI-1 and DATI-2 reports. The criteria for data inclusion and the methodology are described in detail elsewhere¹. Briefly, compounds that were detected more than 15% of the time were selected for inclusion in the study. Also included were compounds that had 12-month average concentrations comparable to a health benchmark. For any values that were not detected, the method detection limit (MDL) divided by two was substituted. Compounds that do not have a health benchmark or had average concentrations well below their respective benchmarks were not included in DATI-2 or this Grand Rapids report.

Changes in the level of estimated cancer risk are shown in **Table ES-1**. The estimates of cancer risk should not be viewed as actual cancer cases resulting from air pollution, but as the upper bound (i.e., high) estimates of extra risk based on lifetime (i.e., 70 years) exposure.

The findings indicate that:

1. The primary cancer risk drivers for Grand Rapids in 2001 to 2002 was from formaldehyde and 1,3 butadiene.
2. The risk drivers from 2006 to 2007 in Grand Rapids were formaldehyde and benzene, both of which are mobile source pollutants. This may be attributable to the fact that the air toxics monitoring site that was operational in 2006 to 2007 in Grand Rapids was located near a major roadway.
3. The concentrations of arsenic, cadmium, manganese, nickel and lead in Grand Rapids were generally lower than concentrations measured in the Detroit metropolitan area during both time intervals. Levels at the background site in Houghton Lake and Ypsilanti were either about the same as those measured in Grand Rapids, or for the case of Houghton Lake, some elements had lower concentrations than Grand Rapids.
4. The level of risk due to arsenic, cadmium and nickel is either lower in Grand Rapids or about equal to other urban areas in Michigan.

¹ Michigan Department of Natural Resources and Environment "Detroit Air Toxics Initiative: Risk Assessment Update" December 22, 2010. (The name of the agency was changed in April 2011 to the Michigan department of Environmental Quality)

5. No monitoring data, or an insufficient number of detected analytes were available in 2001 to 2002 for cadmium, carbon tetrachloride and chloroform, so the level of risk could not be estimated.
6. There is not a significant hazard posed by manganese in Grand Rapids. Levels appear to be typical for an urban area that is not heavily industrialized.

Table-ES -1 Risk Bin Changes in Grand Rapids from 2001-2002 to 2006 – 2007

Incremental Increase in Lifetime Cancer Risk	DATI-1 Monitoring Period Pollutants from 2001 - 2002	DATI-2 Monitoring Period Pollutants from 2006 - 2007
100 to 400 in one million	None	None
10 to 100 in one million	Formaldehyde Benzene 1,3 butadiene	Formaldehyde Benzene
1 to 10 in one million	Arsenic Acetaldehyde	Arsenic Acetaldehyde Carbon Tetrachloride 1,3 Butadiene Chloroform
0 to 1 in a million	Nickel Methylene Chloride	Cadmium Nickel Methylene chloride

1. INTRODUCTION AND OVERVIEW

The unique nature of the ambient air monitoring database generated by the Michigan Department of Environment Quality (MDEQ) lent itself nicely to a variety of data analysis activities that were funded by the United States Environmental Protection Agency's (EPA's) section 103 FY '07 Community-Scale Air Toxics Ambient Monitoring Grant program. These analyses were conducted by MDEQ and its partners in the grant, Sonoma Technology, Inc (STI), the Lake Michigan Air Directors Consortium (LADCO) and the University of Illinois at Chicago (UI-C). The title of the project is: Analysis of Air Toxics Data: Quality Assurance Implications, Source Apportionment Uncertainty Analysis and Updated Risk Assessment.

Due to the diverse nature of the data set, the goals of this project spanned a variety of analyses addressed various components of the NATTS program including:

- Perform source apportionment using both the air toxics and fine particulate datasets
- Analyze trends to compare changes in air toxics in Detroit with other cities nationwide and assess spatial diversity
- Evaluate inter laboratory data comparability
- Quantify the level of filter blank contamination
- Assess the impact of alterations in MDLs on the ability to discern trends
- Determine the impact of the performance evaluation program on inter laboratory data comparability
- Estimate changes in the levels of risk in Southeast Michigan
 - Determine how levels of risk in Southeast Michigan compare with Grand Rapids

In November, 2005 MDEQ finalized an analysis of risk in Southeast Michigan called the Detroit Air Toxics Initiative (DATI) that used data collected from 2001 to 2002². The analysis of risk was updated in this most recent grant monitoring data using 2006 to 2007 ambient data³. This updated DATI report was vetted through a steering committee based in Southeast Michigan and a communications plan was developed. As a second facet of the analysis, the risks between Detroit and Grand Rapids, the two largest urban areas in Michigan were compared, which is the objective of this report. Background information about how the analysis was conducted appears in Section 2 and is described in greater detail in the full DATI-2 report. That section consists of:

- a description of toxic compounds in the air
- a review of the air toxics monitoring program in Michigan
- a discussion of the different categories of air pollutants and the methodology used to sample for them

² See http://www.michigan.gov/deq/0,1607,7-135-3310_4105-139044--,00.html for more on the Detroit Air Toxics Initiative (DATI) Fiscal Year '03 Community Assistance and Risk Reduction Grant.

³ See http://www.michigan.gov/deq/0,1607,7-135-3310_4105-139044--,00.html for more on the Detroit Air Toxics Initiative Risk Assessment Update (DATI -2) Fiscal Year '08 Community Assistance and Risk Reduction Grant.

- a summary of pollutants that were deemed to be the primary risk drivers in Southeast Michigan during DATI -1
- an explanation of the methods used to compare risk
- a thorough discussion of the updated risk and risk drivers in Southeast Michigan during DATI-2

The reader is advised to also review details in the full DATI-2 report at:

http://www.michigan.gov/deq/0,1607,7-135-3310_4105-139044--,00.html

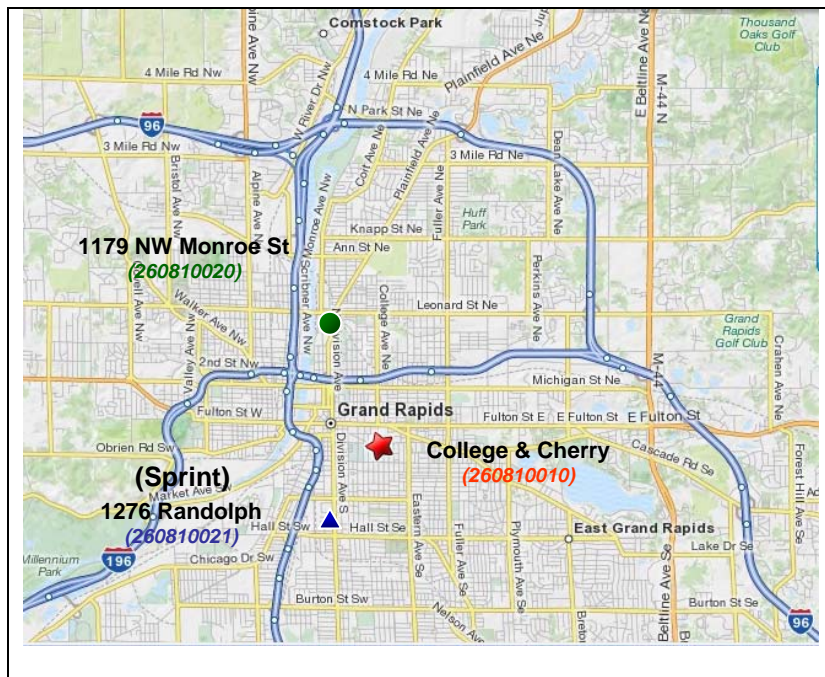
This report focuses on the changes in ambient concentrations in Grand Rapids of toxics previously identified as risk drivers by the DATI-1. The risk posed by these compounds is also discussed. The findings for Grand Rapids are compared and contrasted to the results from Southeast Michigan.

2. BACKGROUND

MDEQ has collected air toxics measurements at various locations in the Grand Rapids area since 1995 when sampling for trace metals on a once every twelve day schedule began at two locations: the intersection of College and Cherry (260810010) and at 1276 Randolph Street (260810021), also known as the Sprint site. In addition, carbonyl and VOC measurements were collected using various sampling frequencies at the Randolph Street site (260810021). On December 23, 2004, the Randolph Street site was closed and monitoring was transferred to 1179 NW Monroe Street (260810020). On April 11, 1998 the collection of trace metal samples was discontinued at the College and Cherry (260810010). The locations of all three sites are shown in **Figure 1**. The location of the College and Cherry site (260810010) is included on the map as a reference only because no data generated from College and Cherry was used in this report. The Monroe Street site (260810020) lies 4.3 miles north of the previous (Randolph Street) site.

Figure 1: Air Toxic Monitoring Stations in Grand Rapids

(Sites are positioned at the symbol locations)



The Monroe Street (260810020) site contains a plethora of air quality measurements, including criteria gases and fine particulate. Many of these measurements were not collected at the Randolph Street site. The move enhanced the diversity of measurements and quality of the data set at the Monroe St. site. Air toxics measurements were collected at the Randolph Street site (260810021) during DATI-1 and at the Monroe Street site (260810020) during DATI-2. The exact dates of operation and sampling frequency for each compound category can be found in **Table 6** of the DATI-2 report.

This report compares data in three ways:

1. It examines differences between the Grand Rapids Data sets in two time periods 2001 - 2002 (Randolph Street (260810021)) and 2006 – 2007 (Monroe Street (260810020)).
2. It compares the 2001 – 2002 data collected in Grand Rapids (Randolph Street (260810021)) with Detroit.
3. It contrasts the 2006 – 2007 data collected in Grand Rapids (Monroe Street (260810020)) with Detroit.

Table 1 compares the measurements made in DATI-1 and DATI-2 with those made in Grand Rapids. The Detroit Pilot Project was funded by EPA and Wayne County Department of the Environment, Air Quality Management Division. Because both agencies were contributing funds for the project, and the project design committee was interested in characterizing as many categories of toxic air contaminants as possible, polynuclear aromatic hydrocarbons (PAHs), or semi-volatile compounds as they are also called, were measured in Southeast Michigan in DATI -1. The cost for the laboratory analysis for PAHs exceeds \$400 per sample, so the PAHs could not be measured at many sites and not in Grand Rapids. Also, the determination of hexavalent chromium (Cr⁺⁶) in DATI-1 was performed to further develop the method. Until that time, only California measured Cr⁺⁶. Since 2003, Cr⁺⁶ has been part of the National Air Toxics Trend Site (NATTS) network and is measured at the Dearborn (261630033) site.

Table 1: Locations and Types of Air Sampling Performed in Southeast Michigan and Grand Rapids

Site Name	VOC	Carbonyl	Metal	Cr +6	SVOC
Allen Park	DATI-1	DATI-1	1 & 2	DATI-1	DATI-1
Dearborn	1 & 2	1 & 2	1 & 2	1 & 2	DATI-1
Houghton Lake	1 & 2	1 & 2	1 & 2		
N. Delray	1 & 2	1 & 2	1 & 2		DATI-1
NE Detroit		DATI-1	1 & 2		DATI-1
River Rouge	DATI-1	1 & 2	1 & 2	DATI-1	DATI-1
S. Delray	DATI-1	DATI-1	1 & 2		DATI-1
Ypsilanti	1 & 2	1 & 2	1 & 2		
Southfield Freeway	DATI-1	DATI-1	DATI-1	DATI-1	DATI-1
Grand Rapids*	1 & 2	1 & 2	1 & 2		

* Grand Rapids was sampled during DATI-1 but not made part of the DATI-1 report

VOC = volatile organic compound, Cr+6 = hexavalent chromium, SVOC = semivolatle organic compounds

The key time periods of monitoring data for this risk assessment included approximately 12 months of air monitoring data for each assessment; 3/15/2001 through 4/15/2002 and 2/28/2006 through 3/28/2007. These time frames coincide with those periods that were used in DATI-1 and DATI-2. The time period 2/28/2006 through 3/28/2007 was selected as reflective of five years after the DATI-1 study performed by the AQD's Toxics Unit. Due to severe budget reductions, a number of chemicals are no longer monitored at some of the sites and some monitoring locations have been discontinued entirely.

The first priority for selecting chemicals of concern for the current analysis was derived from the risk assessment done in the DATI-1 project. The process for describing priority chemicals of concern is described in the DATI-1 Risk Assessment Report⁴ (p. 26, Section 6.4) and in Heindorf MA⁵, 2005. There were 12 cancer risk drivers and an important non-carcinogen (manganese) identified during DATI -1 as compounds of potential concern (COPCS). Additionally, the DATI-1 report cited potential concerns for diesel exhaust and acrolein.

Three c

Table 3 below indicates which chemicals were found with a frequency of detection greater than the 15% inclusion limit. Any detection frequencies less than 15% are shaded gray. Blank cells in the table indicate that the analyte was not measured at that site. The table also outlines how the detection of air toxics in Grand Rapids relates to the sites in Southeast Michigan and how the detection varies from 2001-2002 to 2006-2007.

⁴ See http://www.michigan.gov/deq/0,1607,7-135-3310_4105-139044--,00.html for more on the Detroit Air Toxics Initiative (DATI) Fiscal Year '03 Community Assistance and Risk Reduction Grant.

⁵ Heindorf MA. 2005. Detroit Pilot Project Report: Descriptive Statistical Data Summary. Draft Report. MDEQ-AQD.

Table 3. Percent Detected Above the Method Detection Limit for Priority Chemicals

Chemical Name	Study Period	Grand Rapids	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
1,3-Butadiene	DATI-1	18%	67%	56%	ns*	ns	83%	0%	33%	80%	ns
1,3-Butadiene	DATI-2	27%	ns	92%	ns	2%	ns	18%	ns	ns	17%
1,4-Dichlorobenzene	DATI-1	4%	9%	16%	ns	ns	19%	35%	17%	18%	ns
1,4-Dichlorobenzene	DATI-2	7%	ns	86%	ns	2%	ns	11%	ns	ns	7%
Acetaldehyde	DATI-1	100%	97%	98%	100%	97%	100%	100%	97%	100%	100%
Acetaldehyde	DATI-2	100%	ns	100%	ns	100%	ns	100%	100%	ns	100%
Acrylonitrile	DATI-1	7%	0%	1%	ns	ns	0%	46%	2%	0%	Ns
Acrylonitrile	DATI-2	0%	ns	3%	ns	0%	ns	0%	ns	ns	3%
Arsenic (TSP)	DATI-1	23%	100%	100%	100%	0%	100%	100%	100%	100%	100%
Arsenic (TSP)	DATI-2	100%	100%	98%	100%	100%	ns	100%	100%	100%	100%
Benzene	DATI-1	71%	100%	99%	ns	ns	100%	100%	100%	100%	ns
Benzene	DATI-2	100%	ns	100%	ns	98%	ns	100%	ns	ns	100%
Cadmium (TSP)	DATI-1	0%	100%	100%	100%	0%	100%	100%	100%	100%	100%
Cadmium (TSP)	DATI-2	100%	100%	98%	100%	95%	ns	100%	100%	100%	97%
Carbon Tetrachloride	DATI-1	18%	100%	99%	ns	ns	100%	96%	100%	98%	ns
Carbon Tetrachloride	DATI-2	97%	ns	100%	ns	98%	ns	100%	ns	ns	100%
Chloroform	DATI-1	0%	9%	11%	ns	ns	10%	8%	3%	17%	ns
Chloroform	DATI-2	97%	ns	98%	ns	96%	ns	14%	ns	ns	17%
Formaldehyde	DATI-1	100%	98%	98%	100%	100%	98%	100%	97%	100%	100%
Formaldehyde	DATI-2	100%	ns	100%	ns	100%	ns	100%	100%	ns	100%
Manganese (TSP)	DATI-1	100%	100%	100%	100%	100%	100%	100%	100%	100%	100%
Manganese (TSP)	DATI-2	100%	100%	100%	100%	100%	ns	100%	100%	100%	100%
Methylene Chloride	DATI-1	68%	100%	95%	ns	ns	100%	73%	85%	97%	ns
Methylene Chloride	DATI-2	40%	ns	98%	ns	19%	ns	21%	ns	ns	30%
Nickel (TSP)	DATI-1	50%	100%	100%	100%	0%	100%	100%	100%	100%	100%
Nickel (TSP)	DATI-2	100%	100%	100%	100%	97%	ns	98%	100%	100%	100%

*ns = Chemical was not sampled

Note the increase in the frequency of detection for benzene after the Grand Rapids monitoring station was moved from Randolph (Sprint) to its current location at Monroe Street. After the move, increases in frequency of detection also occurred for acrylonitrile, arsenic, cadmium and nickel .

Carbon tetrachloride in 2001 to 2002 data set was only detected 18% of the time. This is surprising since carbon tetrachloride is typically considered to be a “marker compound” with concentrations that are pretty consistent nationwide due to stability and no further emissions. This poor detection frequency indicates there could be a problem with the laboratory data, i.e. the method detection limit should be lower. During the DATI-1 time frame, MDEQ reported a MDL equal to 0.24 ug/m³ where as ERG reported 0.057 ug/m³. Thus, the low detection frequency in 2001 – 2002 for carbon tetrachloride in Grand Rapids may be due to limitations in laboratory sensitivity.

When the detection frequency of carbon tetrachloride reported by the MDEQ laboratory from 2001 – 2002 is compared to 2006 - 2007, the analyte detection is much more likely. However, there was only a minor change in the MDL which went from 0.24 to 0.21 ug/m³. In September 2006, the MDEQ laboratory installed a new Entech concentrator.

3. AIR CONCENTRATIONS OF TOXIC COMPOUNDS IN GRAND RAPIDS

Concentrations of air toxics in Grand Rapids are compared to levels measured in Southeast Michigan by notched box plots in **Figures 2 to 4**. The method detection limit (MDL) divided by two was substituted for analytes that were not detected. Although not a risk driver in DATI-2, lead was also included in **Figure 2** due to the new monitoring requirements for lead.

The ambient concentrations from 2001 to 2002 and from 2006 to 2007 are shown side by side for each pollutant, using the same scale for each graph. Occasionally, outlying data points are present in the data set which makes it difficult to discern differences between the monitoring stations. In these instances a second set of graphs are presented below and shown with a shaded fill to highlight the omission of some of the data points.

When examining air monitoring data, it is also important to consider the types of locations that house the monitoring stations. Both of the air monitoring locations in Grand Rapids were in urban locations influenced by point and mobile sources; neither were in residential neighborhoods. When the Detroit Pilot project was designed a variety of locations were selected so that differences in the profiles of toxic air contaminants could be compared in the 2001 – 2002 data set. The monitoring stations were located in areas:

- impacted by emissions from nearby point sources
- influenced by motor vehicle emissions
- surrounded by residential neighborhoods
- that are rural to provide background concentrations.

There are point source-oriented and mobile-source sites included in the 2001 – 2002 data set that tend to skew ambient concentrations higher. One of the objectives of the pilot project was to investigate differences in the concentrations of toxic compounds at source oriented and mobile oriented sites and in residential and background areas, hence the diversity. Monitoring was not conducted at these point source influenced sites in 2006 – 2007 study for budgetary reasons and because MDEQ had already investigated impacts from siting on ambient concentrations. Instead, the 2006 – 2007 network focused on long term trend sites. When the 2001 – 2002 averages are compared in **Figures 2 to 4**, there may be more site-to site variability that is due to differences in the types of settings housing the monitors. A few of the point source-oriented or mobile source oriented measurements were retained for the 2006 – 2007 study. The sites that were closed include: the mobile source monitor at 696 and Lodge; the point source oriented monitor at S Delray. **Table 1** identifies which monitors were shut down in 2006 – 2007.

Figure 2 compares the concentrations of trace metals at various sites in Michigan that were measured in 2001 to 2002 with the levels five years later. In 2001 to 2002, levels of arsenic and cadmium in Grand Rapids were frequently reported as below the **reporting** level. For the Detroit Pilot Project, laboratories were instructed by the Environmental Protection Agency to report values as low as they could go. Because this involves more work for the laboratory and Grand Rapids was not considered part of the Detroit Pilot

Figure 2: Comparison of Air Toxic Metal Concentrations in Grand Rapids with Southeast Michigan

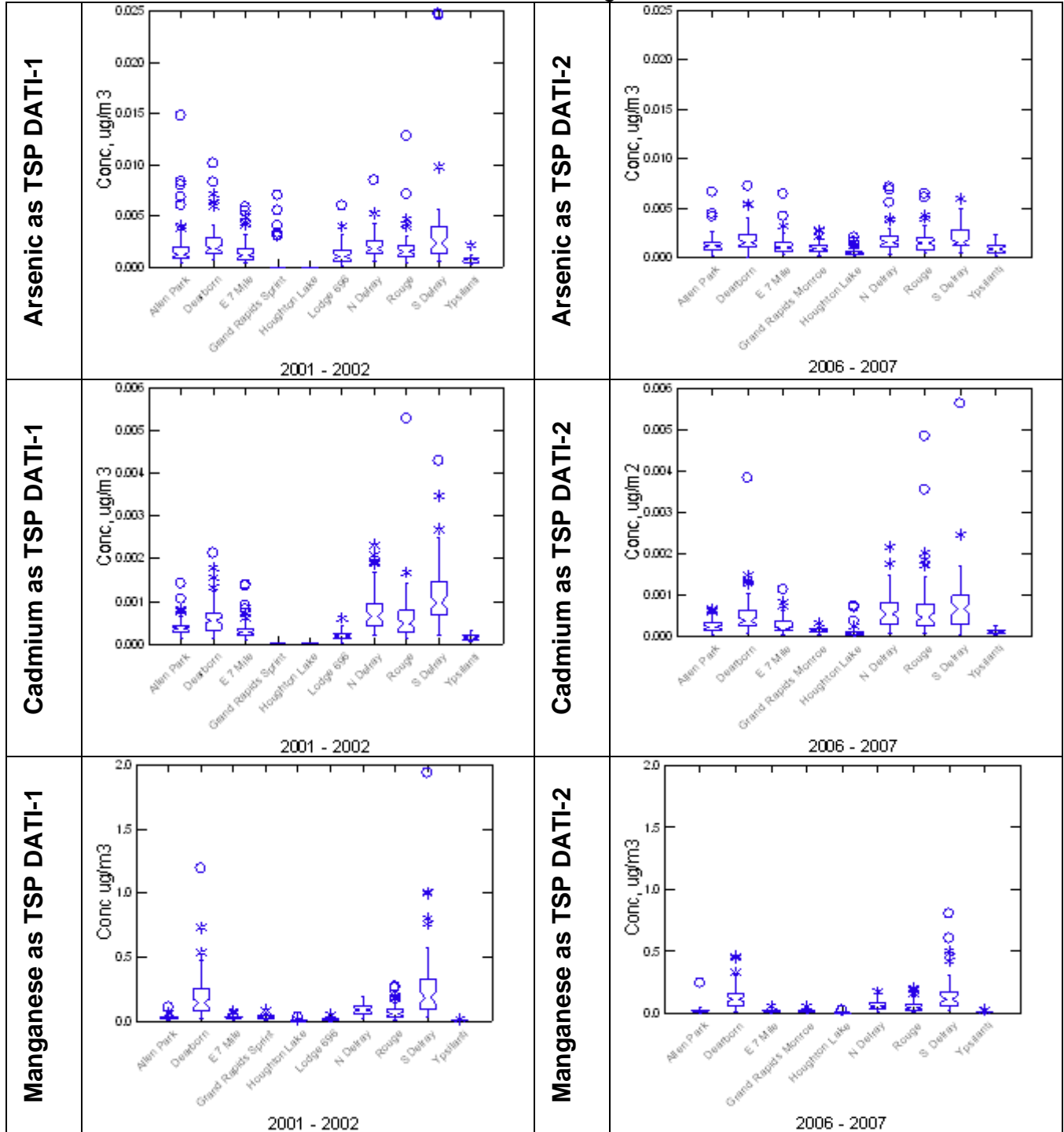
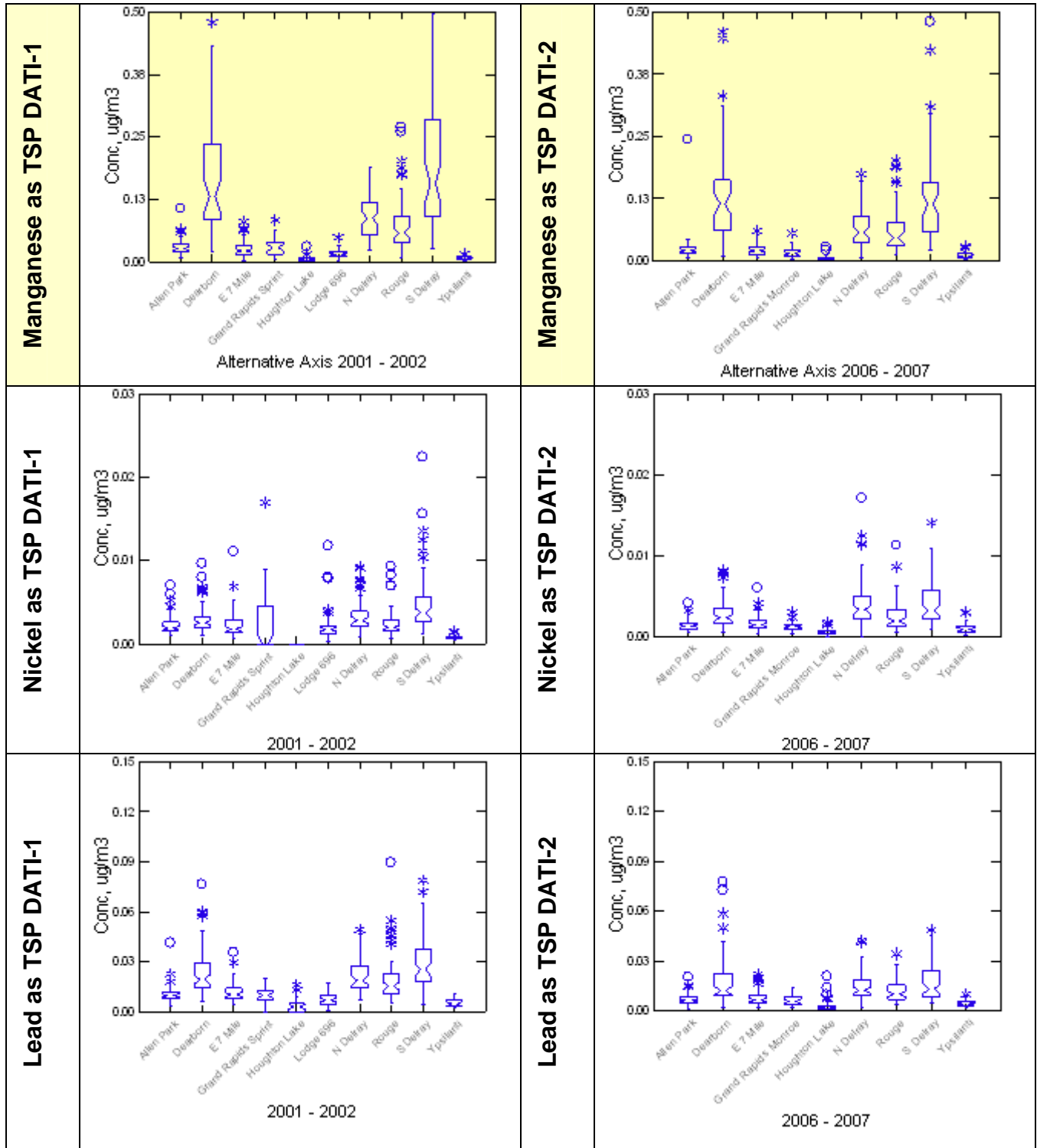


Figure 2 : Comparison of Air Toxic Metal Concentrations in Grand Rapids with Southeast Michigan, Continued



Project, the MDEQ laboratory reported many values as “less than the reporting level⁶” but not as a numerical estimate. The “<RDL” fields were treated the same as a not detected quantity and the MDL/2 was substituted. RDLs are higher than MDLs, how much so is analyte specific. The less than RDL reporting practice was used for both data sets generated in Grand Rapids. As a result of using the less than RDL reporting practice for Grand Rapids and not at other stations, more non detected values appear in the Grand Rapids data set than for other stations. So, for 2001 – 2002, the Grand Rapids data may be biased low. In the 2006 to 2007 data, Grand Rapids shows much less variation in the levels of arsenic and cadmium than the stations in Southeast Michigan. Median concentrations are less in Grand Rapids as well. The less than RDL reporting technique could be responsible for this trend.

Figure 2 shows some outlying data points for manganese, nickel and lead. When the graphs are re plotted using a different axis, the decreases in average manganese, nickel and lead concentrations in Grand Rapids over time become more apparent. The change in site location could contribute to this reduction, especially if local point source emissions impact the monitoring station. Examination of the 2001 to 2002 manganese data shows that the levels in Grand Rapids are similar to E 7 Mile in Detroit and Allen Park. These sites are removed from Detroit’s industrial urban core and hence, less impacted by point sources. The sprint site in Grand Rapids has similar concentrations and is more representative of an urban background concentration. The location at Monroe St in Grand Rapids is even less impacted by industry, so the reduction is likely to be a real change in urban levels.

Figure 3 compares levels of selected VOCs in Grand Rapids with sites in Southeast Michigan. Because Dearborn is part of the National Air Toxics Trend Site (NATTS) network, its samples are analyzed by the national contract lab, Eastern Research Group. All the rest of the VOC samples generated from 2006 to 2007 in Michigan are sent to the MDEQ laboratory. The detection limit differences and hence concentrations that were plotted between Dearborn and the other sites are influenced by differences in laboratory sensitivity and reported values of MDLs.

Other laboratory reporting issues that impact data analysis include methodology changes. In 2001, the MDEQ laboratory added 1,3 butadiene to the list of compounds determined in the VOC method. This may have contributed to some of the spread in the data for the Grand Rapids Sprint site. In 2006 to 2007, the range of values reported decreases and could be a result of improvements in laboratory technique. Many of the sites show very similar concentrations for 1,3 butadiene in 2006 to 2007. The similarity between the levels of 1,3 butadiene at most sites is likely because 1,3 butadiene is a mobile source pollutant and is ubiquitous in urban environments.

Similarities in the 2006 – 2007 concentrations of 1,4 dichlorobenzene, acrylonitrile, and carbon tetrachloride between the non-NATTS sites are also due to the similar detection frequencies and laboratory sensitivity.

Annual averages of benzene and methylene chloride concentrations decreased over the five-year interval of this comparison. In 2001 – 2002 there was a major point source located near the S Delray site that contributed to the elevated concentrations of benzene

⁶ The reporting level is the lowest level that laboratory can measure. Anything below this level, the laboratory may know it is there, but not be certain how much is there.

Figure 3: Comparison of Air Toxic VOC Concentrations in Grand Rapids with Southeast Michigan

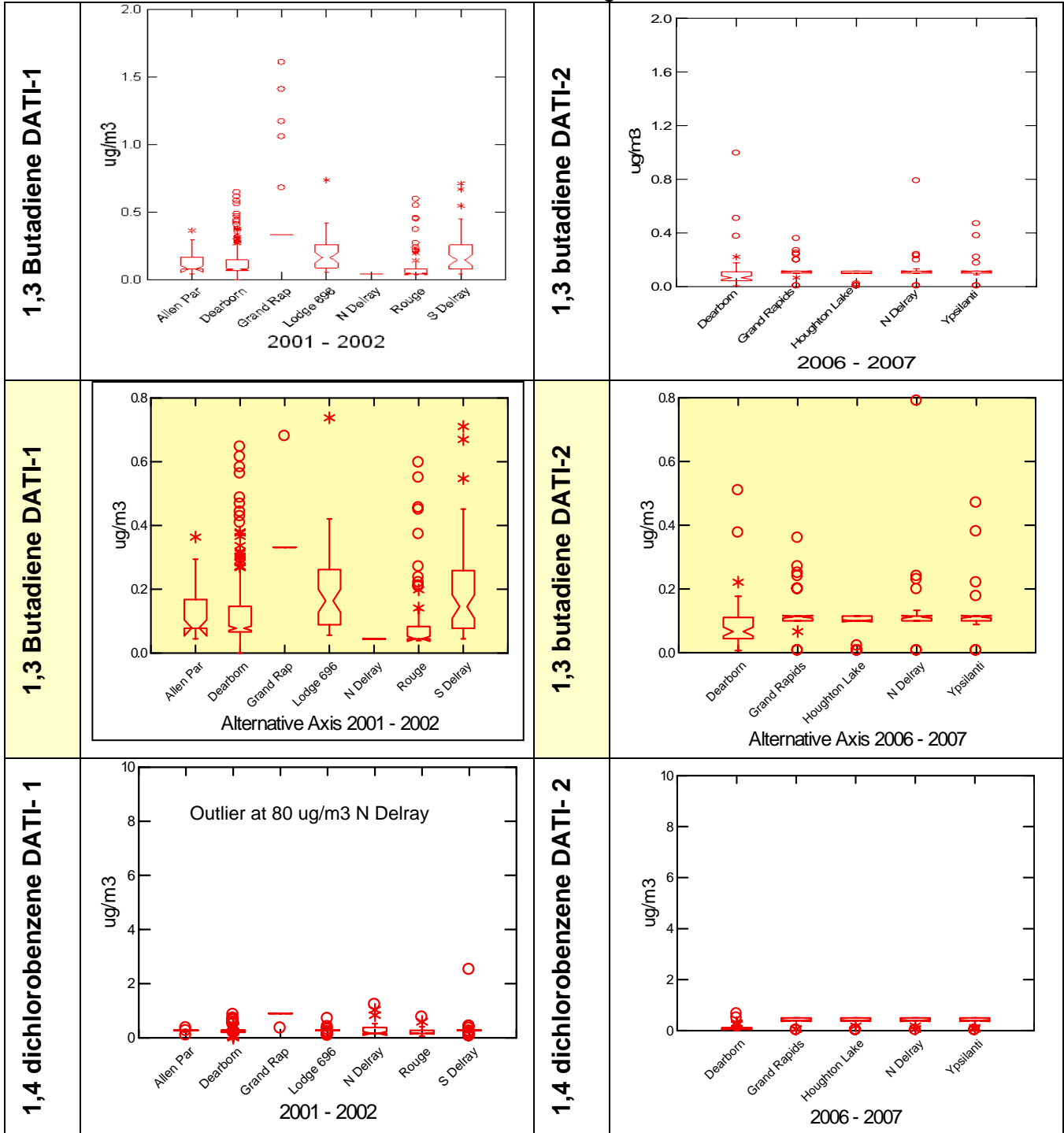


Figure 3: Comparison of Air Toxic VOC Concentrations in Grand Rapids with Southeast Michigan, Continued

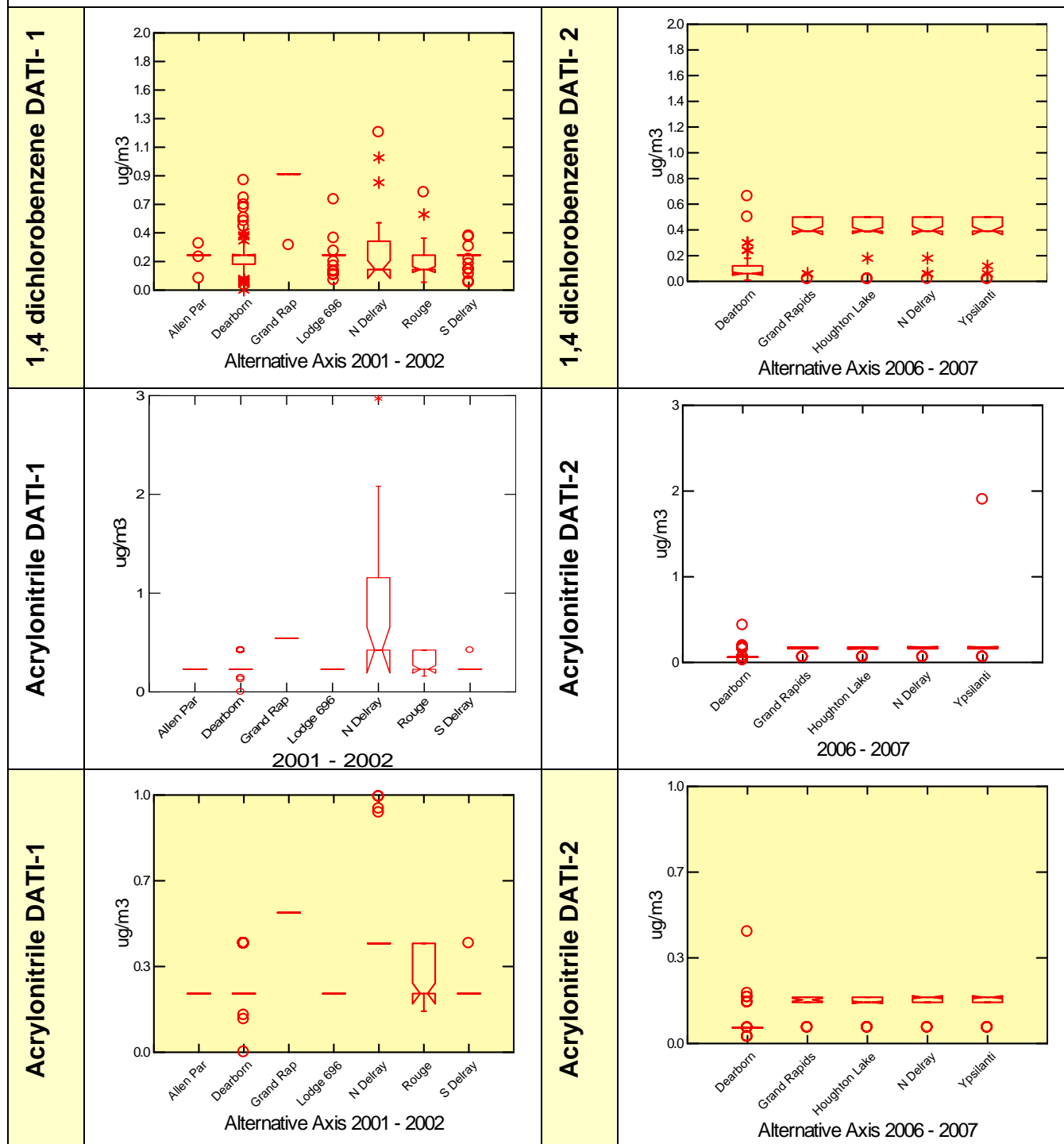


Figure 3: Comparison of Air Toxic VOC Concentrations in Grand Rapids with Southeast Michigan, Continued

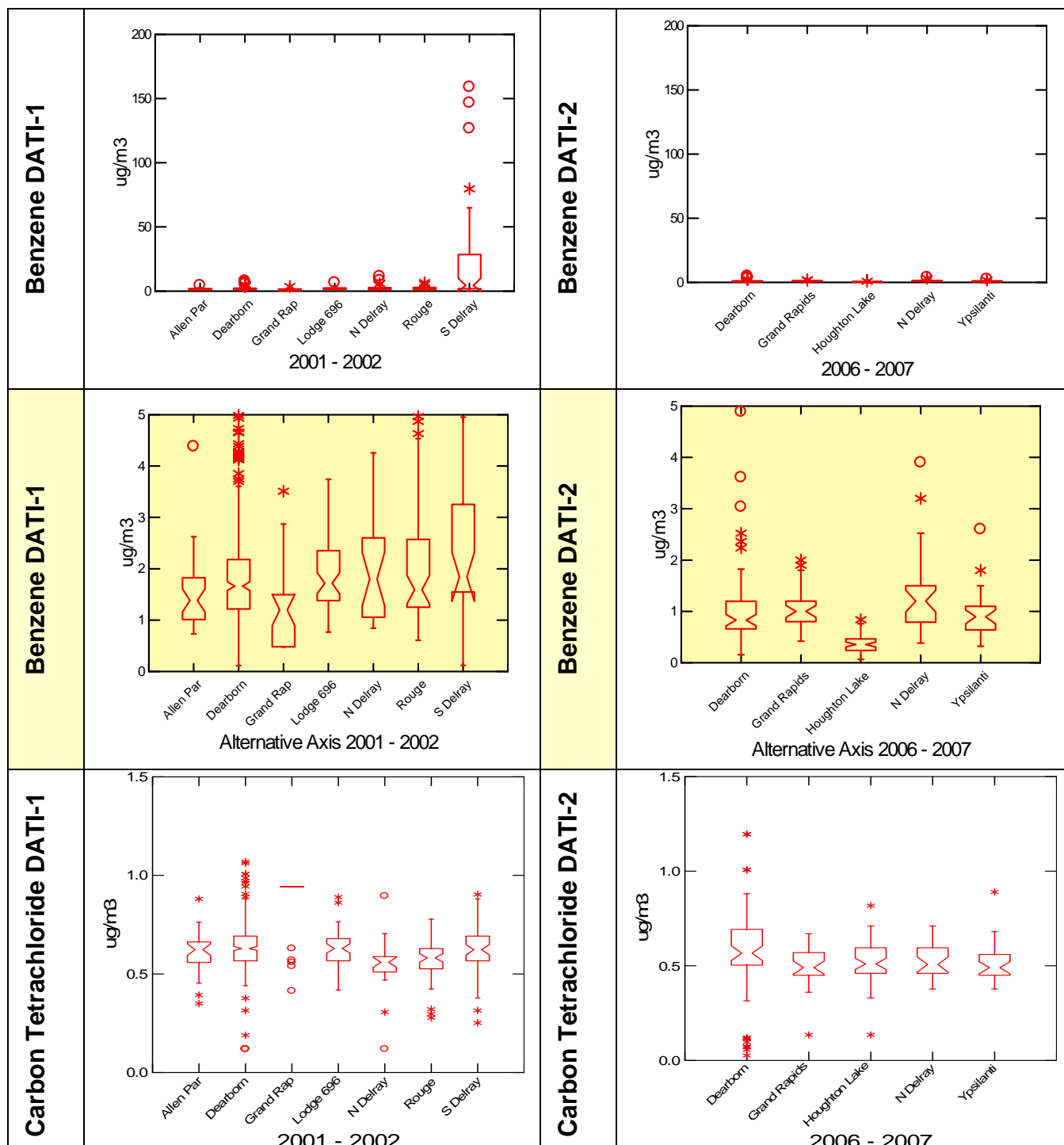


Figure 3: Comparison of Air Toxic VOC Concentrations in Grand Rapids with Southeast Michigan, Continued

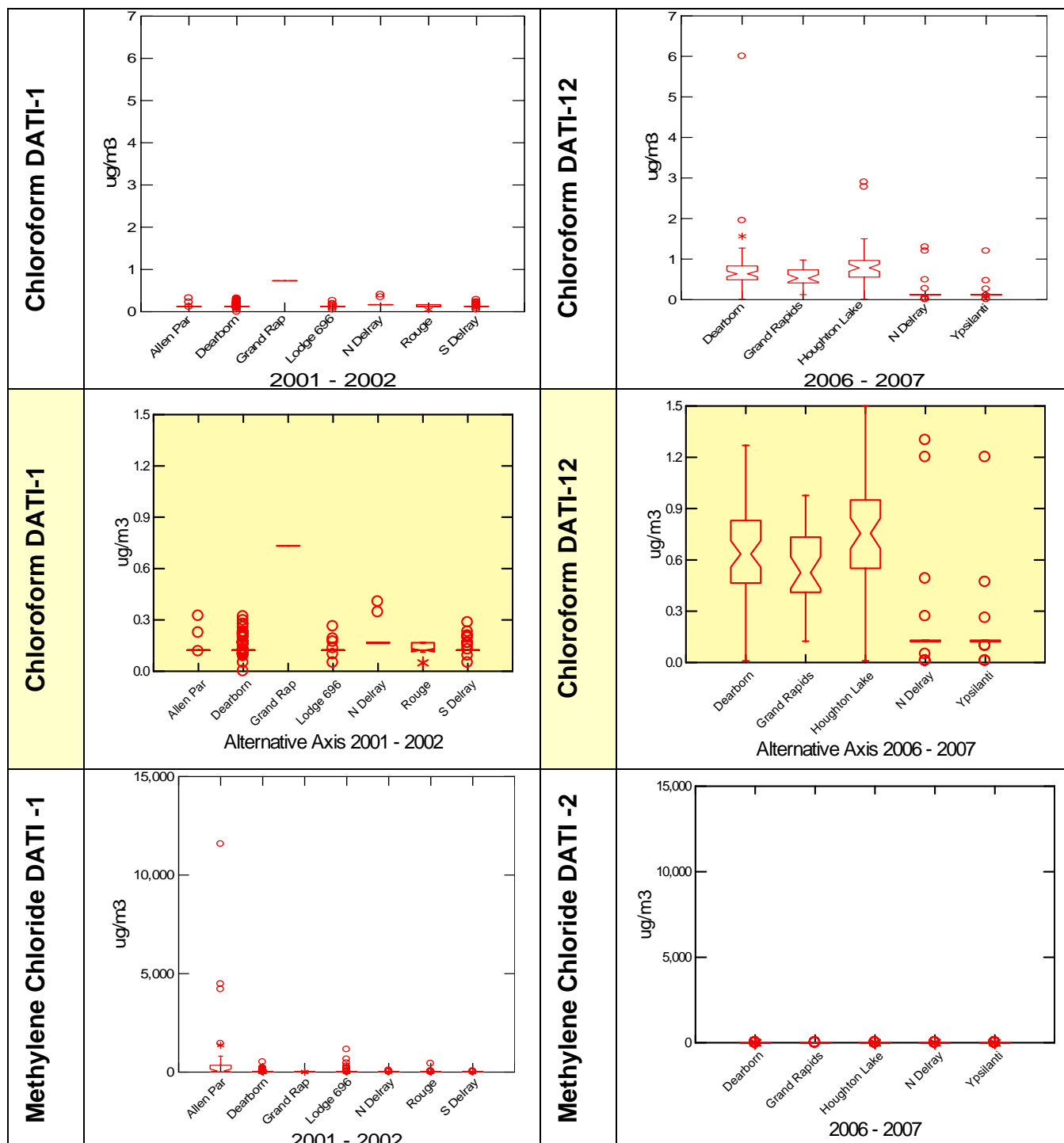
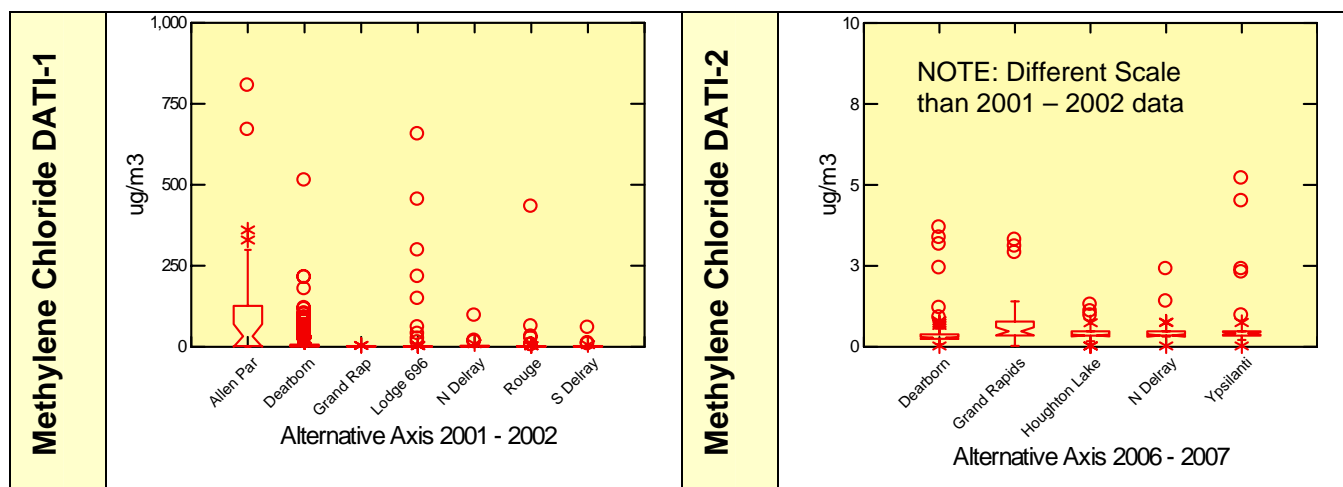


Figure 3: Comparison of Air Toxic VOC Concentrations in Grand Rapids with Southeast Michigan, Continued



that not only impacted the S Delray site, but under certain wind conditions, also impacted Dearborn, N Delray and Rouge Sites. The source closed in 2004. Follow up monitoring (not shown here), confirmed that ambient levels had decreased. Benzene emitted from mobile sources should be more homogeneous. The concentrations of benzene in Grand Rapids were lower in 2001 – 2002 than those in Detroit and may be because of the lack of such a large major point source. The benzene concentrations in 2006 – 2007 in Grand Rapids are about that same as they were in 2001-2002 even though the site moved, suggesting mobile sources are influencing benzene levels at both of the stations.

Figure 3 also shows elevated methylene chloride levels were measured at the Allen Park site in 2001 – 2002. MDEQ identified a possible point source near Allen Park that may have been responsible for the emissions. When follow-up monitoring was conducted in 2003 at Allen Park, (data not shown here) elevated levels were no longer detected. Coincidentally, the possible source of the emissions had also closed.

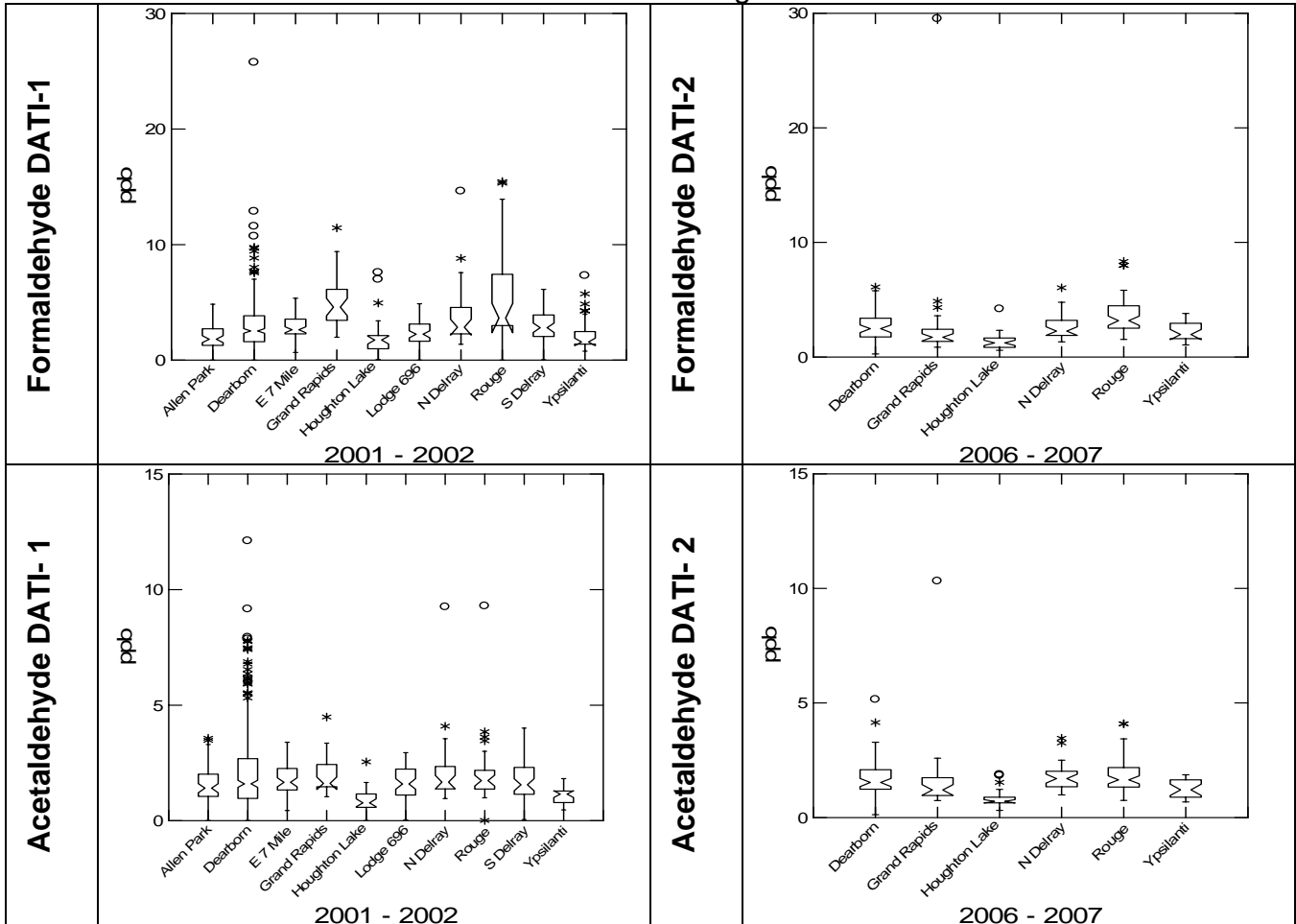
In the DATI-2 report, as well as the Air Toxics Report,⁷ elevated chloroform concentrations at various sites were identified. The tendency of detecting chloroform more frequently in recent times, as well as temporal patterns in the changes in chloroform concentrations, prompted the air monitoring unit to confirm the cleanliness of the sampling lines at Dearborn and N Delray. Zero air was pumped into the sampling system through the probe over a 24-hour period. The samples were analyzed either by the MDEQ or the national contract lab. Chloroform was not detected by either laboratory at either station. This indicates that the sampling system is clean and chloroform values may be real. MDEQ is investigating chloroform levels further.

Figure 4 compares the concentrations of carbonyl compounds in Grand Rapids with levels in Southeast Michigan. The Randolph St site (260810021) in Grand Rapids was

⁷ Analysis of Trends in Air Toxics in Michigan, STI December 2010

selected as a possible source oriented location because it was located near furniture manufacturing. When compared to most sites in Southeast Michigan, levels of formaldehyde at the Randolph St site (260810021) are somewhat higher, confirming the possible influence of point sources on the site in 2001 to 2002. Also, formaldehyde at Rouge tends to be elevated in comparison to other sites. Levels of acetaldehyde and formaldehyde are lowest at background station at Houghton Lake for all years.

Figure 4: Comparison of Air Toxic Carbonyl Concentrations in Grand Rapids with Southeast Michigan



4. ANALYSIS OF RISK IN GRAND RAPIDS

Risk assessment was performed by using methods developed by the AQD, as described below:

For chemicals known to cause carcinogenic effects: An Initial Risk Screening Level (IRSL) is the air concentration at which a carcinogen present in the atmosphere is associated with an acceptably small level of incremental (i.e., increase over the background rate) cancer risk with continuous lifetime inhalation exposure (i.e. 70 years). The EPA determined that a one in a million risk was an acceptable level of excess risk and would be protective of most individuals if exposed to a chemical continuously for 24 hours a day, over 70 years (an assumed lifetime). MDEQ uses this same practice.

Exposure levels for determining life time cancer risk were based on monitoring levels averaged over a year (the annual average). These exposure levels were used to estimate the risk of cancer per million people exposed to each carcinogenic air pollutant separately and in total. The inhalation cancer risk estimates in DATI are based only on exposure to outdoor air toxics and should not be confused with overall cancer rates.

$$\text{Risk} = (\text{Average Exposure Concentration}) / \text{IRSL}$$

where:

Risk = cancer risk to an individual (expressed as an upper-bound risk of contracting cancer over a lifetime);

Average Exposure Concentration = Annual Average Concentration for a specific air toxic;

IRSL = Initial Risk Screening Level (air concentration that has the probability of 1-in-1-million risk of cancer)

Performing the estimate in this way provides an estimate of the probability of developing cancer over a life time due to the exposure in question. Because of the way this equation is written, the underlying presumption is that a person is exposed continuously to the annual average air concentration for their full lifetime (usually assumed to be 70 years).

For chemicals known to cause adverse impacts other than cancer (i.e., non-carcinogens): An Initial Threshold Screening Level (ITSL) is an ambient air concentration of a toxic air contaminant at which no adverse effects are expected in humans. An ITSL is a calculation of a proposed dose level for a toxic chemical below which no adverse effect will occur. This “threshold” dose level must be exceeded before an adverse effect would be expected to occur.

If a chemical presents a possible risk other than cancer, a hazard quotient (HQ) is developed. HQ values less than one indicate no adverse health effects are expected while HQ values greater than one indicate that adverse health effects are possible. It is important to note that a hazard quotient exceeding 1 does not necessarily mean that adverse health effects will occur (EPA, 2002). For the purpose of the current analysis, chemicals with a hazard quotient less than 1 are not considered priority chemicals. Health quotient approximations are determined by taking the average air concentration and dividing it by the ITSL.

$$\text{Hazard Quotient} = (\text{Average Concentration}) / \text{ITSL}$$

The intent of the present initiative is to base the risk assessment on the estimated long-term average exposure levels. It is assumed that this would be best represented by the arithmetic average concentrations for the 1-year monitoring period. Therefore, annual average values of air concentrations are used for comparison to health-based screening levels.

Uncertainty in assessing risks:

Several areas of uncertainty are inherent in risk assessment such as this project. Although efforts have been made to reduce uncertainty in sampling and laboratory analysis, human and mechanical errors and limits of instrumentation can still exist⁸. Estimating exposures to individual people using measurements of air concentrations at fixed site monitoring locations introduces uncertainty. The monitoring locations may not be representative of larger areas. Monitors are not located at industrial property boundaries because this would tend to over estimate air concentrations. Also, air samples for toxic air contaminants, like those monitoring for this study, are not typically collected every day because of resource limitations including both time (collecting and analyzing the samples) and money (cost of analysis).

The use of annual average monitor values, as done in this study, can result in an underestimate or an overestimate of levels on any given day. The 95% confidence intervals were calculated and used to graph error bars included on the individual chemical concentration graphs in Section 6. These error bars help to visualize the distribution of air samples during the year of sampling. This risk assessment also does not include estimated health risks from exposure to compounds which were not monitored or did not have a health benchmark established. This could underestimate cancer and non-cancer risks.

Another source of uncertainty is related to the interpretation of data that are below the method detection limit. The replacement of non-detected values with the estimate of method detection limit (MDL) divided by a factor of 2 may also over or underestimate air concentrations of chemicals that are below the laboratory's analytical ability to measure their existence. Since MDLs have a specific concentration for each compound, this method of estimating air concentrations below the MDL provided more data with which to characterize exposure concentrations. At this time, it is not possible to determine the amount of error introduced into the annual average air concentration of a chemical at a particular location by using this estimation method.

Uncertainty also exists in the determination and application of health protective benchmark levels used for risk assessment. Uncertainty factors are incorporated into the risk assessment algorithms in an effort to minimize potential to misclassify actual risk. For a thorough discussion of uncertainty in risk assessment as it relates to this study, the interested reader is referred to the DATI-1 Risk Assessment Report available at www.michigan.gov/degair under the Air Toxics link or directly at [http://www.michigan.gov/documents/DATI - COMPLETE FINAL REPORT 11-9-05_142053_7.pdf](http://www.michigan.gov/documents/DATI_COMPLETE_FINAL_REPORT_11-9-05_142053_7.pdf)

⁸ Uncertainty in the monitoring data is being examined in other data analysis projects.

Table 4. Priority Chemicals Identified for DATI-2 and AQD Screening Levels

Chemical	Chemical Abstract Service (CAS) Number	Initial Risk Screening Level µg/m³; (ppb) Annual averaging	Initial Threshold Screening Level µg/m³; (ppb) (Ave. time)
Acetaldehyde	75-07-0	0.5; (0.28)	9; (5.0) [24 hr]
Benzene	71-43-2	0.1; (0.03)	30; (9.4) [24 hr]
Formaldehyde	50-00-0	0.08; (0.065)	
Methylene Chloride	75-09-2	2; (0.6)	
Manganese	7439-96-5		0.05; (0.02) [annual]
Nickel	7440-02-0	0.0042; (0.0018)	
Cadmium	7440-43-9	0.0006; (0.0001)	
Arsenic	7440-38-2	0.0002; (0.00007)	
1,3-Butadiene	106-99-0	0.03; (0.014)	2; (0.9) [24 hr]
Acrylonitrile	107-13-1	0.01; (0.005)	2; (0.9) [24 hr]
Carbon Tetrachloride	56-23-5	0.07; (0.011)	100; (15.9) [24 hr]
Chloroform	67-66-3	0.4; (0.08)	
1,4-Dichlorobenzene	106-46-7	0.14; (0.02)	800; (133) [24 hr]

In addition to evaluating data from a select period of time five years after the DATI-1 assessment, staff considered more than four years of data from 2002-2007 for any chemicals not appearing to have a consistently downward trend. The only chemical for which this appeared to be the case was manganese. In response to these findings, the AQD included an initiative in its fiscal year 2007 (FY07) Strategic Plan to address environmental impacts of manganese in Southeast Michigan. The AQD's responsibility for this initiative was to analyze and reduce, where possible, emissions of manganese from existing sources. An AQD Manganese Workgroup was formed in January 2007 to implement this initiative. Once completed the final report will be available online on the MDEQ Air Quality Divisions Air Toxics section of the web site.

Cancer Risk by Chemical

For the purposes of this report, one in a million excess cancer cases potentially attributable to exposure to a toxic air contaminant is considered the appropriate health benchmark. This is the same benchmark used in the DATI-1 for cancer risk assessment. For uniformity of comparison between graphs, units on the y axis use a scale of 0 to 70 in one million excess cancer risks when feasible. The risks will be categorized in three ranges, according to the estimated excess number of cancers per million individuals:

- 1 to 10 in a million risk
- 10 to 100 in a million risk
- 100 to 1000 in a million risk

Details specific to southeast Michigan are supplied in the DATI-2 report. In general, the report found that cancer risk declined from 2001- 2002 to 2006-2007 for arsenic, benzene and methylene chloride. A slight decline was observed at most locations for cadmium, acetaldehyde and 1,3 butadiene. A decline in risk due to 1,4 dichlorobenzene exposure was observed at Dearborn; other sites couldn't be assessed because the frequency of detection was quite low as was the detection of acrylonitrile. The DATI-2 report noted very slight changes in the levels of risk due to exposure to nickel and carbon tetrachloride. Declines were noted for formaldehyde, with some locations exhibiting large reductions in risk. This is interesting because formaldehyde is usually attributed to being a mobile source pollutant. Non uniform reductions in risk were attributed to changes in emissions from point sources. Slight increase in risk from exposure to chloroform was noted previously in this report and is being investigated by MDEQ. This section compares the changes in the level of risk from 2001 – 2002 and from 2006– 2007 in Grand Rapids as illustrated in **Figure 5**.

Figure 5: Levels of Risk in Grand Rapids due to Individual Chemicals

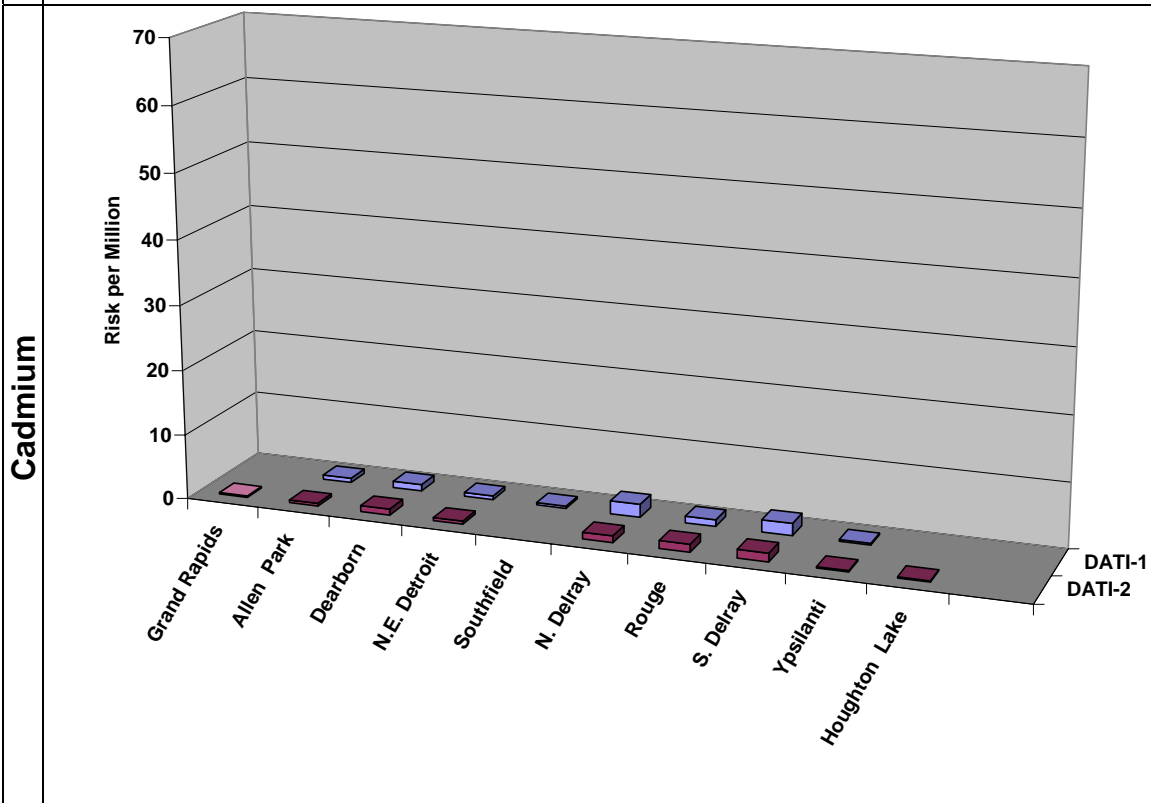
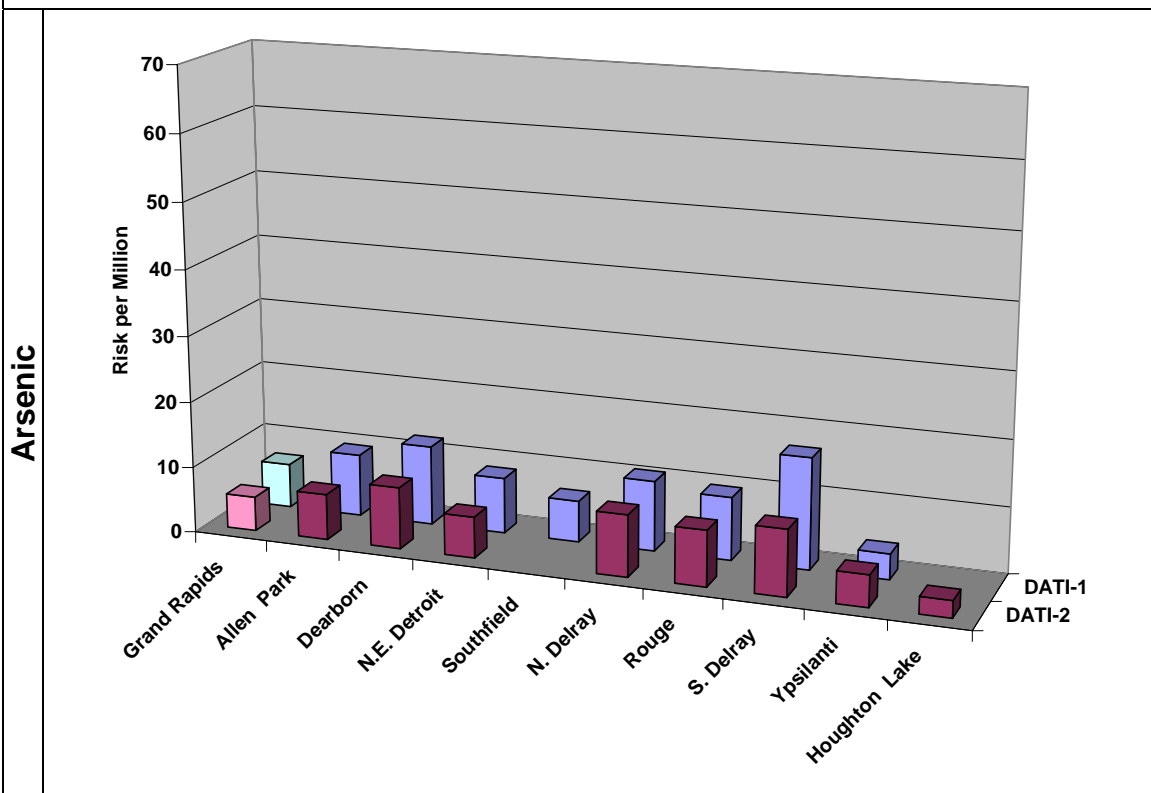


Figure 5: Levels of Risk in Grand Rapids due to Individual Chemicals, continued

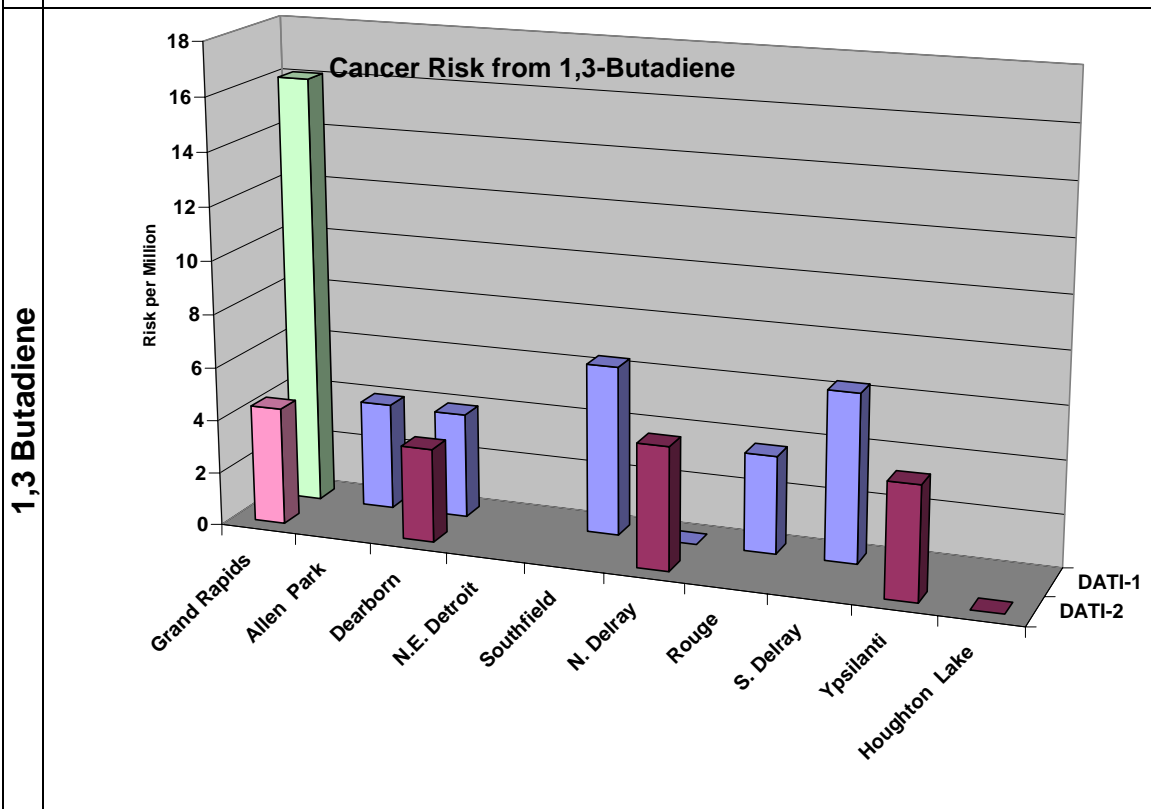
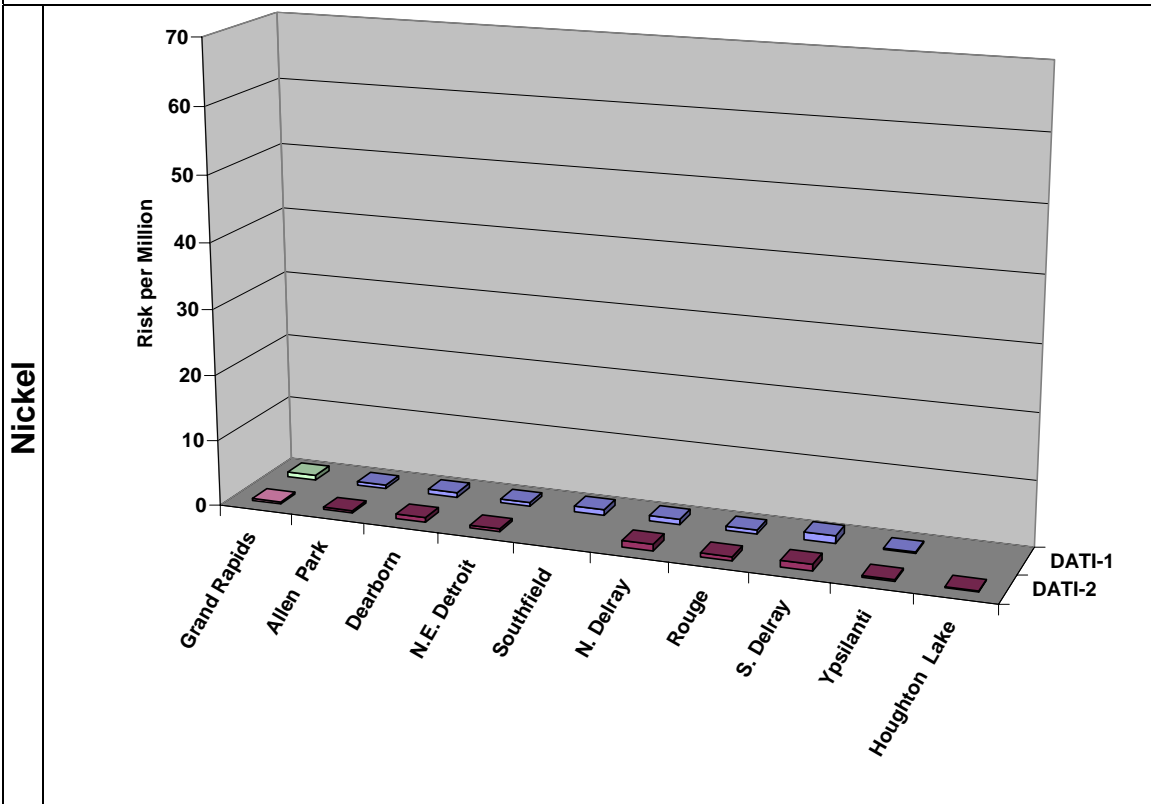


Figure 5: Levels of Risk in Grand Rapids due to Individual Chemicals, continued

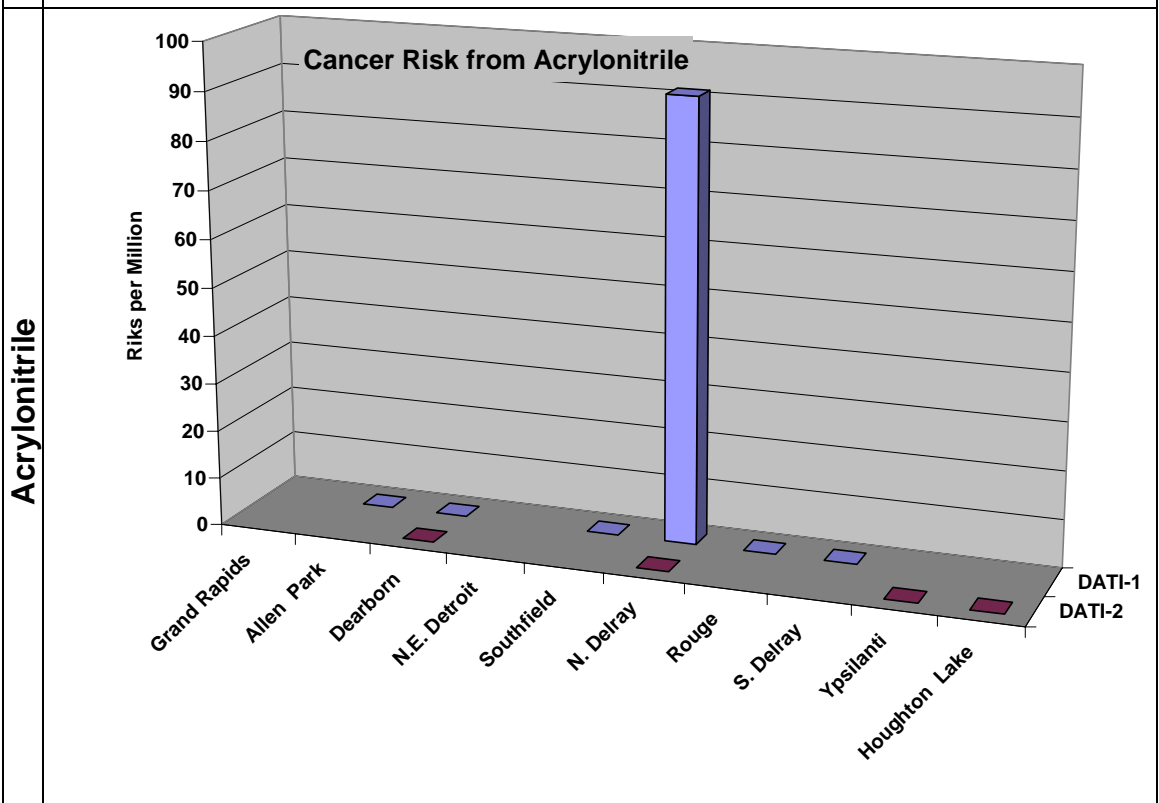
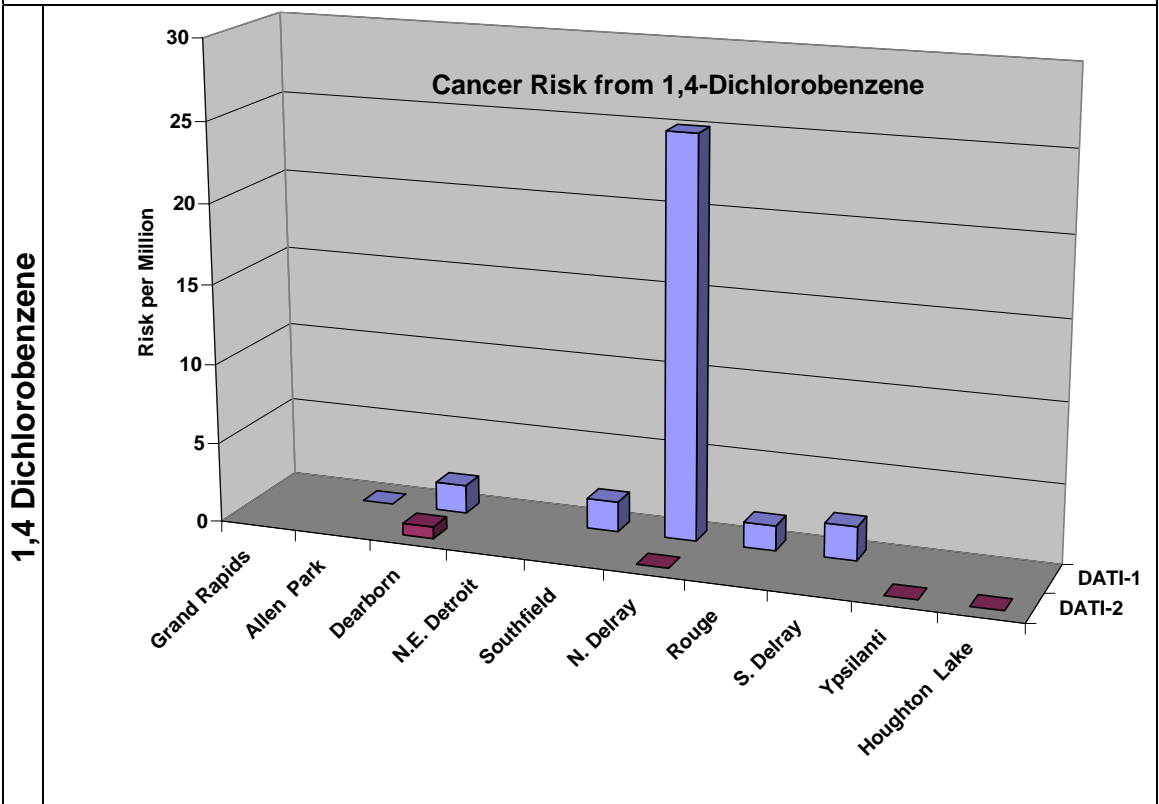


Figure 5: Levels of Risk in Grand Rapids due to Individual Chemicals, continued

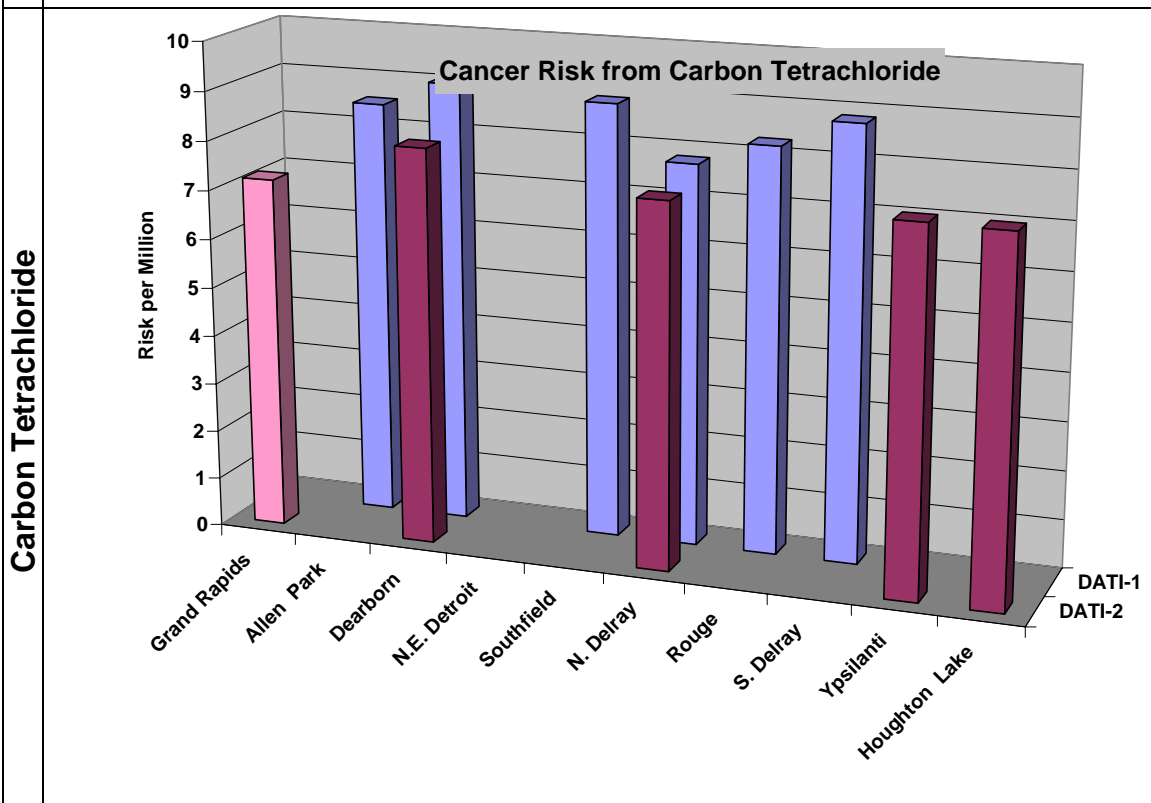
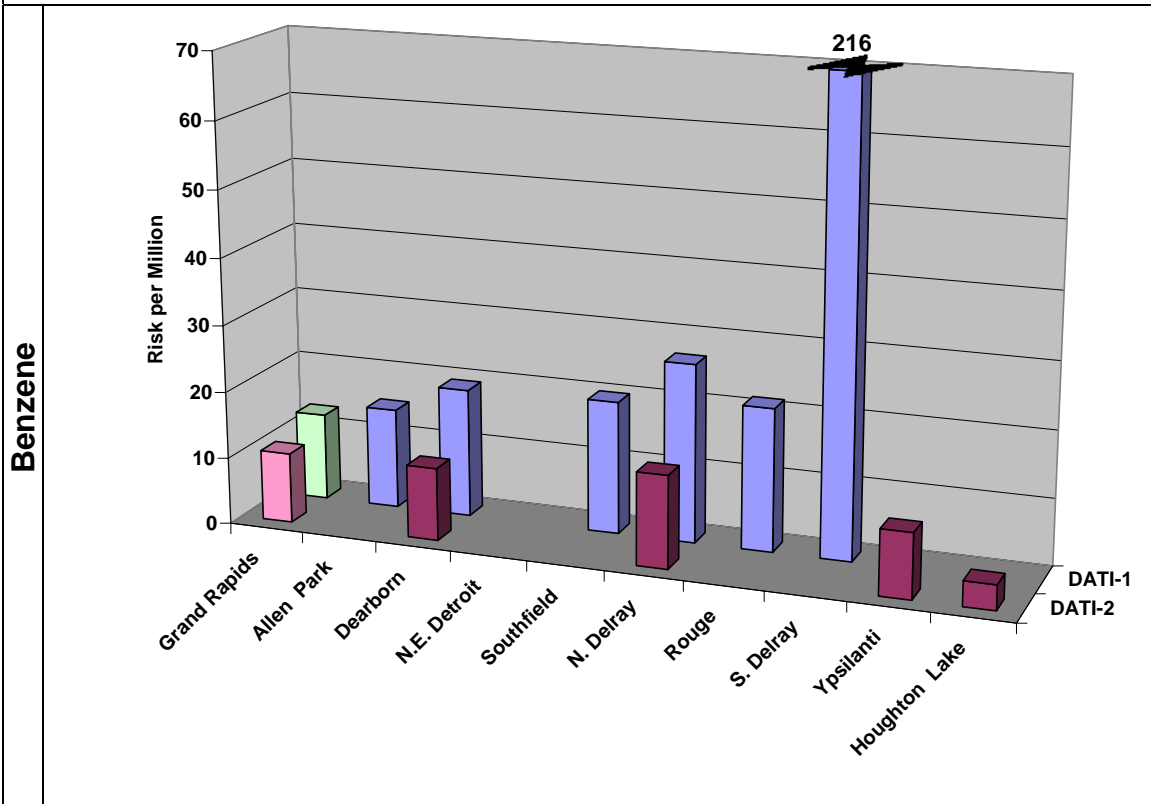


Figure 5: Levels of Risk in Grand Rapids due to Individual Chemicals, continued

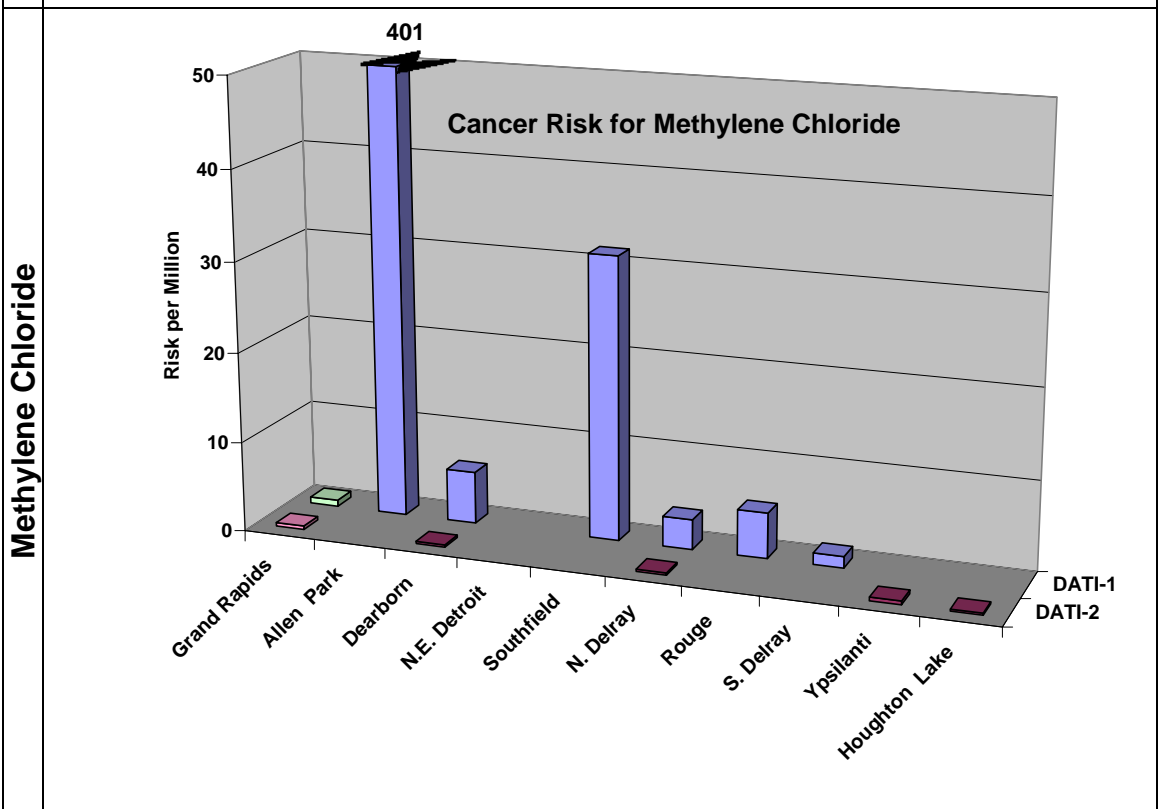
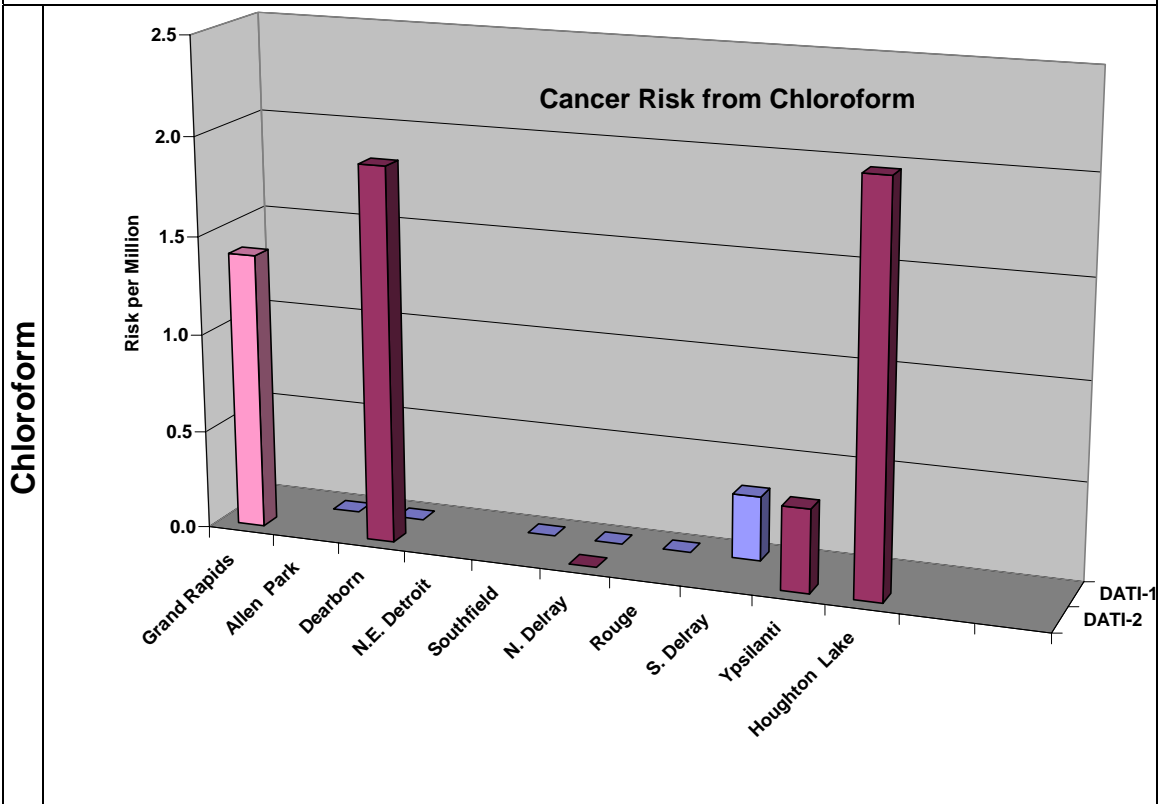
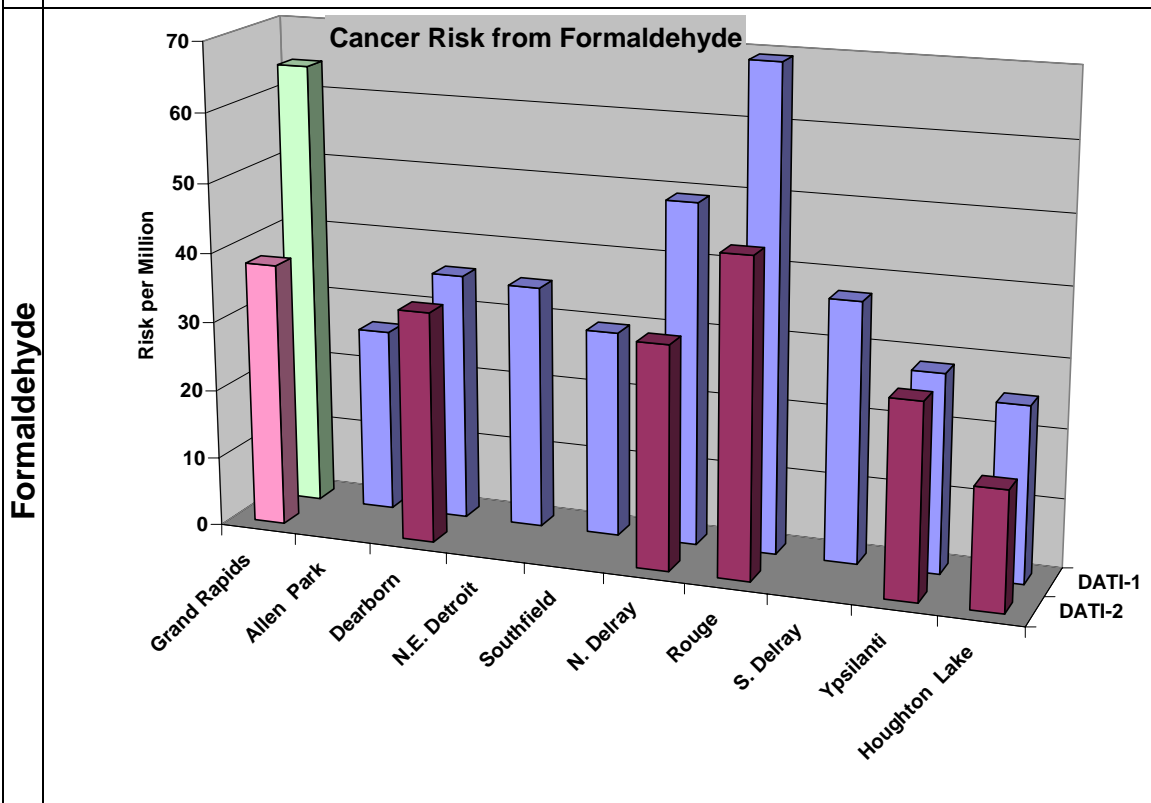
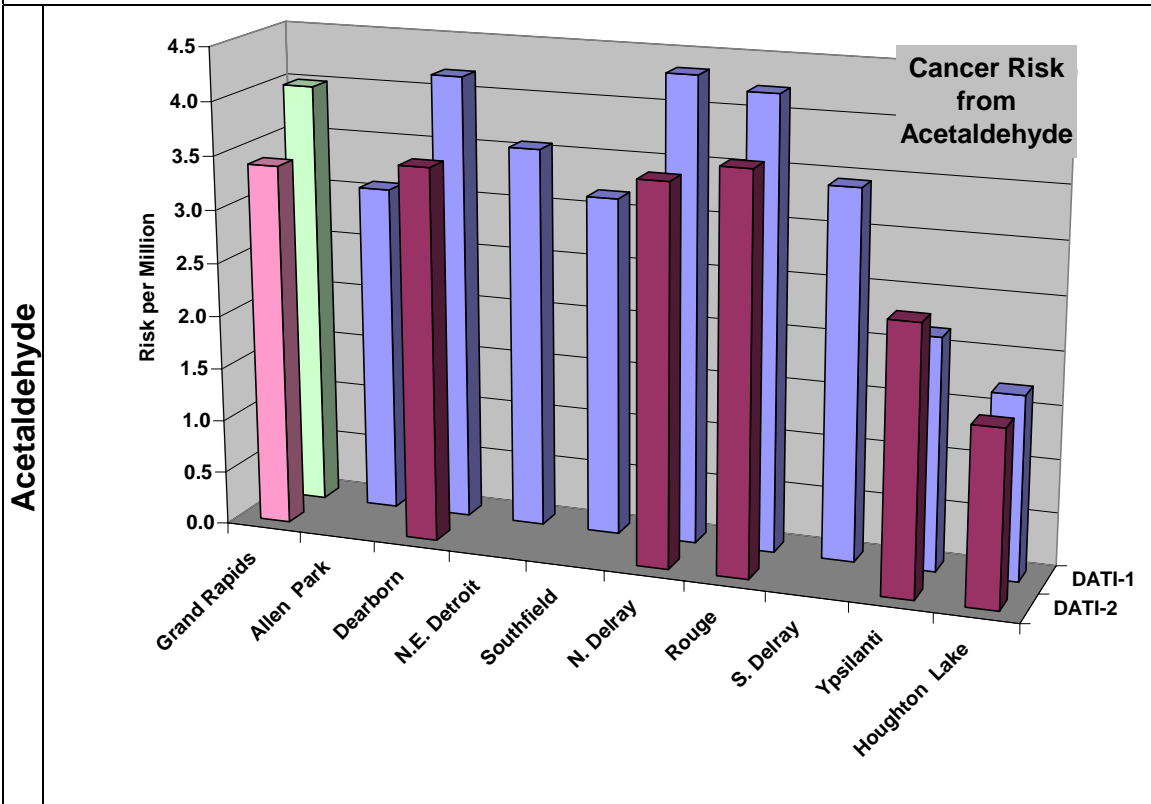
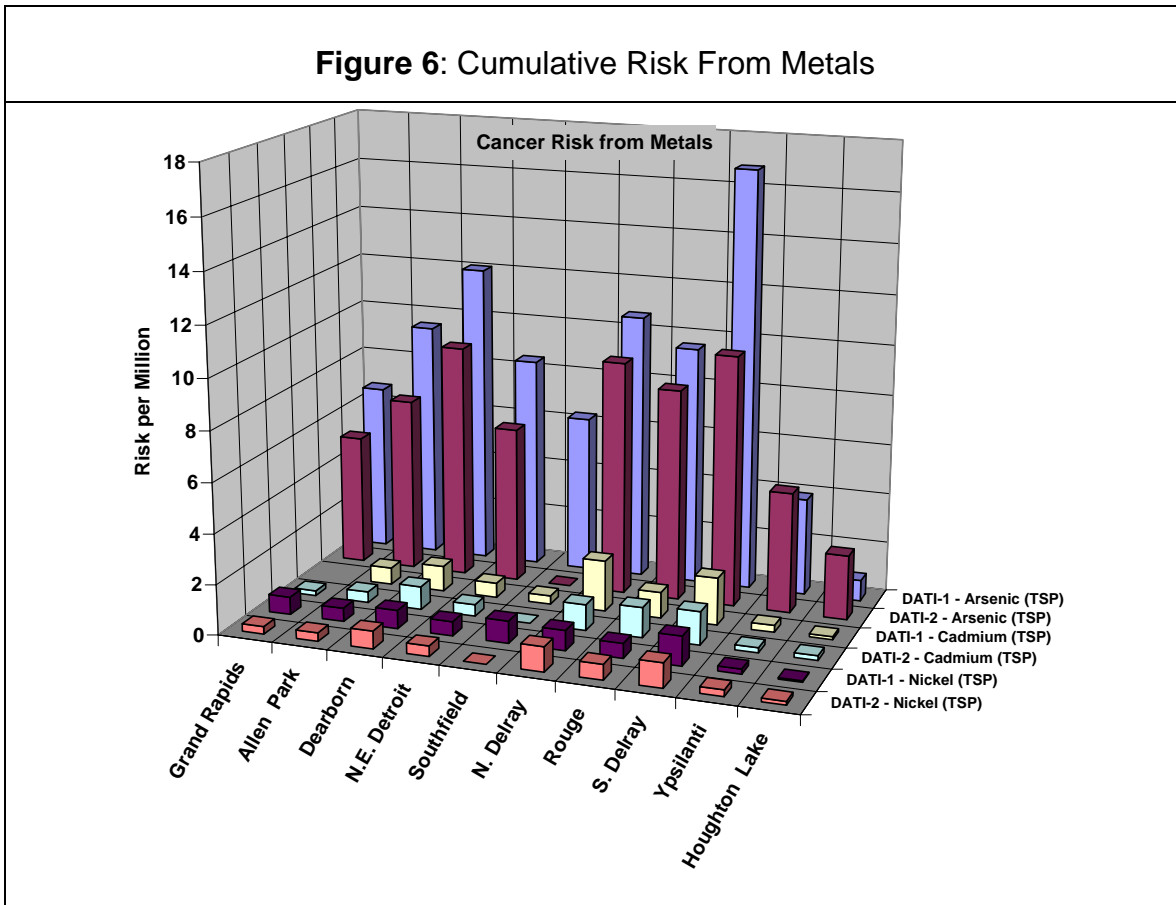


Figure 5: Levels of Risk in Grand Rapids due to Individual Chemicals, continued



DATI-2 also evaluated levels of risk by location at various sites in southeast Michigan. The report found that cancer risk from trace metals declined at most sites, while the risk increased slightly due to arsenic at the urban upwind background site. The risk due to exposure to acetaldehyde and formaldehyde declined at four sites, was unchanged at the urban background site and could not be assessed at the remaining sites due to lack of data. There were only two locations that measured VOCs in 2001- 2002 and 2006 – 2007: Dearborn and N Delray. Many of the VOCs were not detected. Only benzene and carbon tetrachloride met the minimum detection requirements set forth for the risk analysis (i.e. > 15% detection). Benzene showed considerable declines at both locations from the DATI-1 to the current study. Carbon tetrachloride showed slight decline at Dearborn but was essentially unchanged at N. Delray. The Dearborn site showed measurable declines in risks associated with methylene chloride, formaldehyde, acetaldehyde, 1,3-butadiene and 1,4-dichlorobenzene in addition to the benzene and carbon tetrachloride noted above. Chloroform showed slight elevated concentrations at N. Delray, but the sampling frequency was less than our criterion and risk change was not calculated.

A similar analysis was performed for Grand Rapids, comparing Grand Rapids with southeast Michigan stations, as shown in **Figure 6**. The risk due to metals in Grand Rapids is less than that of the Detroit sites but greater than the background site or Ypsilanti.



As seen in **Figure 7**, there are only three monitoring locations for which VOCs were measured during both time periods (i.e., Dearborn and N. Delray in Southeast Michigan and Grand Rapids). Only benzene and carbon tetrachloride met the minimum criteria to be compared at both locations from the DATI-1 time from to the current analysis. Benzene showed considerable declines at both locations from the DATI-1 to the current study. Carbon tetrachloride showed slight decline at Dearborn but was essentially unchanged at N. Delray. The Dearborn site showed measurable declines in risks associated with methylene chloride, formaldehyde, acetaldehyde, 1,3-butadiene and 1,4-dichlorobenzene in addition to the benzene and carbon tetrachloride noted above. Chloroform showed slight elevated concentrations at N. Delray, but the sampling frequency was less than our criterion and risk change was not calculated.

The Grand Rapids data shows greater risk due to 1,3 butadiene in 2001 to 2002 than at the other stations. The differences in laboratory reporting procedures for the Grand Rapids site in 2001 to 2002 could be biasing the data. (i.e. the MDEQ laboratory reported “less than RDL” for non detects in Grand Rapids; concentrations at all other sites was estimated down to the MDL.) RDLs are higher than MDL values. Furthermore, the lab was encouraged to report any concentration detected in a sample, even when below the MDL. This practice was not applied to VOC samples generated in the Grand Rapids area by the MDEQ laboratory as a cost savings measure.

As noted in **Figure 8** below, cancer risk estimates from carbonyls declined at Grand Rapids, Dearborn, N. Delray, Rouge and Houghton Lake. The decline was largely attributed to formaldehyde decreases from the sites in Southeast Michigan and Houghton Lake. Remember that air sampling was conducted at the Grand Rapids-Randolph St site (260810021) during DATI-1 and at the Grand Rapids- Monroe site (260810020) during DATI-2, and the site move complicates the analysis. The Grand Rapids-Randolph St (260810021) site was located in an area impacted by furniture manufacturing which may emit formaldehyde from particle board resins. However, the Grand Rapids-Monroe St (260810020) site is near a highway which is impacted by formaldehyde from motor vehicle emissions.

Figure 7: Cumulative Risk From VOCs

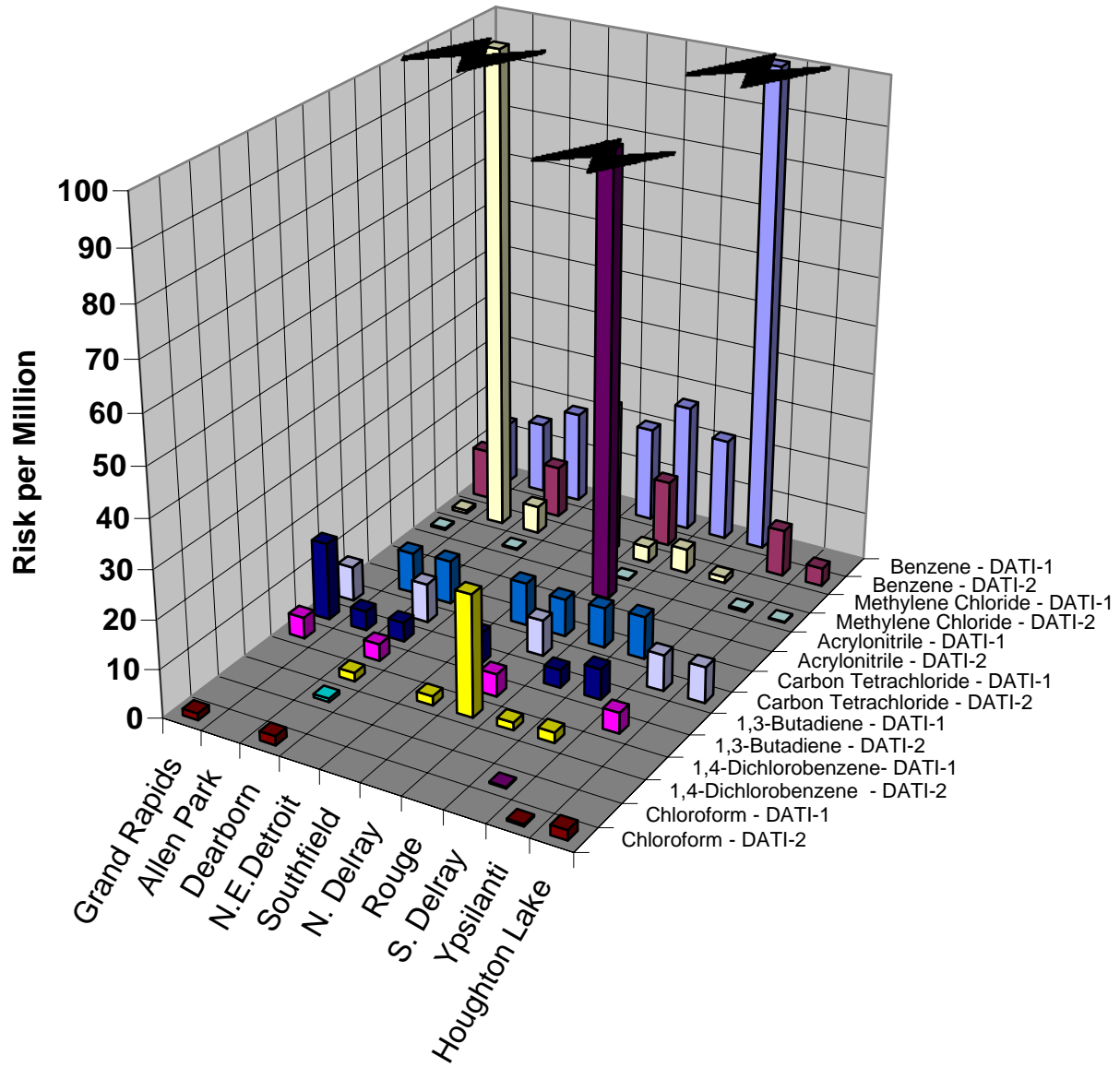
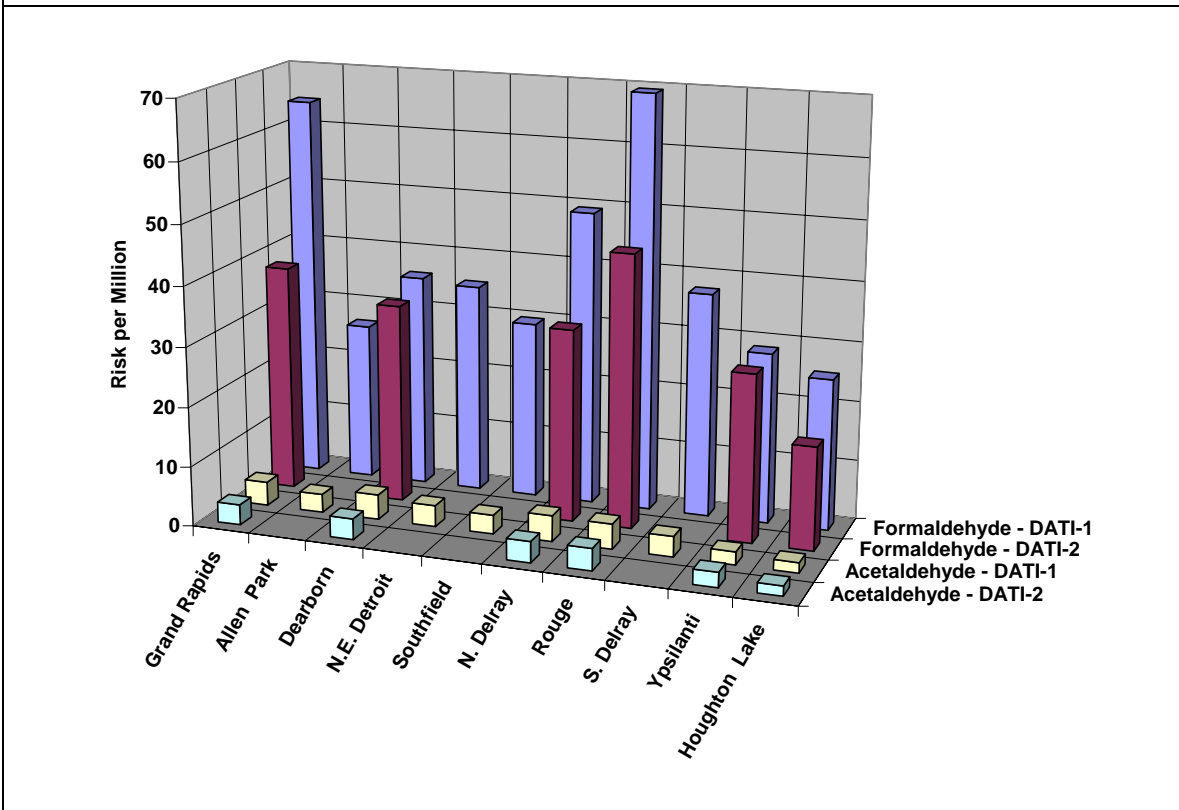


Figure 8: Cumulative Risk From Carbonyls



The full DATI-2 report characterized risk near each monitoring site. **Figure 9** summarizes risk levels corresponding to DATI-1 and DATI-2 time frames for Grand Rapids. Most of the risk is due to exposure to formaldehyde and 1,3 butadiene. The total cancer risk in Grand Rapids during 2001 – 2002 was 105.6 and during 2006 – 2007 was 71.1 per million.

As seen below in **Figure 10**, total cancer risk estimates have gone down for nearly every site. Although levels appear slightly higher at Houghton Lake and Ypsilanti (background sites); this could be the result of more chemicals being monitored at those two sites during the DATI-2 time frame. Total cancer risk in Grand Rapids has also gone down during the more recent time frame.

Figure 9: Cancer Risk at Grand Rapids

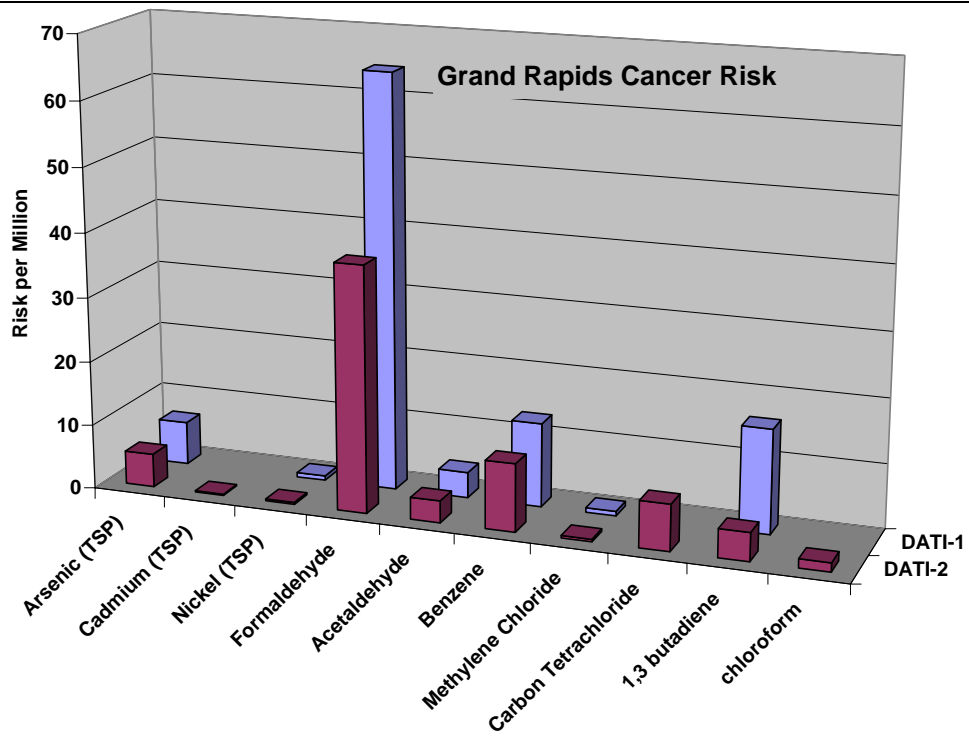
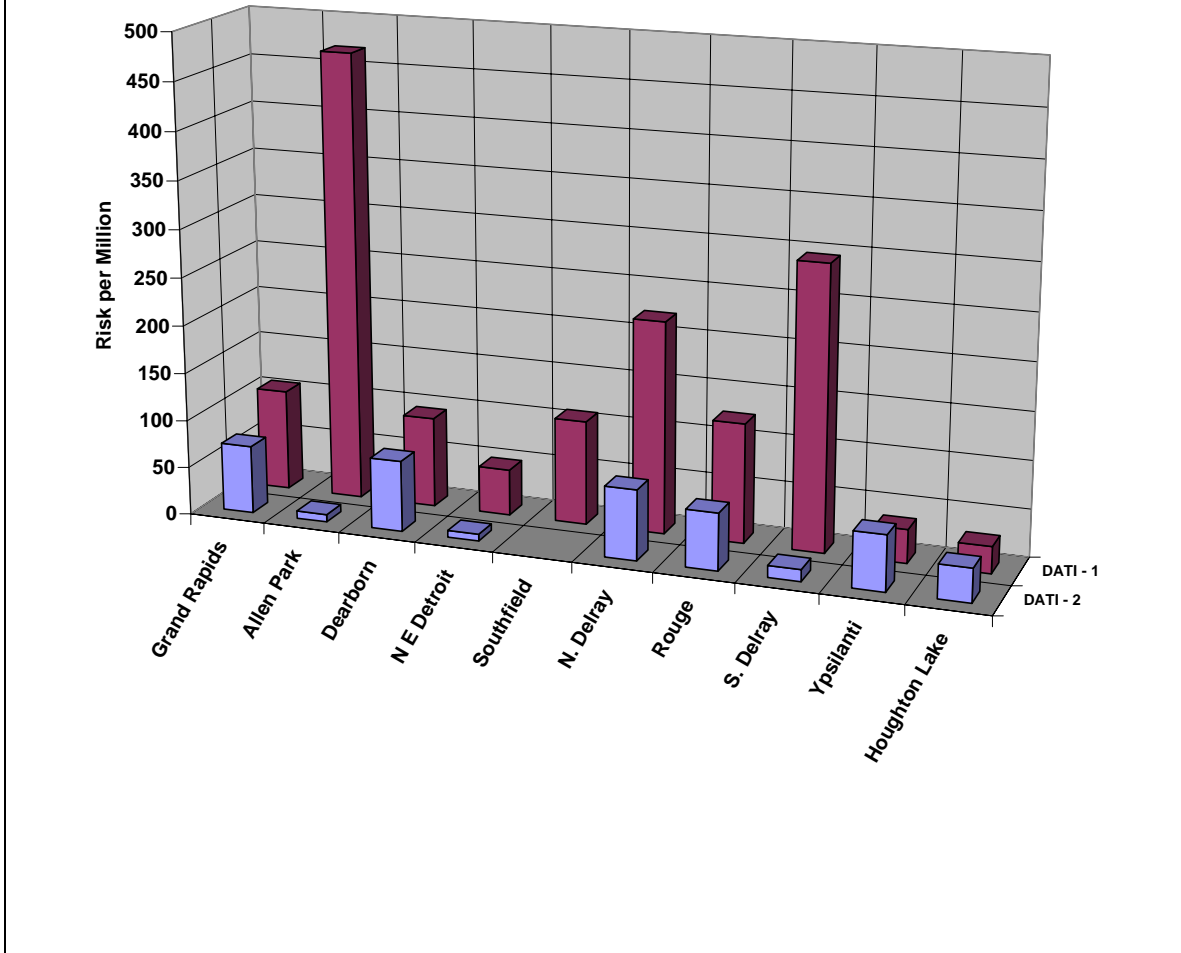


Figure 10: Cumulative Cancer Risk for all Chemicals by Site and Study – Including Grand Rapids

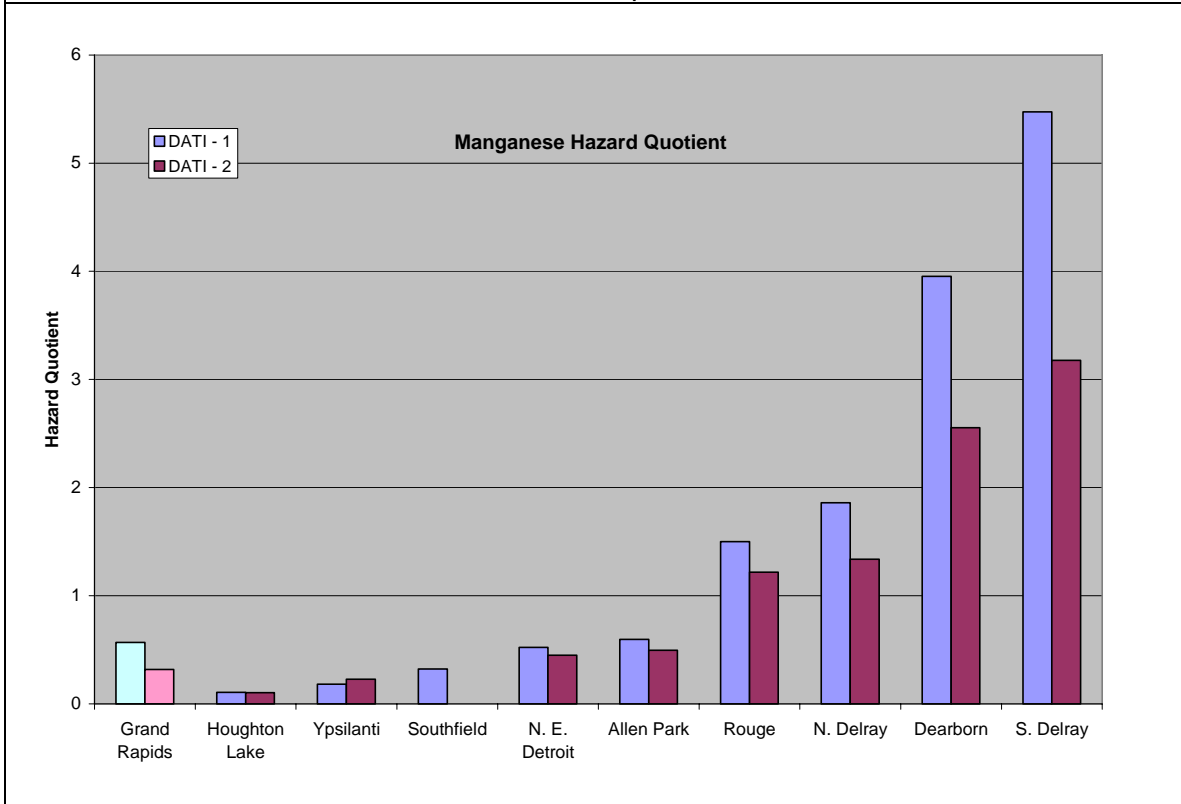


Non-Cancer Data

The risk assessment for chemicals not associated with the development of cancer involved the development of a hazard ranking. The risk associated with an individual chemical was quantified by comparing the estimated exposure to a certain reference level and expressed as a ratio, or hazard quotient (HQ). Hazard quotient values less than or equal to 1 indicates that adverse non-cancer health effects are unlikely to occur. The only chemical with a hazard quotient value higher than 1 in the current analysis was manganese. As noted **Figure 11** below, the manganese hazard quotients for all locations except Ypsilanti are lower than in the DATI-1 analysis. Both DATI-1 and DATI-2 manganese hazard quotients for Ypsilanti are less than 1, as are those at NE Detroit (E 7 Mile) and Allen Park. The River Rouge and N. Delray location manganese HQs are now just above 1. The Dearborn manganese HQ is down appreciably from DATI-1 to about 2.5. The S. Delray manganese HQ is appreciably decreased from DATI-1 and is now just above 3.

The manganese hazard quotient for Grand rapids falls somewhere between that for N. E. Detroit and Allen Park, both of which are sites on the fringe of the urban center city industrial area. Like the other sites in the study, a decline in the hazard quotient was observed for Grand Rapids. The hazard quotient was 0.57 and 0.32 for 2001 to 2001 and 2006 to 2007, respectively, in Grand Rapids.

Figure 11: Hazard Quotient Comparisons for Manganese – DATI-1 vs DATI-2 including Grand Rapids



Conclusions

Although changes in laboratory reporting practices and site locations complicate data analysis activities, some generalized conclusions may be made about air concentrations and risk estimates.

No monitoring data, or an insufficient number of detected analytes were available in 2001 to 2002 for cadmium, carbon tetrachloride and chloroform, so the level of risk could not be estimated.

Elevated concentrations of chloroform were noted during 2006 to 2007 at multiple locations in Michigan. MDEQ is investigating possible causes.

The risk drivers from 2001 to 2002 in Grand Rapids were formaldehyde and 1,3-butadiene, which are both generally attributed to mobile source emissions. The location of the monitoring station was changed in 2005. The risk drivers from 2006 to 2007 were due to formaldehyde and benzene, both of which are mobile source pollutants. This is not surprising since the air toxics site that was operational in 2006 to 2007 in Grand Rapids was located near a major roadway. The previous station was most likely impacted by point sources as well as mobile sources that emitted formaldehyde. The reduction in the level of formaldehyde was most likely due to relocation of the station and reduction in the impact of emissions from point sources.

The level of risk due to arsenic, cadmium and nickel is either lower in Grand Rapids or about equal to other urban areas in Michigan. Risk from manganese in Grand Rapids is typical for an urban area that is not heavily industrialized.

References:

Heindorf MA. 2005. Detroit Pilot Project Report: Descriptive Statistical Data Summary. Draft Report. MDEQ-AQD.

MDEQ, 2005 Detroit Air Toxics Initiative: Risk Assessment Report, November, 2005.

MDEQ, 2010 Detroit Air Toxics Initiative: Risk Assessment Update. December 22, 2010.

MDEQ, 2011 Ambient Air Levels of Manganese in Southeast Michigan: Evaluation & Recommendations by the AQD Manganese Work Group, June 2011.

U.S. EPA, 2004. Air Toxics Risk Assessment Reference Library, Vol. 1. Technical Resources Manual. April 2004. EPA-453-K-04-001A.