# Detroit Air Toxics Initiative

**Risk Assessment Update** 

December 22, 2010

# **Community Data Analysis Risk Assessment Document**

# December 22, 2010

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# **ES-1. EXECUTIVE SUMMARY**

# **Background**

In order to address concerns about exposure to toxic air pollutants in the Detroit area, the Detroit Air Toxics Initiative (DATI) was performed. The DATI effort involved the use of data from a pilot air-monitoring project conducted during 2001 and 2002. An assessment of risk was based on that data. Air Quality staff from the Michigan Department of Natural Resources and Environment have performed an updated evaluation of health risks from exposure to toxic air contaminants in the Detroit area. This report describes the current initiative. The evaluation compared air and health data from 2001-2002 (the focus of the original DATI study) to more recent air monitoring results from 2006-2007. Since the original pilot monitoring project, severe budget reductions have resulted in fewer chemicals being monitored at fewer locations. Therefore, their comparisons are not available for all chemicals at all monitoring sites.

The original DATI project is henceforth referred to as DATI-1 and the current risk assessment as DATI-2. Both projects were made possible with funding from the U.S. Environmental Protection Agency (EPA). This report provides the background, methodology, and results for the risk assessment phase of the current project.

#### **Methods**

Both the DATI-1 and 2 risk assessments used air toxics monitoring data collected in the Detroit area to characterize exposures from toxic chemicals present in the ambient air. The monitoring data was collected from fixed site ambient air monitoring stations. Monitoring data for 60 compounds were evaluated in DATI-2, including metals, volatile organic compounds, semi-volatile organic compounds, and carbonyl compounds. Monitoring occurred at seven Detroit area sites, including six located in Wayne County and one in Oakland County. In addition, data from two additional sites were analyzed to provide comparisons of Detroit to other areas in Michigan. These included a site in Washtenaw County (Ypsilanti) that provides data from a smaller urban area located in a predominantly upwind direction from Detroit, and a site located in rural central Michigan near Houghton Lake.

Only exposures via inhalation were evaluated as part of the risk assessment. Other routes of exposure such as consumption of contaminated food or water, dermal exposures, and other exposures that may occur from deposition of air toxics to land and water were not included in this assessment.

Adverse effects including cancer and non-cancer were evaluated as part of both DATI-1 and DATI-2 projects. In general, risk assessment guidance developed by the U.S. Environmental Protection Agency, or methodologies for implementation of Michigan Department of Natural Resources and Environment Quality air toxic programs, were used to evaluate health risks from exposure to the monitored levels of air toxics.

# STAKEHOLDER GROUP

Part of the grant effort included the development of a community stakeholder group formed to help determine the best strategy for communicating findings of the risk assessment. The final group of 16 members consisted of representatives from government, industry, academia, non-governmental organizations and a community activist. Four meetings were held to assist with development of the communication strategy. The questions posed to the group at the first meeting included: what media would be best used for public outreach; how should the analysis be described for easy understanding; how shall we describe that less data is available for analysis in the DATI-2 project; and whether criteria pollutant data should be included in the

analysis? The group provided invaluable suggestions on formatting and distributing the results. In addition to this full risk assessment report, both a public summary and technical summary will be developed and distributed to a variety of community organizations, academia and nongovernmental organizations. Presentations will be provided at the request of individual groups as resources allow.

# **RESULTS**

<u>**Cancer Risk</u>**: The ambient air levels of 9 chemicals were associated with increased cancer risks of  $1 \times 10^{-6}$  (1 in one million) or higher at one or more monitoring site. These 9 chemicals and their highest estimated risk at any one site are shown in Figure ES-1 below. For comparison purposes, the 14 chemicals from DATI-1 are also included. Again, not all chemicals were monitored during the DATI-2 period as a result of budget reductions.</u>

Incremental Increase in Lifetime Cancer Risk	Pollutants from DATI-1	Pollutants from DATI-2
100 to 400 in one million	methylene chloride naphthalene benzene	
10 to 100 in one million	acrylonitrile formaldehyde 1,4-dichlorobenzene arsenic	formaldehyde benzene
1 to 10 in one million	carbon tetrachloride 1,3-butadiene acetaldehyde cadmium nickel	arsenic cadmium* acetaldehyde* 1,3-butadiene* carbon tetrachloride chloroform naphthalene**
0 to 1 in a million	hexavalent chromium chloroform	hexavalent chromium nickel 1,4-dichlorobenzene acrylonitrile methylene chloride

Figure ES-1 Risk Bin Changes from DATI-1 to DATI-2

\*Although in the same risk bin, concentrations and risks declined from DATI-1

\*\* Not sampled during DATI-2 period. Risk is based on 2005 annual average air concentration

Elevated cancer risk from diesel particulate matter (DPM) was found in both the DATI-1 and DATI-2 studies, however, these risks were not included in the above estimates and comparisons due to the greater uncertainty associated with determining DPM ambient concentrations, estimating risks, and the limited number of sites with surrogate monitoring data. Although these estimated values are relatively uncertain, they serve to provide a general sense of the contribution DPM may add to the cancer risk from air toxics in the Detroit area. The DATI-2 concentration range resulted in an estimated increased cancer risk in of approximately 200 X 10<sup>-6</sup> associated with the estimated levels at Allen Park, the only site with available surrogate (i.e., elemental carbon) data for comparison. In contrast, the DATI-1 risk estimate was over 300 x 10<sup>-6</sup>. These estimated ranges of cancer risk are considered to have significant uncertainty. However, they suggest that diesel emissions may be a significant risk driver in the context of the total cancer risks estimated in this report for the other Detroit-area air toxics.

<u>Non-Cancer Effects</u>: With regard to non-cancer effects, only one compound, manganese exceeded the health protective benchmark values (HQ > 1) at certain sites. **Figure ES-2** shows this information.



Figure ES-2 Hazard Quotient Comparisons for Manganese

As shown in **Figure ES-2**, annual average manganese concentrations at four Detroit sites (South Delray, Dearborn, North Delray, and River Rouge) were 1.5 to 5.5 times higher than the chronic health benchmark value of 0.05  $\mu$ g/m<sup>3</sup> in DATI-1. However, in the DATI-2 time frame, concentrations and hazard quotients fell at every location. There was a slight increase at the Ypsilanti site – however, the levels still did not exceed the hazard quotient of 1.

While the monitored levels of manganese were greater than the chronic health benchmark value at these four sites, they have declined since the DATI-1 study. As noted in the DATI-1 report, the health-based value is set significantly below actual exposure concentrations known to cause adverse effects in humans. Setting a health benchmark value in this manner is done to help ensure that sensitive members of the population (such as the sick, young, and elderly) are protected for a lifetime of exposure to manganese, even though data on effects are only available for healthy adult workers exposed for just a portion of their lifetime. This reduction in the margin of safety between the actual effect levels of manganese and the chronic health

benchmark value is still a concern. This concern is elevated further when considering the suggestive evidence in experimental animals for manganese accumulation in the brain, even at relatively low, environmentally relevant exposures. For sites where historical data are available, annual averages continuing above the benchmark are a concern.

In response to the elevated manganese in the DATI-1 study, the AQD formed a workgroup to address the environmental impacts of manganese in Southeast Michigan. Objectives of the workgroup included performing an analysis of emissions from existing sources and reducing emissions from existing sources where possible. While manganese has traditionally been monitored at the TSP fraction, the PM<sub>10</sub> fraction is now being monitored, and this is the size fraction that will be compared to the Initial Threshold Screening Level (ITSL). Correlations will be drawn between the TSP and PM<sub>10</sub> manganese concentrations. The Manganese Workgroup report is due out by the end of 2010. Elevated manganese is also of concern at some locations in Ohio. The Ohio Environmental Protection Agency (Ohio EPA) is also conducting a manganese initiative. Further information is available on levels found in Ohio in Section 9 and at the Ohio EPA website: <a href="http://www.epa.ohio.gov/dapc/atu/atu.aspx">http://www.epa.ohio.gov/dapc/atu/atu.aspx</a>

<u>Uncertainty</u>: Areas of uncertainty exist in all of the primary steps of the risk assessment – monitoring data collection, as well as in deriving estimates of exposure and toxicity. Substantial uncertainties are present, despite the application of state-of-the-art monitoring methods, inclusion of the air toxics of highest interest, a well-designed and extensive monitoring protocol, and the use of the best available health protective benchmarks.

<u>Comparison of Detroit to Other Areas</u>: The Detroit-area monitoring data were compared to the findings of other air toxics monitoring initiatives for other cities in the U.S. The comparison indicates that:

- a) The pollutants creating the greatest risks vary across the cities studied; however, formaldehyde was a risk driver in nearly all cities reviewed.
- b) The high levels of manganese noted above are generally relatively high in comparison to the other cities except for locations in Ohio which are the focus of special studies.
- c) some studies reported higher levels of the compounds of greatest concern in Detroit, some were comparable, and others were lower; and,
- d) There was a lot of variability in the levels of some of the compounds of concern across the Detroit-area sites, while other cities had more consistency across sites.

# **CONCLUSION**

The risk assessment update termed DATI-2 started with monitoring data for 60 chemicals. From this list of chemicals, 13 chemicals had been identified in DATI-2 as posing the greatest concern. In addition to these 13 air toxics, this assessment also indicates that diesel exhaust may be an important pollutant to focus on for mitigation of air toxics health risks. The current study found that, overall, concentrations fell for the compounds of concern from DATI-1. The causes for the declines are not definitively known, but it is believed that business closures, reduced traffic and air quality control measures are responsible for the reductions.

# 1. INTRODUCTION AND OVERVIEW

The purpose of this report is to provide an update of the assessment of risk from air toxics in the Detroit area and to identify pollutants and sources (when feasible) of greatest concern. The current assessment is designed to describe changes in the risks associated with air pollutant exposure from the original Detroit Air Toxics Initiative (DATI-1). The original (DATI-1) project was initiated by the former Michigan Department of Environmental Quality, now the Michigan Department of Natural Resources and Environment (DNRE), Air Quality Division (AQD). It was funded through the U.S. Environmental Protection Agency's (EPA's) Fiscal Year 2003 Community Assistance and Risk Reduction Initiative. The risk assessment performed for the DATI-1 focused on air toxics monitoring data from the Detroit Pilot Air Monitoring Project, which measured concentrations of toxic chemicals present in the ambient air. The Detroit Pilot Project was an intensive one-year air toxics monitoring study in the Detroit area that ran from April 2001 through April 2002. The Detroit Pilot was funded by the EPA and was a predecessor of the DATI-1-1 as well as to this community air toxics monitoring grant project. The current initiative provides an analysis of air monitoring data from 2006-2007. Air toxics measurements were reduced significantly after this time period as the result of budget cuts. Therefore, not all chemicals could be compared for all monitoring locations.

The aim of this study is to determine if the risk levels, risk drivers or spatial differences have changed appreciably since 2002. A stakeholder group including representatives from the community and Region 5 EPA has reviewed the findings. This stakeholder group has been involved in determining the best method for communicating the findings of this study to the general public.

# 2. AIR TOXICS

Chemicals are emitted to the air from many sources. It is common to reference smoke stacks (or point sources) as the primary source of air pollutants; however, they are also emitted from area sources (clusters of smaller sources that can emit pollutants; e.g., dry cleaners or gas stations) or mobile sources (e.g., sources that are not stationary and emit combustion pollutants such as trucks, cars, and rail engines). The EPA regulates six "criteria" pollutants individually that are of concern in the general (or ambient) air. The six criteria pollutants (carbon monoxide, sulfur dioxide, nitrogen oxides, lead, particulate matter and ozone) are considered separately from toxic air pollutants (air toxics).

Generally, air toxics are classified as either gases or particles. The different classes of compounds are measured using different analytical methods, as described in the next Section. Particles are further segregated by particle size as the smaller particles can get deeper into the lungs and cause more damage. Particles measured for air quality purposes are classified as either total suspended particulate matter (TSP); coarse particulate matter (PM less than 10 microns in diameter, or  $PM_{10}$ ) or fine particulate matter (PM less than 2.5 microns in diameter, or  $PM_{2.5}$ ). An illustration of relative particle sizes is provided in the diagram below



Under the Federal Clean Air Act, Section 112, toxic air pollutants are regulated principally via a discrete list of 188 substances called hazardous air pollutants, or HAPs. In Michigan, toxic air pollutants are regulated under the Michigan Natural Resources and Environmental Protection Act 451, Part 2, R 336.1224-1231 and are termed toxic air contaminants (TACs). Air toxics are pollutants, aside from the criteria pollutants, that are known or suspected to have the capability of causing cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects, and are the subject of this report. Air "toxics" included in this grant includes 60 chemicals monitored by the AQD as shown in **Table 1**.

Metals	VOCs		
Arsenic		Acrolein	Trichloroethene
Barium	1,1,1-Trichloroethane	Acrylonitrile	Hexachloro-1,3-Butadiene
Beryllium	1,1,2,2-Tetrachloroethane	Benzene	Methyl Ethyl Ketone
Cadmium	1,1,2-Trichloroethane	o-xylene	Methyl Isobutyl Ketone
Chromium	1,1-Dichloroethane	Bromoform	Methyl Methacrylate
Chromium VI	1,1-Dichloroethene	Bromomethane	Methyl Tert-Butyl Ether
Cobalt	1,2,4-Trichlorobenzene	Carbon Disulfide	Methylene Chloride
Copper	1,2-Dibromoethane	Carbon Tetrachloride	n-Hexane
Iron	1,2-Dichloroethane	Chlorobenzene	
Lead	1,2-Dichloropropane	Chloroethane	Carbonyls
Manganese	1,3-Butadiene	Tetrachloroethene	Acetaldehyde
Mercury	1,4-Dichlorobenzene	Chloromethane	Formaldehyde
Molybdenum	2,2,4-Trimethylpentane	Chloromethyl Benzene	Propionaldehyde
Nickel	2-Chloro-1,3-Butadiene	Ethyl Acrylate	
Vanadium	Acetonitrile	Ethylbenzene	
Zinc	Chloroform	Vinyl Chloride	
	Toluene	Styrene	

Air toxics measurements of ambient air in Detroit have been taken for several years. The DATI-1<sup>1</sup> risk assessment and risk reduction project was based on 2001-2002 air toxics monitoring data for the greater Detroit metropolitan area as well as background sites. That assessment identified key drivers or causes of human health inhalation risks and locations that had relatively high risk estimates. The AQD conducted the monitoring and risk assessment in consultation with EPA Region 5 and a stakeholder group. Those findings are presented in a public summary, a technical summary, and a fully detailed report<sup>1</sup>. A summary of findings from the DATI-1-1 study can be found in Appendix A. As analysis methods have improved and changed, a more diverse set of measurements have been collected. The current data analysis project follows up on the detailed analysis of risk conducted in the DATI-1 project using 2001-2002 data and analyzes risk approximately five years later.

# 3. AIR TOXICS MONITORING

This follow-up risk assessment to the DATI-1 used air toxics monitoring data collected in the Detroit area to characterize exposures from toxic chemicals present in the ambient air. The DNRE conducts air monitoring for toxics and/or fine particulate matter (which can be separately analyzed by individual chemical species) at 13 locations statewide. Monitoring sites studied for the present risk assessment include eight in the greater Detroit area: Allen Park, Northeast Detroit (N.E. Detroit, also called East 7 Mile), River Rouge, South Delray (S. Delray), Dearborn, Southfield (also called Lodge), Ypsilanti and North Delray (N. Delray, also called Southwestern High School). The Ypsilanti site serves as an urban background monitor. Houghton Lake is used as a background monitor to examine differences between the Detroit area sites and a site in a rural, non-industrial setting. These sites were selected since they were evaluated in the DATI-1 project (see **Figure 1** and **Figure 2**).

The seven monitoring locations for DATI shown in **Figure 1** below include six in Wayne County and one in Oakland County. **Figure 2** shows all monitoring locations, including the background sites at Houghton Lake (rural) and Ypsilanti (urban).

<sup>&</sup>lt;sup>1</sup> See <u>http://www.michigan.gov/deq/0,1607,7-135-3310\_4105-139044--,00.html</u> for more on the Detroit Air Toxics Initiative (DATI) Fiscal Year '03 Community Assistance and Risk Reduction Grant.



Figure 1. DATI Monitoring Stations in Wayne and Oakland Counties

Figure 2. DATI Monitoring Stations



The key time period of monitoring data for this risk assessment included approximately 12 months of air monitoring; 2/28/2006 through 3/28/2007. This time frame 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. This is reflected in **Table 2** where spaces do not contain information about DATI-2. As a result, not all chemicals were collected at these sites during DATI-2. For this risk assessment effort, the primary focus is on

those sites and chemicals common to both the DATI-1 risk assessment and this project (see **Table 2**). Dearborn and North Delray had the most types of samples (e.g., VOC, Carbonyl and Metal) in common for comparing DATI-1 and DATI-2.

	Chemical Classification						
Site Name	Metal	Carbonyl	voc	Cr +6	SVOC		
Allen Park	1 & 2	DATI-1	DATI-1	DATI-1	DATI-1		
Dearborn	1 & 2	1 & 2	1 & 2	1 & 2	DATI-1		
Houghton Lake	1 & 2	1 & 2	DATI-2				
N. Delray (SWHS)	1 & 2	1 & 2	1 & 2		DATI-1		
NE Detroit	1 & 2	DATI-1			DATI-1		
River Rouge	1 & 2	1 & 2	DATI-1	DATI-1	DATI-1		
S. Delray	1 & 2	DATI-1	DATI-1		DATI-1		
Ypsilanti	1 & 2	1 & 2	DATI-2				
Lodge	DATI-1	DATI-1	DATI-1	DATI-1	DATI-1		

Table 2. Locations and Types of Air Sampling Used During DATI-1 and DATI-2

Chemicals are divided into groupings based on the type of laboratory method used for analysis of the monitoring media. A description of each group of compounds is provided below.

# <u>Metals</u>

Metals are inorganic chemicals emitted as particles of various sizes. The size of the particle influences how deeply the particle can penetrate into the lungs. The different sized particles consequently present different potential toxicities due to varying size fractions. Therefore, particles are sampled using different size categories. Total suspended particles (TSP) are particles with an aerodynamic diameter less than 50 micrometers ( $\mu$ m). These larger particles do not remain in the air as long and do not penetrate as deeply into the lungs. Therefore, the health risk is usually less than smaller size fractions. PM<sub>10</sub> includes particles with aerodynamic diameter less than 2.5 µm. Metal samples are collected by drawing air through a size-selective inlet and depositing them onto different types of filters. The metal chemicals are extracted from the filters, digested and analyzed using either inductively coupled plasma mass spectrometry, inductively coupled atomic emission spectroscopy or x-ray fluorescence spectroscopy. Filters from some of the fine particulate monitoring sites are also analyzed for particulate precursors such as sulfate, nitrate, organic carbon, and elemental carbon or trace metals.

# <u>Carbonyls</u>

Carbonyls are organic compounds that are less volatile and more polar compounds than the volatile organics described below. They contain either a ketone or aldehyde functional group.

Polar compounds cannot be analyzed in the laboratory the same way as non-polar compounds. Therefore, carbonyl compounds are collected by passing air through a silica gel-filled cartridge treated with a chemical that creates a colorimetric reaction. The cartridges are extracted with a solvent and analyzed using high pressure liquid chromatography with a fluorescence detector. Carbonyls are generally respiratory irritants. In this report, carbonyls of principle concern are acetaldehyde and formaldehyde. Both are carcinogenic with effects in the respiratory tract.

# <u>VOCs</u>

Volatile organic compounds (VOCs) are organic chemicals that readily produce vapors at room temperature and normal atmospheric pressure, including gasoline and solvents such as toluene, xylene, and tetrachloroethylene ("perc"). They form photochemical oxidants (including ground-level ozone) that affect health, damage materials, and cause crop and forest losses. Many are also hazardous air pollutants. The samples are collected by filling 6 liter stainless steel summa canisters with air, which is then analyzed using gas chromatography/mass spectrometry.

#### Hexavalent Chromium (Cr+6)

This chemical is technically in the metal category as total chromium. However, the valence state of the element of +6 is of most concern from a health standpoint as it is considered to be a carcinogen at quite low levels. Not all monitoring stations measure the individual valence states of chromium. **Table 2** contains the column to indicate which sites can detect hexavalent chromium, specifically.

# <u>SVOCs</u>

Semi-volatile organic compounds are organic chemicals that less readily produce vapors at room temperature and pressure. Examples include naphthalene or polynuclear aromatic hydrocarbons (PAHs) such as benzo(a)pyrene and phthalates such as bis(2-ethylhexyl)phthalate. The classification of chemicals into groups such as volatile and semi-volatile relates to the method used to detect them on analysis as well as describing their behavior in the environment.

# 4. POTENTIAL CONCERNS FROM AIR TOXICS

Exposure to air toxics in urban areas may be of appreciable concern because people and sources of emissions are concentrated in the same geographic area. As noted in Section 2, air toxics have the potential to cause serious health effects if exposures are excessive. Understanding which air toxics in an urban area contribute the most to potential health risks can provide valuable information in developing strategies to reduce these risks. A brief summary of available data on each of the chemicals determined as priority for this study (see Section 5 Methods for Comparing Risk for description) is provided below. Note: the effects described below in people were discovered primarily by examining individuals whose exposure was in the workplace, or extrapolated from findings in animal studies. The exposure levels in these studies were generally higher than those found in the environment. In order to extrapolate down to lower levels of exposure, the process of risk assessment is used, as described in Section 5.

**Acetaldehyde -** Acetaldehyde is ubiquitous in the ambient environment. Acetaldehyde is mainly used as an intermediate in the synthesis of other chemicals. It may be formed in the body from the breakdown of ethanol. It is an intermediate product of higher plant respiration and formed as a product of incomplete wood combustion in fireplaces and woodstoves, coffee

roasting, burning of tobacco, vehicle exhaust fumes, and coal refining and waste processing. Residential fireplaces and woodstoves are the two highest sources of emissions, followed by various industrial emissions. Acute (short-term) exposure to acetaldehyde results in effects including irritation of the eyes, skin, and respiratory tract. Symptoms of chronic (long-term) intoxication of acetaldehyde resemble those of alcoholism. Acetaldehyde is considered a probable human carcinogen based on inadequate human cancer studies and animal studies that have shown nasal tumors in rats and laryngeal tumors in hamsters.

**Acrylonitrile -** Exposure to acrylonitrile is primarily occupational; it is used in the manufacture of acrylic acid and modacrylic fibers. Acrylonitrile may be released to the ambient air during its manufacture and use. Acute exposure of workers to acrylonitrile has been observed to cause mucous membrane irritation, headaches, dizziness, and nausea. No information is available on the reproductive or developmental effects of acrylonitrile in humans. Based on limited evidence in humans and evidence in rats, EPA has classified acrylonitrile as a probable human carcinogen.

**Arsenic** – A naturally occurring element, arsenic is found throughout the environment; for most people, food is the major source of exposure. Certain forms of arsenic (i.e., inorganic) are mainly used to preserve wood. Copper chromated arsenate (CCA) is used to make "pressure-treated" lumber. CCA is no longer allowed for residential uses in the U.S.; it is still used in industrial applications. Organic arsenic compounds are used as pesticides, primarily on cotton fields and orchards. Breathing high levels of inorganic arsenic can give you a sore throat or irritated lungs. Nervous system disorders have occurred in workers acutely exposed to inorganic arsenic. Breathing low levels of inorganic arsenic for a long time can cause a darkening of the skin and the appearance of small "corns" or "warts" on the palms, soles, and torso. Almost nothing is known regarding health effects of inhaled organic arsenic compounds are less toxic than inorganic forms. Inorganic arsenic exposure in humans, by the inhalation route, has been shown to be strongly associated with lung cancer, while ingestion of inorganic arsenic in humans has been linked to a form of skin cancer and also to bladder, liver, and lung cancer. Inorganic arsenic has been classified as a human carcinogen.

Benzene – Benzene is found in the air from emissions from burning coal and oil, gasoline service stations, and motor vehicle exhaust. Acute inhalation exposure of humans to benzene may cause drowsiness, dizziness and headaches, as well as eye, skin and respiratory tract irritation, and, at high levels, unconsciousness. Chronic inhalation exposure has caused various disorders in the blood in individuals working in industries that use the chemical. Reproductive effects have been reported for women exposed by inhalation to high levels, and adverse effects on the developing fetus have been observed in animal tests. Some women who breathed high levels of benzene for many months had irregular menstrual periods and a decrease in the size of their ovaries, but we do not know for certain that benzene caused the effects. It is not known whether benzene will affect fertility in men. Increased incidences of leukemia (cancer of the tissues that form white blood cells) have been observed in humans occupationally exposed to benzene. Benzene has been classified as a human carcinogen. Benzene can cause harmful effects on the bone marrow and can cause a decrease in red blood cells leading to anemia. It can also cause excessive bleeding and can affect the immune system, increasing the chance for infection. It is important to note, however, that exposure to ambient levels of benzene will not result in most health effects noted above.

**1,3-Butadiene** – About 75 percent of manufactured 1,3-butadiene is used to make synthetic rubber. Synthetic rubber is widely used for tires on cars and trucks. 1,3-Butadiene is also used to make plastics including acrylics. Small amounts are found in gasoline. Most of the

information on the health effects of 1,3-butadiene comes from studies where the exposure was from breathing contaminated air. Breathing very high levels of 1,3-butadiene for a short time can cause central nervous system damage, blurred vision, nausea, fatigue, headaches, decreased blood pressure and pulse rate, and unconsciousness. There are no recorded cases of accidental exposures at high levels that resulted in death in humans, but this could occur. Breathing lower levels may cause irritation of the eyes, nose and throat. Studies of workers who had longer exposures with lower levels have shown an increase in heart and lung damage. but these workers were also exposed to other chemicals. We do not know for sure which chemical (or chemicals) caused the effects. We also do not know what levels in the air will cause these effects in people when breathed over many years. Animal studies show that breathing 1,3-butadiene during pregnancy can increase the number of birth defects. Other effects seen in animals that breathed low levels of 1,3-butadiene for one year include kidney and liver disease and damaged lungs. Some of the animals died, 1.3-butadiene may reasonably be anticipated to be a carcinogen. This is based on animal studies that found increases in a variety of tumor types from exposure to 1,3-butadiene. Studies on workers are inconclusive because the workers were exposed to other chemicals in addition to 1,3-butadiene.

**Cadmium** – Soils and rocks, including coal and mineral fertilizers, contain some cadmium. The main sources of cadmium in the air are the burning of fossil fuels such as coal or oil and the incineration of municipal waste. Cadmium does not corrode easily and has many uses, including batteries, pigments, metal coatings, and plastics. The general population is exposed from breathing cigarette smoke or eating cadmium contaminated foods. The acute effects of cadmium in humans through inhalation exposure consist mainly of effects on the lung, such as pulmonary irritation. Chronic inhalation or oral exposure to cadmium leads to a build-up of cadmium in the kidneys that can cause kidney disease. Other long-term effects from excess exposure include the development of fragile bones. Cadmium has been shown to be a developmental toxicant in animals, resulting in fetal malformations and other effects, but no conclusive evidence exists in humans. An association between cadmium exposure and an increased risk of lung cancer has been reported from human studies, but these studies are inconclusive due to confounding factors such as exposures to other chemicals. Animal studies have demonstrated an increase in lung cancer from long-term inhalation exposure to cadmium. The EPA has classified cadmium as a probable human carcinogen.

**Carbon Tetrachloride** – Carbon tetrachloride may be found in both ambient outdoor and indoor air. Carbon tetrachloride is most often found in the air as a colorless gas. It is not flammable and does not dissolve in water very easily. It was used in the production of refrigeration fluid and propellants for aerosol cans, as a pesticide, as a cleaning fluid and degreasing agent, in fire extinguishers, and in spot removers. Because of its harmful effects, these uses are now banned and it is only used in some industrial applications. High exposure to carbon tetrachloride can cause liver, kidney, and central nervous system damage. Human symptoms of acute inhalation and oral exposures to carbon tetrachloride include headache, weakness, lethargy, nausea, and vomiting. These effects can occur after ingestion or breathing carbon tetrachloride, and possibly from exposure to the skin. The liver is especially sensitive to carbon tetrachloride because it enlarges and cells are damaged or destroyed. Kidneys also are damaged, causing a build up of wastes in the blood. If the exposure is low and brief, the liver and kidneys can repair the damaged cells and again function normally. Effects of carbon tetrachloride are more severe in persons who drink large amounts of alcohol. Studies in humans have not been able to determine whether or not carbon tetrachloride can cause cancer because usually there has been exposure to other chemicals at the same time. Swallowing or breathing carbon tetrachloride for years caused liver tumors in animals. Mice that inhaled carbon tetrachloride also developed tumors of the adrenal gland. The EPA has classified carbon tetrachloride as a probable human carcinogen.

**Chloroform** – Chloroform may be released to the air as a result of its formation in the chlorination of drinking water, wastewater and swimming pools. Other sources include pulp and paper mills, hazardous waste sites, and sanitary landfills. Exposure to chloroform can occur when breathing contaminated air or when drinking or touching the substance or water containing it. Breathing high levels (e.g., 900 ppm) of chloroform can cause dizziness, fatigue, and headaches. Breathing chloroform or ingesting chloroform over long periods of time may damage your liver and kidneys. It can cause sores if large amounts touch your skin. The major effect from acute inhalation exposure to chloroform is central nervous system depression. Chronic exposure to chloroform by inhalation in humans has resulted in effects on the liver, including hepatitis and jaundice, and central nervous system effects, such as depression and irritability. It is not known whether chloroform causes reproductive effects or birth defects in people. Animal studies have shown that miscarriages occurred in rats and mice that breathed air containing 30 to 300 ppm chloroform during pregnancy and also in rats that ate chloroform during pregnancy. Offspring of rats and mice that breathed chloroform during pregnancy had birth defects. Abnormal sperm were found in mice that breathed air containing 400 ppm chloroform for a few days. Chloroform has been shown to be carcinogenic in animals after oral exposure, resulting in an increase in kidney and liver tumors. The EPA has classified chloroform as a probable human carcinogen.

**Chromium** – Chromium occurs in the environment primarily in two valence states, trivalent chromium (Cr III) and hexavalent chromium (Cr VI). Exposure may occur from natural or industrial sources of chromium. Chromium III is much less toxic than chromium (VI). The respiratory tract is also the major target organ for chromium (III) toxicity, similar to chromium (VI). Chromium (III) is an essential element in humans. The body can detoxify some amount of chromium (VI) to chromium (III). Shortness of breath, coughing, and wheezing were reported from a case of acute exposure to chromium (VI), while perforations and ulcerations of the septum, bronchitis, decreased pulmonary function, pneumonia, and other respiratory effects have been noted from chronic exposure. The concentrations of chromium in air that can cause these effects may be different for different types of chromium compounds, with effects occurring at much lower concentrations for chromium (VI) compared to chromium (III). However, the concentrations causing respiratory problems in workers are at least 60 times higher than levels normally found in the environment.

**1,4 Dichlorobenzene -** 1,4-Dichlorobenzene is used mainly as a fumigant for the control of moths, molds, and mildews, and as a space deodorant for toilets and refuse containers. 1,4-Dichlorobenzene is also used as an intermediate in the production of other chemicals, in the control of tree-boring insects, and in the control of mold in tobacco seeds. The general population is mainly exposed to 1,4-dichlorobenzene through breathing vapors from 1,4-dichlorobenzene products used in the home, such as mothballs and toilet deodorizer blocks. The median indoor air concentration of 1,4-dichlorobenzene, via inhalation in humans, results in irritation of the skin, throat, and eyes. Chronic 1,4-dichlorobenzene inhalation exposure in humans results in effects on the liver, skin, and central nervous system (CNS). No information is available on the reproductive, developmental, or carcinogenic effects of 1,4-dichlorobenzene caused kidney tumors in male rats and liver tumors in both sexes of mice by gavage (experimentally placing the chemical in their stomachs). The EPA has classified 1,4-dichlorobenzene as possible human carcinogen.

**Formaldehyde** – Formaldehyde is used mainly to produce resins used in particleboard products and as an intermediate in the synthesis of other chemicals. It is also used as a

preservative in some foods and in many products used around the house, such as antiseptics, medicines, and cosmetics. Exposure to formaldehyde may occur by breathing contaminated indoor air, tobacco smoke, or ambient urban air. Acute and chronic inhalation exposure to formaldehyde in humans can result in respiratory symptoms, and eye, nose, and throat irritation. It is possible that people with asthma may be more sensitive to the effects of inhaled formaldehyde. Limited human studies have reported an association between formaldehyde exposure and lung and nasopharyngeal cancer. Some studies of people exposed to formaldehyde in workplace air found more cases of cancer of the nose and throat than expected, but other studies did not confirm this finding. In animal studies, rats exposed to high levels of formaldehyde in air developed nose cancer. Animal inhalation studies have reported an increased incidence of nasal cancer. Formaldehyde has been determined to be a probable human carcinogen.

**Manganese** – Manganese is a naturally occurring metal that is found in many types of rocks. Manganese is used principally in steel production to improve hardness, stiffness, and strength. It may also be used as an additive in gasoline to improve the octane rating of the gas. Manganese is an essential nutrient, and eating a small amount of it each day is important to stay healthy. However, inhaling manganese does not provide the body benefits and can be harmful to the brain and nervous system. Workers exposed to inhaled manganese have had health effects include behavioral changes and other nervous system effects, which include movements that may become slow and clumsy. This combination of symptoms when sufficiently severe is referred to as "manganism." Manganism is characterized by feelings of weakness and lethargy, tremors, a mask-like face, and psychological disturbances. Visual reaction time, hand steadiness, and eve-hand coordination were affected in chronically-exposed workers. Impotence and loss of libido have been noted in male workers afflicted with manganism. Other less severe nervous system effects such as slowed hand movements have been observed in some workers exposed to lower concentrations in the work place. Nervous system and reproductive effects have been observed in animals after high oral doses of manganese.

**Methylene Chloride -** Methylene chloride is predominantly used as a solvent. Methylene chloride is predominantly used as a solvent in paint strippers and removers; as a process solvent in the manufacture of drugs, pharmaceuticals, and film coatings; as a metal cleaning and finishing solvent in electronics manufacturing; and as an agent in urethane foam blowing. Methylene chloride is also used as a propellant in aerosols for products such as paints, automotive products, and insect sprays. Occupational and consumer exposure to methylene chloride in indoor air may be higher than from ambient air, especially from spray painting or other aerosol uses. People who work in these places can breathe in the chemical or it may come in contact with the skin. The acute effects of methylene chloride inhalation in humans consist mainly of nervous system effects including decreased visual, auditory, and motor functions, but these effects are reversible once exposure ceases. The effects of chronic exposure to methylene chloride suggest that the central nervous system (CNS) is a potential target in humans and animals. Human data are inconclusive regarding methylene chloride and cancer. Animal studies have shown increases in liver and lung cancer and benign mammary gland tumors following the inhalation of methylene chloride.

**Naphthalene -** Exposure to naphthalene happens mostly from breathing air contaminated from the burning of wood, tobacco, or fossil fuels, industrial discharges, or moth repellents. Acute (short-term) exposure of humans to naphthalene by inhalation, ingestion, and dermal contact is associated with hemolytic anemia (may damage or destroy some of your red blood cells), damage to the liver, and neurological damage. Cataracts have also been reported in workers acutely exposed to naphthalene by inhalation and ingestion. Chronic (long-term) exposure of

workers and rodents to naphthalene has been reported to cause cataracts and damage to the retina. Hemolytic anemia has been reported in infants born to mothers who "sniffed" and ingested naphthalene (as mothballs) during pregnancy. Naphthalene has caused cancer in animals. Michigan regulates naphthalene as a carcinogen in the Air Pollution Control Rules.

**Nickel** – Nickel occurs naturally in the environment at low levels. Nickel is an essential element in some animal species, and it has been suggested it may be essential for human nutrition. Nickel may be released to the environment from the stacks of large furnaces used to make alloys or from power plants and trash incinerators. The nickel that comes out of the stacks of power plants attaches to small particles of dust that settle to the ground or are taken out of the air in rain or snow. It usually takes many days for nickel to be removed from the air. If the nickel is attached to very small particles, it can take more than a month to settle out of the air. Respiratory effects have also been reported in humans from inhalation exposure to nickel. Human and animal studies have reported an increased risk of lung and nasal cancers from exposure to nickel refinery dusts and nickel subsulfide. Animal studies of soluble nickel refinery dust and nickel subsulfide as human carcinogens, and nickel carbonyl as a probable human carcinogens. Human and animal studies have reported an increased risk of lung and nasal for soluble nickel refinery dust and nickel subsulfide as human carcinogens, and nickel carbonyl as a probable human carcinogens. Human and animal studies have reported an increased risk of lung and nasal cancers from exposure to nickel refinery dusts and nickel subsulfide as human carcinogens, and nickel carbonyl as a probable human carcinogens. Human and animal studies have reported an increased risk of lung and nasal cancers from exposure to nickel refinery dusts and nickel subsulfide.

#### **References:**

Agency for Toxic Substances and Disease Registry (ATSDR), Division of Toxicology and Environmental Medicine, ToxFAQs, <u>http://www.atsdr.cdc.gov/toxfaqs/index.asp</u>

U.S. EPA, Technology Transfer Network, Air Toxics Web, <u>www.epa.gov/ttn/atw</u>

# 5. METHODS USED FOR COMPARING RISK

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 Report<sup>1</sup> (p. 26, Section 6.4) and in Heindorf MA, 2005. There were 12 cancer risk drivers or causes and an important non-carcinogen (manganese) identified during DATI -1 (**Table 3**).

Metals	Carbonyls	SVOCs	VOCs
arsenic	acetaldehyde	naphthalene	1,3-butadiene
cadmium	formaldehyde		1,4-dichlorobenzene
manganese (non-carcinogen)			acrylonitrile
nickel			benzene
			carbon tetrachloride
			methylene chloride

#### Table 3. DATI-1 Priority Chemicals

Criteria were then developed to determine which chemicals would be included in the current analysis. The first criterion was whether the chemical was measured in the greater Detroit area during the time frame of interest. The second criterion involved the number of detections as a percentage of number of samples collected. For the purpose of this report, only the substances with at least 15% detection frequencies are considered to be adequately representative of

exposure levels for use in quantitative risk assessment. In other words, if a chemical was not detected in 85% or more of the samples analyzed, it was eliminated from consideration in the current risk assessment. The third criterion for inclusion after determining whether or not the chemical was considered a chemical of concern in the DATI-1 analysis was to make sure that it was potentially a chemical of concern during the second monitoring period. Summary statistics were calculated for all chemicals evaluated. If a chemical was a carcinogen and did not show average risk levels above 1 in a million (the excess risk level determined to be the break point of concern), the chemical is not described as a priority chemical. These criteria were selected to ensure consistency with the DATI-1; to follow the recommendations of the EPA (2004) and to ensure adequate numbers of samples are available to provide a sound analysis. **Table 4** below indicates which chemicals were found with a frequency of detection greater than the 15% inclusion limit.

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

Table 4.	Percent Detected	Above the Method	<b>Detection Limit</b>	for Priority Chemicals

\**ns* = Chemical was not sampled

Concentrations from DATI-1 and DATI-2 are provided in charts showing each chemical and location. The concentrations are described in Section 6. below. Confidence intervals (95%) were developed and show in the midst of concentration bars as vertical lines.

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 Levels (IRSL) is the level at which a carcinogen present in the atmosphere could create an excess of a one-in-a million-risk of cancer incidence in a given population. 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).

When establishing IRSLs, priority is given to using EPA-established inhalation cancer potency values. If the EPA has established an inhalation cancer potency value for a chemical that is published in the Integrated Risk Information System (IRIS), that value is used to establish the IRSL. If there is no inhalation cancer potency value in IRIS, but there is one listed in the EPA's Health Effects Assessment Summary Tables (HEAST), then that value may be used to establish the screening level. If the EPA has not established an inhalation cancer potency value, and there is adequate inhalation toxicity data available, the toxicologist establishes the IRSL using this data and the procedures identified in Rule 229 of the DNRE Air Pollution Control Rules.

 $Risk = \frac{Average...Concentration}{IRSL}$ 

If no inhalation cancer potency value is available from the EPA, or can be determined from the data, the toxicologist evaluates the information available from the oral route of exposure. If the EPA has established an oral potency value in IRIS or HEAST, and data are not available to indicate that oral route to inhalation route extrapolation is inappropriate, this value is used to establish the IRSL. If the EPA has not established an oral potency value, the toxicologist establishes the IRSL following the procedures identified in rule 229 of the DNRE Air Pollution Control Rules. All chemicals with IRSLs are considered to have exposures associated with some level of risk. It has been the policy of DNRE that any cases in excess of an additional 1 in a million, which are attributable to environmental exposures is considered unacceptable risk.

#### 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. ITSLs are set at some fraction of the observable threshold dose determined in studies using laboratory animals or from human data. The fraction or "margin of safety" that is applied depends largely on the quality of the toxicological data base for a specific chemical. When data is judged to be lacking in quality (or quantity) a smaller fraction of the threshold dose is used for the ITSL (Final Report MI Air Toxics, 1989). The IRSL and initial threshold screening level (ITSL) values are available on the DNRE website at http://www.deq.state.mi.us/itslirsl/ and in **Table 5** below.

If a chemical presents a possible risk other than cancer, a hazard quotient (HQ) is developed. The HQ is the level at which no adverse effects are expected. **HQ values less than one indicate no adverse health affects 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.  $Hazard \dots Quotient = \frac{Air \dots Concentration}{----}$ 

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 exist<sup>2</sup>. 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 two 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 <a href="www.michigan.gov/deqair">www.michigan.gov/deqair</a> under the Air Toxics link or directly at <a href="http://www.michigan.gov/documents/DATI\_-">http://www.michigan.gov/deqair</a> under the Air Toxics link or directly at <a href="http://www.michigan.gov/documents/DATI\_-">http://www.michigan.gov/deqair</a> under the Air Toxics link or directly at <a href="http://www.michigan.gov/documents/DATI\_-">http://www.michigan.gov/documents/DATI\_-</a>

<sup>&</sup>lt;sup>2</sup> Uncertainty in the monitoring data is being examined in other data analysis projects.

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

Table 5. Priority Chemicals Identified for DATI-2 and AQD Screening Levels

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 work-group with representatives from the Air Quality Evaluation Section, Permit Section, and Southeast Michigan District Office was formed to work on this effort. The AQD Manganese Workgroup (Workgroup) began meeting in January 2007. The Workgroup was charged with identifying significant sources of manganese air emissions in Southeast Michigan and providing recommendations for further actions to reduce emissions. The final report should be available online by the beginning of 2011.

#### **References:**

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

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

# 6. RESULTS

This section describes how the air monitoring network has evolved since the DATI-1 risk assessment report was prepared. As noted above in Section 2, fewer monitors and fewer chemicals were available for review for the current risk assessment project. As shown in **Table 6** below, due to severe budget reductions in 2007, the following chemicals were **not** monitored at the noted sites during the time frame relevant to DATI-2:

- Allen Park VOCs and Carbonyls (acetaldehyde, formaldehyde, propionaldehyde), hexavalent chromium and SVOCs (e.g., semi-volatile compounds or polynuclear aromatic hydrocarbons (PAHs) such as benzo(a)pyrene and phthalates such as bis(2ethylhexyl)phthalate – see Appendix B for full list.)
- Dearborn Semi-volatile compounds
- N. Delray (SWHS) Semi-volatile compounds
- N.E. Detroit (E. 7 Mile) Carbonyls and semi-volatile compounds
- River Rouge VOCs, hexavalent chromium and semi-volatile compounds
- S. Delray VOCs, Carbonyls and semi-volatile compounds
- Southfield (Lodge/696) No compounds monitored during DATI-2

History of Air Toxics Monitoring in Michigan																			
Trace Metals (C	Once every 6 days)	)		Y	ellov	v ver	tical	bar	s co	mpa	re d	ata s	sets	use	d in	DAT	1-1	and	DATI-2
Site			995	996	997	998	999	000	100	002	003	004	900	900	200	800	000	010	Commente
Flint		260490021	-	-	-	-	-	~	61	~	61	61	~				61	~	
Grand Ranids (C	ollege & Cherov)	260810010																	F
Grand Rapids (C	onroo St)	260810070							ŧ	#									G
Grand Rapids (M	onroe St)	260910020																	G
Mucming	print/ Randolph St)	200010021												ŧ					
Vvyoming Houghton Lako		200012002																	
Muskegen		201130001							-										
Southfield (Lodge	(606)	201210023												ŧ					G
Southileid (Lodge	(696)	201200001												ŧ					
Vecilenti		201330003																	
Allen Dede		201010000												-					G E
Divor Dougo		201030001												-					
River Rouge		201030005							-					-					
N E Detroit (E 7	Mile)	201030015							-					-					
N.L. Detroit (L /	wine)	201030013												-					
Decroit (S Deiray	)	201030027												-					
Dearborn		201030033																	
Carbonyls (Onc	e every 6 days or o	once every 12 da	ys)																1
Site		AQS ID	199	199(	1997	1998	1995	2000	200	2002	2003	200	200	2006	2001	2001	200	2010	Comments
Holland		260050003																	D
Kalamazoo		260770008																	D, E
Grand Rapids (M	onroe St)	260810020																	G
Grand Rapids (S	print/ Randolph St)	260810021												F					G
Houghton Lake		261130001																	1
Southfield (Lodge	/696)	261250001												Ē					G
Ypsilanti		261610008																	G
Allen Park		261630001												Ē					к
River Rouge		261630005																	н
Detroit (N Delray A	KA SW HS)	261630015																	G
N.E. Detroit (E 7	Mile)	261630019												F					D, F
Detroit (S Delray	)	261630027												ŧ					F
Dearborn		261630033																	F
VOCs (Once ever	y 6 days or once e	very 12 days)																	1
			8	8	6	8	66	8	2	6	8	2	8	8	5	8	8	5	
Site		AQS ID	3	19	3	3	3	3	3	8	8	3	2	2	2	3	8	2	Comments
Holland		260050003												L.					D
Kalamazoo		260770008																	D, E
Grand Rapids (M	onroe St)	260810020																	G
Grand Rapids (S	print/ Randolph St)	260810021																	G
Houghton Lake		261130001																	J
Southfield (Lodge	/696)	261250001																	G
Ypsilanti		261610008																	G
Allen Park		261630001																	G
River Rouge		261630005	_																G
Detroit (N Delray A	KA SW HS)	261630015												_					G
N.E. Detroit (E 7	Mile)	261630019																	D,F
Detroit (S Delray	)	261630027																	F
Dearborn		261630033																	F
Key to Comments	8:																		
A:	On 3/31/07 suite c	hanged from Be,	V, 0	Cr, Mr	1, Co,	Ni, C	u, Zn	, As,	Mo,	Cd, B	a, Pb	, Fet	o onl	y: Mn					
C:	PM10 sized trace r	metals also coller	cted	here	1, 00,	141, C	u, 21	, AS,	mo,	Cu, D	a, FL	, 1 - 1		y. As	, cu,	191, 10		++++	
D:	Sampling is on ozo	one action days;	PAM	S site	•														
E:	Data was collected	d using previous	AQS	SIDn	umbe	r: 26	0770	905.	Site I	ocatio	on is	the s	ame						
F: G:	sampling is once e Sampling is once e	every six days	s I	+++	++++	$\parallel \parallel$	$\left  \right  \left  \right $	$\parallel \parallel$		++++	$\parallel \parallel$	$\left  \right  \left  \right $	$\left  \right  \left  \right $	+++		++++	$\parallel \parallel$	+++	
H:	Sampling is once e	every twelve day	's th	rough	2002	2, the	n one	e ev	ery s	six da	ys th	rougi	1 200	7					
l:	Sampling is once e	every twelve day	's thr	rough	2002	2, the	n ond	ce ev	ery s	six da	ys in	2003	, the	n ond	e ev	ery tv	welve	e day	s
J: K·	Sampling is once e Sampling is once e	every twelve day	's thi	rough	2005	o, the the	n ond	ce ev	ery s	six da	ys in vs in	2006	, the	n onc	e ev	ery tv	welve	e day	s
L:	Sampling is once e	every twelve day	is un is thr	rough	2004	, the ), the	n ond	ce ev	ery s	six da	ys ⊪ ys th	roual	1       1 201	0	$\parallel \parallel$	$\parallel \parallel \mid$			

# **Table 6.** Monitoring Dates, Location and Frequency

When the Detroit Pilot Project was conducted in 2001 to 2002, the DNRE operated nine sites in southeast Michigan as well as a background site at Houghton Lake. Parameters measured included: VOCs, carbonyls, trace metals as TSP, PAHs and hexavalent chromium. Sampling occurred on various intervals, depending on the site, and ranged from daily to once every 12 days. Changes to the air toxics monitoring network are summarized in **Table 6**.

With the completion of the Pilot Project, the Southfield (696/Lodge) site was shut down. This site was included in the pilot project so data from the Allen Park mobile source oriented site could be compared to another mobile source oriented site. Monitoring activities were reduced to measuring VOCs, carbonyls and trace metals as TSP at five sites. The sampling frequency was reduced to once every six days at most sites, with once every 12 day sampling occurring at a few.

In the intervening years since the pilot project, additions have been made to the monitoring network as well as cuts. Trace metals as  $PM_{10}$  were added to the National Air Toxics Trend Site at Dearborn in 2003. Hexavalent chromium was added to Dearborn in 2004. Two new sites were established at Newberry and 2000 W. Lafayette to investigate levels of particulate downwind from the proposed Detroit Intermodal Freight Terminal (DIFT) and from the Ambassador Bridge in 2005. In 2006, the DNRE began collecting filter blanks to determine levels of contamination on quartz and glass fiber filters. PAHs were added to the NATTS site at Dearborn in 2008.

The most appreciable changes to the monitoring network occurred on April 1, 2007, when monitoring activities were discontinued at a number of monitoring stations due to the budget reductions. The suite of 14 trace metals was reduced to measuring only manganese, arsenic, cadmium and nickel at Allen Park, N Delray (SWHS), S. Delray and River Rouge. Trace metals monitoring was totally eliminated at Grand Rapids, the background site at Houghton Lake, Ypsilanti and N.E. Detroit (E. 7 Mile) in Detroit. Trace metals monitoring at Flint was decreased to only manganese. VOC monitoring was completely discontinued at Grand Rapids, Ypsilanti and the background site at Houghton Lake. Monitoring for carbonyls was completely discontinued at Grand Rapids, Ypsilanti and the background site at Houghton Lake.

#### Methylene Chloride

In the DATI-1 analysis, elevated levels of methylene chloride were observed at Allen Park. The elevated concentrations appeared at random, indicating that there were no contamination issues at the site or laboratory. Two samples were collected and sent to two different laboratories, which confirmed that the levels were indeed elevated. Therefore, these concentrations were determined to be true values. However, a source of the methylene chloride could not be positively identified. Between 2002 and 2005, additional sampling was performed to confirm the elevated concentrations of methylene chloride had disappeared.

#### Naphthalene

In the DATI-1 analysis, elevated levels of naphthalene, 2-methyl naphthalene and benzene were observed at S Delray. The source closed in May 2004, so the DNRE initiated PAH sampling and confirmed that the elevated levels had disappeared.

# Acrolein

In addition to modifications to Michigan's monitoring network, changes have occurred on a national level that impact the air quality measurements that MDNRE collects. Acrolein is a highly reactive VOC that is quite difficult to measure. Although some laboratories have demonstrated progress in the development of a suitable method, the national contract lab may have issues reporting this compound. Therefore, acrolein is not described in depth in this report due to the low confidence in the accuracy of the analytical method. Currently, there is not a good method for the determination of acrolein, nationally. Also, laboratories that report acrolein all over the nation are having issues with stability of the calibration standard, which contributes to poor accuracy.

#### 6.1. Pollutant Changes Since the DATI-1 Risk Report

This section compares data collected in DATI-1 with more recent measurements. Concentrations are given in units of microgram per cubic meter of air ( $\mu$ g/m<sup>3</sup>). Vertical error bars represent 95% confidence intervals. The confidence intervals are measures of the statistical significance of the difference in concentrations between DATI-1 and DATI-2. Confidence intervals were determined using Microsoft Excel. Because manganese levels in the DATI-1 were elevated above levels of other pollutants, data is displayed using two graphs to illustrate both the trends between all of pollutants and to allow a better view of the relationships between the metals with lower ambient concentrations between DATI-1 and DATI-2 time periods as noted in Section 5 (i.e., 95% confidence intervals as well as f and t-tests for statistical significance). If no bar appears in a chart for a given chemical or location, which means the chemical was not measured at that site or time period, or that it did not meet the criteria for inclusion in risk assessment (see Section 5).

# 6.2. Metal Concentrations by Chemical

This section compares changes in the levels of trace metals between DATI-1 and DATI-2.

**Figure 3** provides a comparison of arsenic concentrations for all locations during both time periods. All sites showed downward concentration trends except the urban background location at Ypsilanti. There is no known reason for an increase in the arsenic concentration at Ypsilanti. In 2007, there were some precision difficulties in the laboratory analysis for arsenic and staff will continue to investigate whether changes in analytical methods may have played a role in the appearance of an increase.



Figure 3. Arsenic Concentrations - DATI-1 and DATI-2

**Figure 4** illustrates trends in cadmium concentrations. Mean levels of cadmium are virtually unchanged at Dearborn and River Rouge. Confidence intervals between DATI-1 and DATI-2 overlap at most sites obscuring our ability to identify actual differences in concentration. Levels of cadmium may show a decrease at N. Delray, S. Delray and N. E. Detroit. Stronger downward trends are observed at Allen Park and Ypsilanti. Statistical analysis was performed to determine whether changes were appreciably different. A readily apparent change was seen at Ypsilanti for cadmium.

NS means not sampled; ND means not detected



Figure 4. Cadmium Concentrations - DATI-1 and DATI-2

\*NS means not sampled; ND means not detected

As noted below (**Figure 5**), the level of hexavalent chromium may show a slight increase in concentration between DATI-1 and DATI-2. However, there is much variability in the data. It is important to note, however, that these measurements are nanograms per cubic meter – 1000 times lower than the usual  $\mu$ g/m<sup>3</sup> units used elsewhere in this report. Hexavalent chromium is volatile, difficult to sample and measure. As noted by the figure below, the error bars overlap between DATI-1 and DATI-2. Statistical analysis indicated that this difference is not appreciable. Methods for detection are continually being improved and some method changes may have impacted the results from DATI-2. AQD staff will continue to investigate this issue.

ICP/MS laboratory analysis of glass fiber filters provides chromium in many oxidation states and is expressed as total chromium (**Figure 6**). A different sampling technique and analytical method are used to determine hexavalent chromium (**Figure 5**). Hexavalent chromium is the most toxic isomer of chromium and is of concern for cancer risk. During the DATI-1 assessment, staff tried to discern the ratio of hexavalent chromium (Cr<sup>+6</sup>) and total chromium to determine whether total chromium measurements could provide a surrogate measure of risk from chromium. As noted in **Figure 7** below, a total of 4 monitoring locations were assessed to determine this ratio, which varied from about 1.0 to 2.5% For the DATI-2 assessment, a measure of the ratio of chromium to total chromium was done at the Dearborn location. **Figure** 

**8** shows the difference in ratios from DATI-1 (four locations) and DATI-2 (1 location). For the DATI-2 assessment, only those samples with detectable chromium were assessed. The detection frequency was much higher in DATI-2 (92%) than in DATI-1 (55%) due to changes in sampling and analysis designed to improve the sensitivity of the method. Dearborn is the only location where hexavalent chromium is currently measured. Error bars represent the 95% confidence interval of the ratios, not a pooling of the individual chemical concentrations. There is no appreciable difference between DATI 1 and 2 for Hexavalent chromium.



#### Figure 7. Ratio of CR+6/CR DATI-1



DATI-1 Ratio of Cr+6/Cr

Figure 8. Percent of Cr+6/CR During DATI-1 and DATI-2 at Dearborn



**Figure 9** describes changes in manganese concentrations at all monitored locations between DATI-1 and DATI-2. Downward trends were noted at all locations except for a slight increase at Ypsilanti and no change at Houghton Lake and Allen Park. The annual average air concentrations of manganese at S. Delray and Dearborn during DATI-2 showed an appreciable reduction (42% and 35%, respectively) compared to DATI-1.



Figure 9. Manganese Concentrations – DATI-1 and DATI-2

NS	means	not	sam	pled

**Figure 10** illustrates changes in nickel concentrations for all locations monitored during DATI-1 and DATI-2. Allen Park, Dearborn, N.E. Detroit, and S. Delray show downward trends. N. Delray, S. Delray and Ypsilanti show upward trends. There was no sampling for nickel in the DATI-2 time frame at the Southfield location due to budget constraints noted in Section 3 and due to the fact that that site was only available during the Detroit Pilot sampling project for toxics.



Figure 10. Nickel Concentrations – DATI-1 and DATI-2

# 6.2.1 Metal Concentration by Location

This section of the report compares the levels of trace metals at each monitoring location.

As shown in **Figure 11** and **Figure 12**, all metals at Allen Park indicate a downward trend, with nickel showing the greatest decrease between DATI-1 and DATI-2 time periods. Annual average air concentrations of cadmium and nickel were appreciably lower during DATI-1 than during DATI-2 (also see **Figures 4** and **10** in Section 6 above). Again, note that two graphs are provided for the monitoring sites with and without manganese since the highly elevated manganese (especially in DATI-1) make the bars for the other metals difficult to see in the combined graph. The different ranges in the graphs are for comparison purposes only.



**Figure 13** and **Figure 14** illustrate changes in metal concentrations at the Dearborn site between DATI-1 and DATI-2. The annual average manganese air concentration was statistically decreased (p<0.05) at Dearborn from DATI-1 to DATI-2.



**Figure 15** and **Figure 16** depict changes in metal concentrations at the N. Delray monitoring location between DATI-1 and DATI-2. Annual average air concentrations of nickel appear to be increasing at N. Delray ( $0.0034 \ \mu g/m^3$  to  $0.0041 \ \mu g/m^3$  for DATI-1 and DATI-2, respectively).


**Figure 17** and **Figure 18**, show concentration differences in metals at N.E. Detroit for the two time periods. A downward trend was indicated for all metal chemicals. The reduction in nickel concentration was appreciable at N.E. Detroit.



Except for manganese, **Figure 19** and **Figure 20** show minimal changes in metal concentrations at the River Rouge monitoring location for the two time periods of DATI-1 and DATI-2. The reduction in the levels of manganese was appreciable.



**Figure 21** and **Figure 22** indicate changes in monitored metal concentrations at the S. Delray location for both the DATI-1 and DATI-2 time periods. All the metals show downward trends at this location. Arsenic shows the largest reduction in ambient levels.



**Figure 23** plots the concentrations of trace metals at the Southfield and Houghton Lake monitoring sites. Since Southfield was a short term site, no follow-up monitoring was conducted after the pilot was completed. Houghton Lake is included as a background reference. The concentrations are shown here for completeness and to allow the reader to perform comparisons with other sites.



**Figure 24** and **Figure 25** illustrate concentrations of metal chemicals monitored at the Ypsilanti location for both the DATI-1 and DATI-2 time periods. Upward trends are indicated in the figures for all the metals.



# 6.2.2. Carbonyl Concentrations by Location

**Figure 26** depicts changes in carbonyl concentrations at all locations in the DATI-1 and DATI-2 time periods. Except for acetaldehyde levels at Ypsilanti, the concentrations of carbonyl compounds are

trending downward or staying the same at all sites. The concentrations of formaldehyde at N. Delray and River Rouge were statistically lower at p<0.05.



Figure 26. Carbonyl Concentrations – All Sites – DATI-1 and DATI-2

## 6.2.3. Carbonyl Concentrations by Chemical

**Figure 27** and **Figure 28** show individual carbonyl concentration changes by location for acetaldehyde and formaldehyde respectively.

Acetaldehyde concentrations declined at all locations except Ypsilanti, as shown in **Figure 27**. None of the changes in the concentration of acetaldehyde are appreciable upon visual examination.

Formaldehyde levels showed downward trends at all locations except Ypsilanti (which remained constant). Concentration declines were appreciable for the Rouge and S. Delray locations.



# 6.2.4 VOC Concentration by Location

No VOC data was collected at the Allen Park, River Rouge, S. Delray and Southfield locations during the DATI-2 time period due to budget reductions as mentioned in **Section 3**. VOC data was only collected for the DATI-2 time period at the background sites of Ypsilanti and Houghton Lake, as seen in the graphs below. Since there are not DATI-1 data for comparison, the concentrations at the background sites will be used only for baseline information and will also appear in the risk assessment portion of Section 7.

**Figure 29** below shows lower concentrations of all VOC at Dearborn during the DATI-2 time period with the exception of chloroform. Although chloroform was measured in the DATI-1 time period, it did not meet the minimum criteria for data inclusions at that time.



Figure 29 Dearborn VOC Concentrations

**Figure 30** shows concentrations of VOCs at Houghton Lake during DATI-1. It is included for comparative purposes.



Figure 30. Houghton Lake VOC Concentrations

Levels of benzene, carbon tetrachloride and methylene chloride decreased at the N. Delray site during this time period, as shown in **Figure 31**. The decrease in methylene chloride is especially notable. Although 1,3-butadiene was monitored in the DATI-1 time period, it only met the minimum criteria for inclusion in the DATI-2 time frame.

Figure 31. VOC Concentrations at N. Delray



**Figure 32** shows the concentration of VOCs that were measured at Ypsilanti during DATI-1. It is included for comparative purposes.



Figure 32. Ypsilanti VOC Concentrations

## 6.2.5. VOC Concentration by Chemical

This section compares the concentrations of selected VOCs between each location.

Levels of 1,3 butadiene are shown in **Figure 33** below. The 1,3-butadiene levels are difficult to compare between the current analysis and the DATI-1 project. The only location where this chemical was measured at levels above the detection limit was at Dearborn. A very slight decrease was seen in 1,3-butadiene levels at Dearborn.





	N. Delray	S. Delray	River Rouge	Dearborn	Allen Park	Southfield	Ypsilanti	Houghton Lake
DATI-1	>85% ND	0.19	0.11	0.12	0.1200	0.19	NS	NS
DATI-2	0.1386	NS	NS	0.11	NS	NS	0.1278	>85% ND

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect)

As noted in **Figure 34** below, the concentration of 1,4-dichlorobenzene at Dearborn also decreased. No other sites had data for both time periods that could be compared for this compound.





	N. Delray	S. Delray	River Rouge	Dearborn	Allen Park	Southfield	Ypsilanti	Houghton Lake
DATI-1	3.51	0.30	0.22	0.25	>85% ND	0.26	NS	NS
DATI-2	>85% ND	NS	NS	0.10	NS	NS	>85% ND	>85% ND

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (nondetect)

**Figure 35** shows average levels of acrylonitrile. During the DATI-1 period, some of the highest acrylonitrile levels in the U.S were measured in SE Michigan. All the acrylonitrile air concentrations (n=29) during the DATI-2 period were below the analytical method detection limit. An annual average air concentration was not calculated because it did not meet criteria for inclusion in risk assessment. However, it is noteworthy that the method detection limit was 0.31  $\mu$ g/m<sup>3</sup>, so even if the air concentrations of acrylonitrile were just below the MDL, a likely overestimate, it indicates that levels may have decreased from an average of 3.51  $\mu$ g/m<sup>3</sup> to below 0.31  $\mu$ g/m<sup>3</sup>. The sensitivity of the analytical method has not been reduced so is not responsible for a reduction in the frequency of detection.



Figure 35. Acrylonitrile Concentrations

	N. Delray	S. Delray	River Rouge	Dearborn	Allen Park	Southfield	Ypsilanti	Houghton Lake
DATI-1	0.91	>85% ND	>85% ND	>85% ND	>85% ND	>85% ND	NS	NS
	>85%							
DATI-2	ND	NS	NS	>85% ND	NS	NS	>85% ND	>85% ND

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect).

Benzene concentration changes are shown in **Figure 36**. Dearborn and N. Delray are the only two locations that sampled benzene during both time periods. Both locations show appreciable reductions in benzene levels. Benzene was not monitored at South Delray for DATI-2, however, as mentioned in the DATI-1 report (Figure 20, pg. 73), benzene concentrations were substantially lower when monitored in 2004 and 2005. During this time period, the 12-month annual average benzene air concentration at South Delray was approximately 8  $\mu$ g/m<sup>3</sup> (compare to DATI-1 average of 21.6  $\mu$ g/m<sup>3</sup>).

Figure 36. Benzene Concentrations



The use of carbon tetrachloride has been discontinued in many applications. However, past uses have resulted in residual levels in the atmosphere (see **Figure 37.** below). Carbon tetrachloride accumulates in the lower atmosphere and has an estimated atmospheric lifetime of 50 years. Therefore, levels are expected to decline slowly. The California Air Resources Board conducted an analysis of California levels of carbon tetrachloride in ambient area and compared them to background levels<sup>3</sup>. They documented global background levels of 0.69  $\mu$ g/m<sup>3</sup> and 0.94  $\mu$ g/m<sup>3</sup>. The average concentrations measured in Michigan are just below that range. The concentrations have declined at N. Delray and Dearborn, albeit not appreciably.

<sup>&</sup>lt;sup>3</sup> Public Hearing to Consider the Adoption of a Regulatory Amendment Identifying Carbon Tetrachloride as a Toxic Air Contaminant, Release Date: July 24, 1987



Figure 37. Carbon Tetrachloride Concentrations

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect).

**Figure 38** appears to indicate elevated chloroform levels in the DATI-2 time period. Unfortunately, there was no monitoring location that had levels meeting criteria for analysis during both DATI-1 and DATI-2 time frames. This finding prompted further investigation. More in depth analysis showed that there were 39 samples (representing an 11.4% detection frequency) with evaluated concentrations in the DATI-2 time period. Of those samples, the average value was 0.135  $\mu$ g/m<sup>3</sup> (substituting the MDL/2 for values that were less than the level of detection) and the maximum detected value was 0.318  $\mu$ g/m<sup>3</sup>. During DATI-1, chloroform at N. Delray had a lower detection frequency (7.7%). The average concentration, using the MDL/2 substitution technique was 0.182  $\mu$ g/m<sup>3</sup> and the maximum value was 0.405  $\mu$ g/m<sup>3</sup> at N. Delray. During the DATI-2 time period, chloroform was detected at the N. Delray location just below the 15% non-detect criterion at 14% detection frequency. The average value corrected by MDL/2 was 0.21  $\mu$ g/m<sup>3</sup>. These findings indicate that the DATI-1 average value of 0.182 at N. Delray and the DATI-2 average value of 0.21 show a slight increase in concentration albeit a rough comparison.

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. Zero air was pumped into the sampling system through the probe over a 24-hour period. The samples were analyzed by the DNRE lab and no

chloroform was detected. This indicates that the sampling systems are clean and values may be real. The DNRE is investigating chloroform levels further.





	N. Delray	S. Delray	<b>River Rouge</b>	Dearborn	Allen Park	Southfield	Ypsilanti	Houghton Lake
DATI-1	>85% ND	0.13	>85% ND	>85% ND	>85% ND	>85% ND	NS	NS
DATI-2	>85% ND	NS	NS	0.76	NS	NS	0.17	0.82

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect).

As seen in **Figure 39**, methylene chloride was found at extremely high concentrations at Allen Park in the DATI-1 analysis. High levels were also seen at the Southfield monitoring location. Elevated values occurred at random intervals through out the year, not following a pattern that could indicate contamination issues. Staff identified one possible source of methylene chloride, but could not confirm their responsibility. Follow up samples taken in subsequent years show appreciably reduced levels of methylene chloride. The possible culprit was no longer engaging in the activities that staff had identified as causing the elevated concentrations.





NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (nor detect). Split bar for Allen Park was created to show the very high level of 803 µg/m<sup>3</sup> in DATI-1 while maintaining the scale to allow lower levels to remain visible.

## 7. RISK ASSESSMENT UPDATE

## 7.1. Cancer Risk by Chemical

This section describes an estimate of cancer risk for individual chemicals that were monitored between 2/28/2006 to 3/28/2007, which is approximately five years after the data was collected and used in the DATI-1 risk assessment. 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

## 7.1.1. Metal Results by Chemical

As noted in **Figure 40** below, cancer risk estimates for arsenic declined from the DATI-1 estimates at all locations except Houghton Lake and Ypsilanti (Lodge was not sampled for the current time frame). All risk estimates for arsenic fall within the lower range of 1 to 10 in 1 million excess risk.





Allen		N.E.	Houghton		Ν.		S.	
Park	Dearborn	Detroit	Lake	Lodge	Delray	Rouge	Delray	Ypsilanti
9.5	12.0	8.5	>85% ND	6.3	10.6	9.6	16.8	3.9
6.9	9.3	6.2	2.6	NS	9.3	8.5	10.0	4.8
	Allen Park 9.5 6.9	Allen Park Dearborn 9.5 12.0 6.9 9.3	Allen ParkN.E. Dearborn9.512.06.99.3	Allen ParkN.E. DearbornHoughton Lake9.512.08.5>85% ND6.99.36.22.6	Allen ParkDearbornN.E. DetroitHoughton LakeLodge9.512.08.5>85% ND6.36.99.36.22.6NS	Allen ParkDearbornN.E. DetroitHoughton LakeN. LodgeN. Delray9.512.08.5>85% ND6.310.66.99.36.22.6NS9.3	Allen ParkN.E. DearbornHoughton DetroitN. LodgeN. DelrayRouge9.512.08.5>85% ND6.310.69.66.99.36.22.6NS9.38.5	Allen ParkN.E. DearbornHoughton LakeN. LodgeN. DelrayS. Delray9.512.08.5>85% ND6.310.69.616.86.99.36.22.6NS9.38.510.0

NS means not sampled. ND means not detected.

The risk from cadmium has very slightly declined at most locations (see **Figure 41** below). The risks noted from the DATI-1 comparison were only slightly elevated above the 1 in a million risk level. The risks from DATI-2 are less than or just above the 1 in a million risk level. With all estimates below or very close to the 1 in a million excess risk level, cadmium alone is not considered a risk driver. It may, however, contribute to overall risk when combined with other chemicals.





Figure 42. Cadmium Cancer Risk - Expanded Axis



Note: Graph included for comparison to **Figure 41.** Scale was changed from 0 to 70 in a million cancer risk to 0 to 2.5 in a million risk in order to better show the lower concentrations.

The risk from exposure to hexavalent chromium (Cr+6) has increased very slightly at Dearborn (see Figure 43 below). Risk is still below the 1 in a million risk level, thus hexavalent chromium is not considered a risk driver. It may, however, contribute to overall risk when combined with other chemicals.



Figure 43. Dearborn Hexavalent Chromium Risk

**Figure 44** shows that very slight changes were noted in the cancer risk from nickel between for some sites between DATI-1 and DATI-2. Levels of risk at Allen Park, N.E. Detroit and S. Delray decreased very slightly whereas risk at N. Delray and Ypsilanti showed an extremely slight increase. All other sites showed risk at the same level as DATI-1. With all estimates at or below 1 in a million excess risk for nickel, it may contribute to overall risk, but cannot be considered a risk driver as a single chemical.



Figure 44. Nickel Cancer Risk

	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	0.5	0.7	0.6	0.1	0.9	0.8	0.6	1.2	0.2
DATI-2	0.3	0.7	0.4	0.1	NS	1.0	0.6	1.0	0.3

## 7.1.2. Carbonyl by Chemical

As noted in **Figure 45** below, cancer risk estimates from acetaldehyde showed slight decreases at all locations where measurements were taken during both time frames. All measurements still fall within the lower portion of the 1 to 10 in a million bin. It is interesting to note that values do not tend to vary much from location to locations. This is likely due to the fact that the main source of acetaldehyde is mobile source pollution.

Figure 45. Acetaldehyde Cancer Risk



	Allen		N.E.	Houghton		N.		S.	
	Park	Dearborn	Detroit	Lake	Lodge	Delray	Rouge	Delray	Ypsilanti
DATI-1	3.1	4.2	3.6	1.7	3.2	4.3	4.2	3.4	2.2
DATI-2	NS	3.5	NS	1.6	NS	3.5	3.7	NS	2.5

NS means not sampled.

For all the sites where monitoring was conducted during both time frames, formaldehyde risk estimates for cancer showed declines (see **Figure 46**). The largest declines were seen at the N. Delray and Rouge locations. During the DATI-1 analysis, it was suspected that a point or area source was contributing an excess amount of formaldehyde to the levels emitted by mobile sources. Because total vehicle miles travelled have declined, it would be expected that formaldehyde levels would decrease at most monitoring locations in a uniform fashion. However, the reductions at N. Delray and Rouge are larger than seen at other locations. Therefore, in addition to the known reduction in vehicle miles travelled, it appears that the point or area source responsible for the excess levels in DATI-1 may have ceased or reduced their emissions of formaldehyde.



Figure 46. Formaldehyde Cancer Risk

	Allen		N.E.	Houghton		Ν.		S.	
	Park	Dearborn	Detroit	Lake	Lodge	Delray	Rouge	Delray	Ypsilanti
DATI-1	26.5	35.8	35.1	25.3	29.7	49.2	69.4	37.5	28.6
DATI-2	NS	33.4	NS	17.2	NS	32.3	45.6	NS	28.0

#### 7.1.3. VOCs by Chemical

As seen in **Figure 47** below, cancer risk estimates for 1,3-butadiene declined slightly at the Dearborn location, though they remain above the 1 in a million risk level for the sites monitored (i.e., N. Delray, Dearborn and Ypsilanti).

Figure 47. 1,3-Butadiene Cancer Risk



	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	4.0	3.9	NS	NS	6.4	>85% ND	3.7	6.3	NS
DATI-2	NS	3.5	NS	>85% ND	NS	4.6	NS	NS	4.3

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect).

Cancer risk from 1,4-Dichlorobenzene declined at the Dearborn location to less than the 1 in a million threshold (see **Figure 48**). However, all other locations had either no monitoring data or failed to meet the frequency of detection criterion. At the N. Delray location, 89% of the samples fell below the detection limit.

Figure 48. 1,4-Dichlorobenzene Cancer Risk



	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	>85% ND	1.8	NS	NS	1.9	25.0	1.6	2.1	NS
DATI-2	NS	0.7	NS	>85% ND	NS	>85% ND	NS	NS	>85% ND

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect).

Cancer risk estimates for acrylonitrile during the DATI-2 time frame could not be calculated due to either the number of samples above detection was less than the minimum criterion or because monitoring had to be reduced due to budget restrictions (see **Figure 49**). However, the fact that all 28 sample points were less than the limit of detection can be interpreted to demonstrate that levels have declined.



Figure 49. Acrylonitrile Cancer Risk

	Allen	Desidence	N.E.	Houghton	OcurthCold	N. Dahara	David		Maailaati
	Park	Dearborn	Detroit	Lake	Southfield	N. Deiray	Rouge	S. Deiray	rpsilanti
DATI-1	>85% ND	>85% ND	NS	NS	>85% ND	91.4	>85% ND	>85% ND	NS
DATI-2	NS	>85% ND	NS	>85% ND	NS	>85% ND	NS	NS	>85% ND

NS means not sampled, >85% ND means greater than 85% of samples were below the detection limit (non-detect). Graph shown with scale expanded to 100 to accommodate earlier, higher risk for acrylonitrile at S. Delray.

Cancer risk estimates for benzene declined at Dearborn and N. Delray, which were the only two locations that sampled for benzene in both DATI-1 and DATI-2. The background sites were both in the 1 to 10 in a million risk bin. The elevated risk at S. Delray was likely due to a nearby point source that has since shut down.

Figure 50. Benzene Cancer Risk



	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	15.0	19.2	NS	NS	19.8	26.7	21.4	215.9	NS
DATI-2	NS	10.9	NS	3.7	NS	13.9	NS	NS	9.7

Graph included a split bar for benzene at S. Delray since levels of this compound were elevated during the DATI-1 time period.

Cancer risk estimates from carbon tetrachloride showed slight declines from the DATI-1 assessment for the two monitoring locations where this compound was measured during both time periods (see **Figure 51**). However, risk estimates remain in the bin of 1 to 10 in a million risk.

Figure 51. Carbon Tetrachloride Cancer Risk



	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	8.5	9.0	NS	NS	8.9	7.8	8.3	8.8	NS
DATI-2	NS	8.1	NS	7.4	NS	7.4	NS	NS	7.4

**Figure 52** describes chloroform risk values. As described in Section 6, no two locations met the sampling criteria for inclusion in risk assessment for both DATI-1 and DATI-2. However, further analysis of the data showed that N. Delray had a slight increase in chloroform concentration between DATI-1 and DATI-2. Because sampling frequencies did not meet the risk criteria for assessment, they are not calculated in this graph. Staff are continuing to investigate the chloroform levels at N. Delray and Dearborn.





	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	>85% ND	>85% ND	NS	NS	>85% ND	>85% ND	>85% ND	0.3	NS
DATI-2	NS	1.9	NS	2.0	NS	>85% ND	NS	NS	0.4

NS means not sampled. >85% ND means greater than 85% of samples were below the detection limit (non-detect) The scale was reduced from the typical 70 in a million maximum value to allow for better resolution of the bars on the graph..

Cancer risk estimates for methylene chloride show declines for both sites that monitored during the DATI-1 and DATI-2 time periods (see **Figure 53**). The risks fell from above 1 in a million risk levels to below levels of concern (i.e., less than 1 in a million risk). Although not shown in this graph, intermediate monitoring was done for methylene chloride in response to concern over the elevated levels at Allen Park. AQD staff investigated possible sources of the elevated methylene chloride. The source of the elevated levels was tentatively identified and the possible source ceased the operations theorized to contribute to elevated levels. Follow-up monitoring for methylene chloride was conducted at the Allen Park monitoring station from 2002 to 2005 to confirm a decline in ambient levels. The subsequent samples showed the levels had dropped appreciably.

Figure 53. Methylene Chloride Cancer Risk



	Allen Park	Dearborn	N.E. Detroit	Houghton Lake	Southfield	N. Delray	Rouge	S. Delray	Ypsilanti
DATI-1	401.3	5.8	NS	NS	31.5	3.3	5.1	1.3	NS
DATI-2	NS	0.3	NS	0.2	NS	0.3	NS	NS	0.4

A split bar was incorporated for Allen Park during the DATI-1 time period to show the elevated levels while still maintaining the comparison scale with a maximum value of 70 in a million excess risk.

## 7.2. Cancer Risk by Location

## 7.2.1. Risk from Metals by Location

As seen in **Figure 54** to **Figure 62** below, cancer risk from arsenic at Allen Park, Dearborn, N. Delray, NE Detroit, Rouge, S. Delray declined from the DATI-1 time period. Risk at the urban background site of Ypsilanti increased slightly and all other sites could not be compared due to the lack of monitoring data meeting the minimum criteria for inclusion.

\*Note all flat, striped boxes indicate that the chemical was monitored at that site during the specified time period, but did not meet minimum data quality requirements for inclusion in the study. The scale was altered to a maximum estimated excess risk of 18 (as opposed to the typical 70) for ease of viewing.











## 7.2.2. Total Cancer Risk from Metals

Cancer risks from metals are combined in **Figure 63** below, for all sites with available comparison data. All sites showed declines except for a slight increase in risk from arsenic at the urban background site of Ypsilanti.





\*Note that bar that is flat to bottom of the graph indicates that the chemical was not monitored at the given site for the time frame indicated. All cancer risk estimates are shown, even when less than the 1 in a million risk cut-off so that DATI-1 and DATI-2 risks can be more easily compared.

## 7.2.3. Cancer Risk of Carbonyls by Location

As seen in **Figure 64** through **Figure 72** below, risk estimates attributed to carbonyls declined at Dearborn, Houghton Lake, N. Delray, and River Rouge. Risk at Ypsilanti was essentially unchanged. All other sites were not comparable due to missing data.











Note – Graph 71 and 72 for Ypsilanti depict 3d format (71) vs. flat (72) styles for comparison purposes.

# 7.2.4. Total Carbonyl Risk

As noted in **Figure 73** below, cancer risk estimates from carbonyls declined at Dearborn, N. Delray, Rouge and Houghton Lake. The decline was largely attributed to formaldehyde decreases.



Figure 73. Cumulative Cancer Risk from Carbonyls for All Sites

## 7.2.5. VOC Risk by Location

As seen in **Figure 74** through **Figure 79** below, there are only two monitoring locations for which VOCs were measured during both time periods (i.e., Dearborn and N. Delray). 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.



Split bar indicated in **Figure 74** to show the elevated cancer risk at Allen Park from methylene chloride exposure.





# 7.2.6. Total Cancer Risk by Location

As seen below in **Figure 80** through **Figure 85**, 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 from more chemicals being monitored at those two sites during the DATI-2 time frame.








#### 7.2.7 Additional Data from 2005 re: S. Delray

A cancer risk driver from the DATI-1 was naphthalene. Although this compound was not measured during the time period chosen for the current study (i.e., 2/28/2006 to 3/31/2007), intermittent monitoring was performed in 2005 in response to the elevated levels measured during the pilot project. The monitoring data collected at S, Delray in 2005 showed declines in naphthalene level risk by a appreciable margin. The decrease may be attributed to a nearby source that closed. **Figure 86** below was added to show the risk changes in total cancer risk from VOCS and SVOCs for comparison to the DATI-1 time frame. As seen, the considerable declines in risk were found due to benzene and naphthalene decreases at the S. Delray location.



### 8. 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 in **Figure 87** below, the hazard quotients for all locations except Ypsilanti are lower than in the DATI-1 analysis. Both DATI-1 and DATI-2 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 HQs are now just above 1. The Dearborn HQ is down appreciably from DATI-1 to about 2.5. The S. Delray HQ is appreciably decreased from DATI-1 and is now just above 3.



#### Figure 87. Hazard Quotient Comparisons for Manganese – DATI-1 vs. DATI-2

Manganese is a chemical of special concern in the Midwestern states due to elevations in air levels found in Ohio and Michigan. Analyses from the DATI-1 project found levels of manganese in total suspended particulate (TSP-Manganese) at four Detroit monitoring sites exceeded the HQ of 1. In response, the AQD formed a workgroup to address the environmental impacts of manganese in Southeast Michigan. Objectives of the workgroup included performing an analysis of emissions from existing sources and reducing emissions from existing sources where possible. While traditionally Manganese has been monitored at the TSP fraction, the PM<sub>10</sub> fraction is now being monitored, and this is the size fraction that will be compared to the Initial Threshold Screening Level (ITSL). Correlations will be drawn between the TSP and PM<sub>10</sub> Manganese concentration levels. The Manganese Workgroup report is due out by the end of 2010. Further information is available on levels found in Ohio in Section 9 and at the Ohio EPA website: <a href="http://www.epa.ohio.gov/dapc/atu/atu.aspx">http://www.epa.ohio.gov/dapc/atu/atu.aspx</a>

#### 9. COMPARISON OF DETROIT AIR TOXICS INITIATIVE FINDINGS TO OTHER MONITORING INITIATIVES

To investigate how the ambient concentrations of air toxics and levels of risk in Southeast Michigan compare with other urban areas across the U.S., a series of cities were selected. Their locations are shown in the map in **Figure 88**.





**Table 7** compares ambient air concentrations in Detroit with nine other cities that monitored for air toxics within approximately the same time frame as the DATI-2 study. The selected cities performed monitoring between April 2005 (RI) and October 2008 (IN). Monitoring values were converted to  $\mu$ g/m<sup>3</sup> to support direct comparison between cities. For example, CA reported their values in ng/m<sup>3</sup> for their metals, while other locations (e.g., OH; PA and RI reported their values in ppbv. CA reported VOCs and carbonyls in ppb.

In **Table 8**, the values reported in **Table 7** were converted to cancer risk approximations. These approximations were determined by taking the average concentration for each carcinogen and dividing by the AQD cancer risk screening level (initial risk screening level or IRSL) as described in Section 5.

In **Table 9**, manganese, the only non-cancer risk driver detected in Detroit, was used to derive a hazard quotient. A hazard quotient is derived using a ratio of air concentration and health-based screening level as noted in Section 5.

Table 7. Summary of 12 Cancer Risk Drivers & Manganese - Comparisons Between Monitored Concentrations From The Detroit Project and Levels Detected In Other Cities\*

CHEMICALS	Dearborn, MI <sup>†</sup> (2/06- 2/07)	North Delray Detroit, MI <sup>†</sup> (2/06- 2/07)	Addyston, OH (2007)	Austin, TX (6/05- 7/06)	Burbank, CA (6/05- 6/06)	Elizabeth, NJ (2006)	Indianapolis, IN (10/06- 10/08)	Pittsburgh, PA (2006)	Portland, OR (2006)	Tonawanda, NY (7/07-7/08)	Warwick, RI (4/05- 8/06)
1,3-Butadiene	0.11	0.14	5.5	0.33	0.24	0.16	0.12	0.16	0.2	0.24	0.089
1,4- Dichlorobenzene	0.1	<mdl< th=""><th>1.2</th><th>0.35</th><th>0.30</th><th>0.16</th><th>0.72</th><th>0.78</th><th>N/A</th><th>0.24</th><th>0.18</th></mdl<>	1.2	0.35	0.30	0.16	0.72	0.78	N/A	0.24	0.18
Acetaldehyde	1.75	1.77	N/A	1.6	3.4	5.7	0.70	1.8	1.5	1.3	1.5
Acrylonitrile	< MDL	< MDL	3.0	0.18	N/A	0.03	N/A	N/A	N/A	N/A	0.022
Arsenic (TSP)	0.0019	0.0019	N/A	0.0011	0.0007	0.0008	0.0012	N/A	0.0014	N/A	N/A
Benzene	1.1	1.39	1.2	1.9	2.2	1.3	1.9	1.3	1.2	9.8	0.86
Cadmium (TSP)	0.00055	0.0006	N/A	0.00014	0.0014	0.0019	0.00030	N/A	N/A	N/A	N/A
Carbon tetrachloride	0.57	0.52	1.1	0.67	0.57	0.59	0.28	0.50	N/A	0.68	0.50
Chloroform	0.76	<mdl< th=""><th>0.68</th><th>0.09</th><th>0.24</th><th>0.13</th><th>0.063</th><th>0.15</th><th>N/A</th><th>N/A</th><th>0.15</th></mdl<>	0.68	0.09	0.24	0.13	0.063	0.15	N/A	N/A	0.15
Formaldehyde	2.68	2.58	N/A	2.7	4.7	4.6	2.4	2.1	1.9	5.9	3.3
Manganese (TSP)	0.13	0.07	N/A	0.007	0.023	0.022	0.0063	N/A	N/A	N/A	N/A
Methylene Chloride	0.52	0.51	1.3	0.71	1.2	0.79	0.22	0.76	N/A	0.19	0.38
Nickel (TSP)	0.0030	0.0041	N/A	0.0008	0.0036	0.0048	0.0020	N/A	0.001	N/A	N/A

#### ANNUAL AVERAGE CONCENTRATION DISTRIBUTION (µg/m<sup>3</sup>)

\*Values in bold represent the highest annual average of all cities for which data were available. \*\*Highlighted values represent the highest risk driver for each city. <MDL for Dearborn and North Delray had less than 15% detection for that chemical. N/A values for the other comparison cities is an indication that this chemical was not measured in these areas.

<sup>†</sup>The concentration of manganese at South Delray is 0.159 µg/m<sup>3</sup>.

# Table 8. Summary of 12 Cancer Risk Drivers - Comparisons of Cancer Risk Approximations (in-a-million) Between The Detroit Project and Other Cities\*

CHEMICALS	Dearborn, MI (2/06- 2/07)	North Delray Detroit, MI (2/06- 2/07)	Addyston, OH (2007)	Austin, TX (6/05- 7/06)	Burbank, CA (6/05- 6/06)	Elizabeth, NJ (2006)	Indianapolis, IN (10/06- 10/08)	Pittsburgh, PA (2006)	Portland, OR (2006)	Tonawanda, NY (7/07- 7/08)	Warwick, RI (4/05- 8/06)
1,3-Butadiene	3.5	4.6	180.0	11.0	8.1	5.3	4.0	5.2	6.7	8.0	2.9
1,4- Dichlorobenzene	0.7	<mdl< th=""><th>8.6</th><th>2.5</th><th>2.1</th><th>1.1</th><th>5.1</th><th>5.6</th><th>N/A</th><th>1.7</th><th>1.3</th></mdl<>	8.6	2.5	2.1	1.1	5.1	5.6	N/A	1.7	1.3
Acetaldehyde	3.5	3.5	N/A	3.2	6.9	11.0	1.4	3.6	3.0	2.6	3.0
Acrylonitrile	<mdl< th=""><th><mdl< th=""><th>30.0</th><th>18.0</th><th>N/A</th><th>3</th><th>N/A</th><th>N/A</th><th>N/A</th><th>N/A</th><th>2.2</th></mdl<></th></mdl<>	<mdl< th=""><th>30.0</th><th>18.0</th><th>N/A</th><th>3</th><th>N/A</th><th>N/A</th><th>N/A</th><th>N/A</th><th>2.2</th></mdl<>	30.0	18.0	N/A	3	N/A	N/A	N/A	N/A	2.2
Arsenic (TSP)	9.3	9.3	N/A	5.5	3.5	4	6.0	N/A	7.0	N/A	N/A
Benzene	10.9	13.9	12.0	19.0	22.0	13.0	19.0	13.0	12.0	98	8.6
Cadmium (TSP)	0.9	1.0	N/A	0.2	2.3	3.2	0.5	N/A	N/A	N/A	N/A
Carbon tetrachloride	8.1	7.4	15.0	9.6	8.1	8.4	4.0	7.2	N/A	9.7	7.2
Chloroform	1.9	<mdl< th=""><th>1.7</th><th>0.23</th><th>0.61</th><th>0.33</th><th>0.16</th><th>0.37</th><th>N/A</th><th>N/A</th><th>0.37</th></mdl<>	1.7	0.23	0.61	0.33	0.16	0.37	N/A	N/A	0.37
Formaldehyde	33.4	32.3	N/A	34.0	59.0	57.0	30.0	26.0	24.0	74.0	41.0
Methylene Chloride	0.3	0.3	0.7	0.4	0.6	0.4	0.1	0.4	N/A	0.095	0.2
Nickel (TSP)	0.7	1.0	N/A	0.2	0.9	1.2	0.5	N/A	0.3	N/A	N/A

CANCER RISK APPROXIMATIONS (in-a-million)

\*Values in bold represent the highest annual average of all cities for which data were available.

\*\*Highlighted values represent the highest risk driver for each city.

<MDL for Dearborn and North Delray had less than 15% detection for that chemical. N/A values for the other comparison cities is an indication that this chemical was not measured in these areas.

# Table 9. Summary of Manganese - Comparisons of Hazard Quotient Approximations (in-a-million) Between The Detroit Project and Other Cities\*

	HAZARD QUUTIENT AFFROXIMATIONS										
CHEMICAL	Dearborn, MI <sup>†</sup> (2/06- 2/07)	North Delray Detroit, MI <sup>†</sup> (2/06- 2/07)	Addyston, OH (2007)	Austin, TX (6/05- 7/06)	Burbank, CA (6/05- 6/06)	Elizabeth, NJ (2006)	Indianapolis, IN (10/06- 10/08)	Pittsburgh, PA (2006)	Portland, OR (2006)	Tonawanda, NY (7/07- 7/08)	Warwick, RI (4/05- 8/06)
Manganese	2.56	1.34	N/A	0.14	0.46	0.04	0.13	N/A	N/A	N/A	N/A

#### HAZARD QUOTIENT APPROXIMATIONS

\*Values in bold represent the highest annual average of all cities for which data were available.

N/A values for the other comparison cities is an indication that this chemical was not measured in these areas.

<sup>†</sup>The hazard quotient approximation for manganese at South Delray is 3.18.

In **Figure 89** and **Figure 90**, the air concentrations from Detroit were compared with nine other cities focusing on the risk drivers for Detroit as total suspended particulate for arsenic, cadmium, and nickel. Dearborn and North Delray averaged higher in arsenic than the other cities listed with the average air concentrations for both locations of  $0.0019 \ \mu g/m^3$ . Arsenic concentrations of the next highest city, Portland, OR had an annual average of  $0.0014 \ \mu g/m^3$ . For cadmium, the highest average was from Elizabeth, NJ with a cadmium annual average concentration of  $0.0019 \ \mu g/m^3$ , while Dearborn and N. Delray had concentrations of  $0.00055 \ \mu g/m^3$  and  $0.0006 \ \mu g/m^3$  respectively. The nickel annual average concentration was highest in Elizabeth, NJ with  $0.0048 \ \mu g/m^3$ , while Dearborn and North Delray showed annual average concentrations of  $0.0030 \ \mu g/m^3$  and  $0.0041 \ \mu g/m^3$  respectively.



Figure 89. Comparison of Air Concentrations for Metals (TSP)

**Figure 90** shows air concentration comparisons between Detroit and nine other cities. Dearborn North and South Delray have higher air concentrations of manganese measured as total suspended particulate than the other cities. The South Delray manganese annual average concentration was highest with 0.16  $\mu$ g/m<sup>3</sup>; followed by Dearborn at 0.13  $\mu$ g/m<sup>3</sup> and North Delray with 0.04  $\mu$ g/m<sup>3</sup>. The third highest annual average concentration for manganese was seen in Burbank, CA with 0.023  $\mu$ g/m<sup>3</sup>. Special studies in Ohio have also shown elevated manganese levels as noted in the next page.



#### Figure 90. Comparison of Air Concentrations for Manganese (TSP)

#### Additional Ohio Studies on Manganese

In addition to the studies mentioned above, the Ohio EPA has been performing investigations into the elevated manganese levels in the towns of Marietta and East Liverpool, Ohio. Both air monitoring initiatives and public health studies are underway in Marietta. Air sampling for manganese was conducted using a high volume total suspended particulate (TSP) sampler, with 24-hour samples, with 24-hour samples collected once every six days. Between 2004 and 2009, concentrations of manganese ranged from 0.058-2.22  $\mu$ g/m<sup>3</sup> equating to hazard indices ranging from 5 to 34. Levels in Marietta in 2007 and 2008 were 0.07 to 0.16  $\mu$ g/m<sup>3</sup>.

#### VOC comparisons

**Figure 91** compares the concentrations of VOCs in ambient air in Detroit with other cities. For all the VOCs considered risk drivers in Detroit, with the exception of chloroform, all other VOC levels were consistent with annual average concentrations found at other cities. The chloroform annual average concentration at Dearborn was 0.76  $\mu$ g/m<sup>3</sup>, while chloroform at North Delray had less than 15% detection, which is considered insufficient for risk assessment in this study. The next highest annual average concentration for chloroform was from Addyston, OH with 0.68  $\mu$ g/m<sup>3</sup>.



Figure 91. Risk Driver Comparisons for Compounds of Interest

Annual average air concentrations of arsenic, manganese, and chloroform were slightly higher in Detroit than other comparison cities. The other risk drivers listed in **Table 7** were within the average annual air concentrations found in other comparable urban areas. Monitoring was conducted in the selected urban areas over the same time frame as the DATI-2 study.

Details about all of the individual air toxics efforts are included in Appendix C.

#### 10. DISCUSSION

Most chemical concentrations and associated risks declined from the DATI-1 assessment. The only chemical in the non-carcinogen category to remain with a hazard quotient above the benchmarks level of 1 is manganese. An initiative to reduce manganese emissions in the Detroit area is underway in the AQD as a result of the DATI-1 risk assessment findings. All but one location which monitored for manganese during both DATI-1 and DATI-2 time periods showed decreased levels of manganese.

The annual average concentrations of manganese exceeded the chronic non-cancer health reference level at four sites during both DATI-1 and DATI-2: South Delray, North Delray, Dearborn, and River Rouge. However, the manganese air concentrations were statistically significantly lower (p<0.05) during DATI-2 for South Delray, Dearborn and North Delray.

Figure 92 shows the manganese level at each site in comparison to the health reference level.



Figure 92. Manganese Concentrations Relative to Health Benchmark

Cancer risk estimates for the following chemicals have decreased, though they continue to remain above 1 in a million risk levels: 1,3-butadiene, 1,4-dichlorobenzene, acetaldehyde, arsenic, benzene, cadmium, carbon tetrachloride, formaldehyde, and methylene chloride. Although the risk for acrylonitrile did not meet the minimum criteria for inclusion in the initial risk assessment of the current study, further investigation revealed that the chemical was not able to be detected in all of the samples. Therefore, it is logical to conclude that the levels of

acrylonitrile have declined, if the laboratory sensitivity has remained the same. Although risk estimates changed very little for nickel, it is of interest that all locations now have associated risk estimates at or below the benchmark of 1 in a million risk.

The only compound appearing to have a slight increase in estimated excess cancer risk from DATI-1 to DATI-2 was chloroform. Chloroform values must be interpreted carefully, as no monitoring location measured chloroform during both DATI-1 and DATI-2 time periods at levels of detection sufficient to warrant analysis under our selection criteria. When values were compared to DATI-1 values measured at Dearborn, the differences in risk between the two time periods were small. This occurred despite having a lower sample detection frequency than ideal. Compared to other locations in the U.S. that have conducted air toxics risk assessments, chloroform values at Dearborn were higher than the other areas. However, the resultant risk estimate is 1.9 in a million, which does not present a reason for public health concern. However, efforts will continue to identify potential sources of chloroform or sources of compounds which could breakdown in the atmosphere and form chloroform.

Incremental Increase in Lifetime Cancer Risk	Pollutants from DATI-1	Pollutants from DATI-2
100 to 400 in one million	methylene chloride naphthalene benzene	
10 to 100 in one million	acrylonitrile formaldehyde 1,4-dichlorobenzene arsenic	formaldehyde benzene
1 to 10 in one million	carbon tetrachloride 1,3-butadiene acetaldehyde cadmium nickel	arsenic cadmium* acetaldehyde* 1,3-butadiene* carbon tetrachloride chloroform naphthalene**
0 to 1 in a million	hexavalent chromium chloroform	hexavalent chromium nickel 1,4-dichlorobenzene acrylonitrile methylene chloride

Table 10. Risk Bin Changes from DATI-1 to DATI-2

\*Although in the same risk bin, concentrations and risks declined from DATI-1

\*\* Not sampled during DATI-2 period. Risk is based on 2005 annual average air concentration

# 10.1. Business closures as a possible explanations for changes in concentrations since DATI-1

Appreciable changes have occurred in Michigan's economic climate since the Detroit Pilot Monitoring project and the DATI-1 risk assessment. Michigan has seen the largest unemployment rate in the nation for several years. The loss of jobs has resulted directly from the closure of many different companies. The Detroit area has been hit especially hard by the recession and many companies have ceased operation. The decline of air toxic concentrations and associated risk may have some relationship to these closures. An assessment was performed by AQD staff to determine how many facilities have either ceased operating or begun new operations between the DATI-1 and DATI-2 time periods. The result of this analysis is shown in **Table 11**.

Company Type	Closed	Opened
Allen Park-Dearborn-		
Delray-River Rouge		
Food products	2	
Automotive supply	3	
Calcium lime products	1	
Paper manufacturing	1	
Plating company	1	
Coating company	2	
Industiral waste	1	
Asphalt manufacturing	1	
Cyclic crude production	1	
Portable sand & gravel		1
Ypsilanti		
Boiler shop	1	
Recycled concrete		1
N.E. Detroit		
Asphalt paving material	1	
Metal parts coating	1	
Automotive products	2	
Cold rolled steel products	1	
Fabricated metal products		1

 Table 11.
 Number of companies closed or opened between DATI-1 and DATI-2 (2002-2007)

Although a specific point source for the acrylonitrile was not identified, the source is clearly no longer emitting at appreciable levels. This is appreciable as the prior DATI-1 levels of acrylonitrile were found higher at the N. Delray monitor than any other location in the country.

#### 10.2. Traffic Volumes Decreasing

Changes in the economic climate in Michigan have resulted in changes in the traffic patterns as well. The Southeast Michigan Council of Governments (SEMCOG) provided data on daily vehicles miles traveled in Southeast Michigan (see **Figure 93**). The geographic area is not limited to the Detroit area, but includes the seven-county SEMCOG region (Livingston, Monroe, St. Clair, Washtenaw, Oakland, Macomb and Wayne). That data show a decrease of over 10 million vehicles per day since 2002, as shown in the graph below:





Mobile source pollutants, including reductions in particulate matter, may be associated with this decrease in vehicles on Southeast Michigan roads.

This is a trend that may continue for some time. Although SEMCOG does not have official vehicle miles traveled (VMT) projections, travel trends closely mirror employment trends. Employment is expected to continue a slight downward trend this year, followed by a leveling out and then to begin a slow rise. However, the forecast shows that the employment in Southeast Michigan in 2035 will still be lower than that in 2008.

#### References

USEPA. 1990a. Cancer Risk From Outdoor Exposure to Air Toxics. EPA-450/1-90-004a.

USEPA. 1990b. The Transboundary Air Toxics Study. USEPA Region 5.

#### **10.3.** National Comparisons

In the DATI-1-1 study, the authors referenced a prior comprehensive analysis of air toxics risk performed by the EPA. The following excerpt from the DATI-1 technical report describes the characterization of risks from air toxics as compiled by the EPA in 1990.

The USEPA (1990a) integrated the findings of several air toxics monitoring studies (including also some modeling of impacts) which were conducted nationwide or in specific geographic areas. The study included up to 90 substances. They found that 12 substances accounted for over 90% of the total inhalation cancer risk. The major contributors, and their contribution to the total cancer risk, were:

- products of incomplete combustion (using Benzo(a)pyrene or B(a)P as the surrogate; 35%);
- 1,3-butadiene (12%);
- *Cr*<sup>+6</sup> (9%);
- benzene (8%);
- formaldehyde (5%); and
- chloroform (5%).

The national average lifetime total cancer risk estimate was 490 to 770 X  $10^{-6}$ . For urban areas generally, the lifetime total cancer risk estimate was in the range of 10 to 1000 X  $10^{-6}$ . The authors noted that,

"The numerical estimates presented in this report should be viewed only as rough indications of the potential for cancer risk caused by a limited group of pollutants found in the ambient air. Many of the risks cited in this report are almost certainly inaccurate in an absolute sense. The best use of the risk estimates is in describing the broad nature of cancer risk posed by these toxic air pollutants and by making relative comparisons of risks between pollutants and sources."

A second noteworthy air toxics risk study is USEPA Region 5 (1990b), which involved an air toxics emissions inventory and modeled dispersion and deposition for the Southeast Michigan / Windsor-Sarnia area. The study included 72 air toxics, including 27 carcinogens. The highest cancer risk drivers, and their percent contribution to the total lifetime inhalation cancer risk estimate for the Canadian grid cell, were as follows:

- formaldehyde (33.3%);
- coke oven emissions (23.1%);
- 1,3-butadiene (16.4%);
- carbon tetrachloride (12.8%);
- Cr<sup>+6</sup> (3.8%);
- polycyclic organic matter (3.3%);
- dioxin (3.2%); and
- all others (4.1%).

The lifetime total inhalation cancer risk estimate was 90 X  $10^{-6}$ , with a maximum for the study area at 120 X  $10^{-6}$ . The authors noted that,

"The risk estimates presented in this report should be regarded as only rough approximations of total cancer cases and individual lifetime risks, and are best used in a relative sense. Estimates for individual pollutants are highly uncertain and should be used with particular caution."

These two examples help demonstrate the varying types of air toxics risk studies which exist, some of the fundamental differences between their design and their findings, and the precautionary notes which accompany them. It is interesting to note that most of the same chemicals identified as responsible for the largest portion of cancer risk nationwide are found to be associated with cancer risk in this DATI-2 analysis.

Although not directly attributable to environmental causes, it may be of interest to the reader to look at national statistics on cancer for comparison purposes. According to the American Cancer Society, the U.S. lifetime chance of getting cancer (all causes) is 1 in 2 for men and 1 in 3 for women. The information is from the US National Cancer Institute's Surveillance Epidemiology and End Results (SEER) Database, and is based on incidence and mortality data for the United States from 2005 through 2007, the most current years for which data are available. This data is not specific to environmental exposures, but encompasses cancer from all causes. Despite not providing a direct comparison to risk from air pollutant exposure, these statistics indicate the large difference between total "expected" cancer risk vs. the estimated cancer risks of 1 to 10 per million individuals.

National and other State air toxics initiatives are described in Section 9 as well as below. In March 2010, the EPA released a report titled "Our Nation's Air," which focuses on air quality trends. The 2002 National-Scale Air Toxics Assessment (NATA) is used in the report. NATA looks at nationwide modeling, monitoring and emissions reporting data and provides an estimate of ambient air levels, inhalation exposure and risk estimates associated with 180 of the 187 hazardous air pollutants regulated by the EPA under the Clean Air Act. According to that report, the national average cancer risk level in 2002 was 36 in a million. Many urban areas and transportation corridors show a risk above the national average. Benzene was the most appreciable carcinogen, contributing over 30 percent of the average individual cancer risk. Diesel exhaust was also widespread, but the risk was not quantified by the EPA. Ambient monitoring data show that for the following compounds of widest concern to public health, levels have been declining at most sites: 1,3-butadiene, benzene, tetrachloroethylene, and 1,4-dichlorobenzene

In a companion study to this project, Sonoma Technology, Inc. performed a comparison of Michigan levels to National levels. They note:

At most of the Michigan sites, and for most pollutants, air toxics concentrations are within or lower than the typical range of pollutant concentrations seen at national urban monitoring sites. ...manganese concentrations at four sites (S Delray, Dearborn, N Delray and Rouge) are high, at or above the 95th percentile of concentrations nationally. Additional work on manganese is being performed by the Manganese Workgroup at the Michigan Department of Natural Resources & Environment (MDNRE). The higher manganese concentrations may be a result of local industrial emissions in the Detroit area. VOC concentrations at most Michigan sites are decreasing over time, with less than 30% of sites showing increasing trends.

A National Air Toxics Trends Report issued in 2009 estimated cancer risks in Wayne County using a different, initial screening methodology. Their estimates are not directly comparable to

the current analysis as they used different methodologies for chemical categories and risk approximation. They provided the following risk approximations for 2007:

Pollutant	Cancer risk approximation (per million)
Chloroform	72.32
Carbon Tetrachloride	9.44
Benzene	8.17
Arsenic compounds	7.62
1,3-Butadiene	3.05
Chloromethane	2.19
Tetrachloroethylene	1.94
1,3-dichlorobenzene	1.45
Cadmium compounds	0.95
Nickel compounds	0.56

Table 12. National Air Toxics Trends Estimates for Wayne County in 2007

#### 11. DIESEL EXHAUST

Diesel exhaust contains a complex mix of fine particulate matter and gases. The majority of the particulate matter in diesel exhaust is the fine ( $PM_{2.5}$  or smaller). Fine particles pose a appreciable health risk because they can pass through the nose and throat and lodge in the lungs. These fine particles can cause lung damage and premature death. They can also aggravate conditions such as asthma and bronchitis. Nationwide, particulate matter, especially fine particles, is responsible for thousands of premature deaths every year. The EPA has determined that diesel exhaust is a likely human carcinogen. Diesel exhaust can also contribute to other acute and chronic health effects.

People with existing heart or lung disease, asthma or other respiratory problems are most sensitive to the health effects of fine particles. The elderly and children are also at risk. Children are more susceptible to air pollution than healthy adults because their respiratory systems are still developing; they have a faster breathing rate and breathe more air per unit of body weight. Diesel exhaust also contains pollutants that contribute to <u>ozone formation</u> (or smog), <u>acid rain</u>, and <u>global climate change</u>. Fine particles from diesel engines contribute to haze, which restricts our ability to see long distances.

Health hazard estimates are generally based on exhaust emissions from diesel engines built prior to the mid-1990s. Current engine use includes some new and many older engines. Diesel engines typically stay in service for a long time. As new and cleaner diesel engines, together with different diesel fuels, replace large numbers of existing engines, the general applicability of the health hazard conclusions will need to be re-evaluated.

Since the DATI-1 study, a great deal of research has been published on the health effects of diesel and on ambient measurement metrics for diesel exhaust. Due to the complex nature of diesel exhaust, measurements in ambient air are difficult. The mix of particles and gases changes depends on a variety of factors, including:

- age and type of engine
- the geographic location and refining process used to derive the fuel
- meteorological conditions when measurements are made
- distance from the roadway
- type of air monitoring device used for measurements

Due to the complex nature of diesel exhaust, it is difficult to capture using any one air monitoring device. Different researchers have used varying methods as surrogate estimates of diesel. Diesel particulate matter has been estimated using black carbon (BC), elemental carbon (EC)/organic carbon (OC), or as some fraction of fine particulate matter (PM<sub>2.5</sub>). All three methods have been used in the analyses below. Each method has its own benefits and drawbacks. For the purposes of comparing results from DATI-1 to DATI-2, the method used in DATI-1 (i.e., EC as part of the PM<sub>2.5</sub> speciation profile) is used and described below.

A method for attributing air pollutants to various sources of emission is source apportionment modeling. This method can also estimate contributions from diesel exhaust. The following data was developed by the Lake Michigan Air Director's Consortium (LADCO). The figures below depict analyses of source apportionment from Detroit area monitors. LADCO analyzed all pertinent data from monitors at Dearborn, Newberry, Allen Park and W. Lafayette. Models calculate regressed concentrations versus wind direction and wind speed to locate areas associated with peak concentrations (i.e., source locations). LADCO concluded that their method successfully identified local point sources of BC, EC and OC. Results were not as clear-cut for PM<sub>2.5</sub> measures, perhaps due to secondary formation of chemicals and local primary sources that are small relative to the total mass. These figures are provided in order to get an idea of the relative contributions of the varying surrogate estimates in the Detroit area.



Figure 94. Photo of monitor locations measuring diesel exhaust surrogates (LADCO data).



Figure 95. PM<sub>2.5</sub> Reconstructed Mass for Michigan Sites

As part of the Speciation Trend Site and National Air Toxics Trend Site programs, aethelometers were set up at the Allen Park and Dearborn monitoring locations. An aethalometer is a type of monitor that measures black carbon, which can be used as a surrogate of diesel exhaust. Data from these monitors is available for 2006 and 2007 and annual average values are depicted below in **Figure 96**.





In the DATI-1 analysis for diesel, black carbon data was not available. Therefore, in order to compare a diesel surrogate for both DATI-1 and DATI-2 time periods, elemental carbon must be used. **Figure 97** below depicts annual average concentrations of elemental carbon at Allen Park for the years 2006 and 2007. The concentrations of elemental carbon at Allen Park may or may not directly relate to those in the City of Detroit, however this is the only location for which data is available for both DATI-1 and DATI-2 time periods and is useful for risk assessment purposes. Allen Park is both a mobile source oriented monitoring site and a population based, or neighborhood scale, location.



Figure 98. EC Values Allen Park from DATI-1



2001

2002

2003

Annual Average Elemental Carbon Allen Park DATI-1

Samples of elemental carbon for DATI-1 were collected from January 2001 to December 2003 at the Allen Park site. The chart below shows Allen Park data for 2001 to 2003.

Table 13. Elemental Carbon Statistics from DATI-1 for Alle	ו Park
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YEAR	# OF SAMPLES	EC CONCENTRATION ARITHMETIC AVERAGE & STANDARD DEVIATION	LOWEST MEASURED VALUE	HIGHEST MEASURED VALUE
2001	N = 95	0.69±0.33 µg/m³	0.00019 µg/m <sup>3</sup>	1.71 µg/m³
2002	N = 112	0.86±0.47 µg/m³	0.264 µg/m <sup>3</sup>	3.78 µg/m <sup>3</sup>
2003	N = 117	0.78±0.39 µg/m <sup>3</sup>	$0.0255 \mu g/m^3$	$2.04 \mu g/m^3$

Samples from the DATI-2 time frame are shown in **Table 14** below.

Table 14.	Elemental	Carbon	Statistics	from	DATI-2 for	Allen Park
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YEAR	# OF SAMPLES	EC CONCENTRATION ARITHMETIC AVERAGE & STANDARD DEVIATION	LOWEST MEASURED VALUE	HIGHEST MEASURED VALUE
2006	N=113	0.79± 0.43 µg/m <sup>3</sup>	0.0149 µg/m <sup>3</sup>	2.59 µg/m³
2007	N=120	0.77± 0.41 μg/m <sup>3</sup>	0.0966 µg/m³	2.81 µg/m³

As shown in **Figure 97, Figure 98, and Table 13** and **Table 14** above, elemental carbon values did not exhibit a wide variation between the DATI-1 and DATI-2 time periods when considering the standard deviation in the data. The EPA provided calculations to estimate surrogate diesel exhaust exposure (diesel particulate matter or DPM) from elemental carbon values as used in DATI-1 will be used for the DATI-2 time period data for comparison purposes:

- 1) amount of EC in DPM: 52 75% and
- 2) ambient EC attributed to diesel exhaust: 46 68%, results in the following equation:
- 3) average estimate of DPM = 0.57EC/0.635 or DPM = EC x 0.89 (USEPA, 2002c)

Table 15. Estimated Diesel Particulate Matter at Allen Park for DATI-1

**DPM Calculations – Allen Park from DATI-1** 

YEAR	LOWER-BOUND DPM = (EC x 0.46)/0.75	UPPER-BOUND DPM = (EC x 0.68)/0.52	AVERAGE DPM = EC x 0.89
2001	0.42 µg/m <sup>3</sup>	0.90 µg/m³	0.61 µg/m³
2002	0.52 μg/m <sup>3</sup>	1.1 µg/m <sup>3</sup>	0.76 μg/m³
2003	0.48 µg/m <sup>3</sup>	1.0 μg/m <sup>3</sup>	0.69 µg/m³

 Table 16.
 Estimated Diesel Particulate Matter at Allen Park for DATI-2

#### DPM Calculations – Allen Park from DATI-2

YEAR	LOWER-BOUND DPM = (EC x 0.46)/0.75	UPPER-BOUND DPM = (EC x 0.68)/0.52	AVERAGE DPM = EC x 0.89
2006	0.48 µg/m <sup>3</sup>	1.03 µg/m <sup>3</sup>	0.70 μg/m³
2007	0.47 µg/m <sup>3</sup>	1.01 μg/m <sup>3</sup>	0.68 µg/m³

The DPM estimates shown in **Table 16** do not differ greatly from the DPM estimates in **Table 15** (which show the DATI-1 values). However, since data is only available from one location, it is not possible to determine how well they reflect values for the Detroit area overall. Because the EC surrogate calculations presented above are based on the USEPA (2002c) nationwide diesel estimates, the resulting DPM estimates can only be extrapolated to Detroit with appreciable uncertainty.

#### **Risk Assessment for Diesel**

#### Non-cancer risk

There is no good acute health benchmark value available for comparison with short-term diesel exposure estimates. For longer (i.e., chronic) exposure risk assessment, the EPA has developed a non-cancer effects reference concentration (RfC) of 5  $\mu$ g/m<sup>3</sup> based on potential for pulmonary effects (USEPA, 2010) Integrated Risk Information Database, <u>www.epa.gov/iris</u>). A hazard quotient can be developed for diesel particulate matter by dividing the average of the DPM estimates from **Table 16** by the Reference concentration:

Average all EC estimates from 2006 and 2007 at Allen Park =  $0.78 \ \mu g/m^3$ Average DPM – EC x  $0.89 = (0.78 \ x \ 0.89) = 0.69 \ \mu g/m^3$ Hazard Quotient =  $0.69 \ \mu g/m^3/5 \ \mu g/m^3 = 0.138$  Because the HQ for DPM is so low, there isn't an expected chronic, adverse non-cancer health association expected from DPM exposure.

### Cancer risk

The California EPA has established a cancer unit risk estimate of  $3 \times 10^{-4} (\mu g/m^3)^{-1}$  for DPM. A DPM estimate from positive matrix factorization (PMF) performed by Sonoma Technology, Inc. (STI) was used in the cancer risk estimation in DATI-1. However, more recent work by STI indicates the EC factor is composed of both diesel and gasoline exhaust. Therefore, the estimate here will include only the DPM calculations based on the Allen Park monitored PM<sub>2.5</sub> speciation data. Using the annual average estimate for DPM from **Table 16**, the estimated cancer risk from diesel exhaust would be:

 $(3x10^{-4} \mu g/m^3)^{-1} x 0.69 \mu g/m^3 = 207 x 10^{-6}$  or 207 in a million risk estimate

Compared to the value for DATI-1 of 300 in a million excess cancer risk estimate, the 207 in a million for Allen Park is lower for the DATI-2 time period. The overall uncertainty in this estimate, however, is fairly large. Diesel cancer risk was not addressed in the NATA 2002 analysis and the NATA 2005 analysis has not been released as of press time for this report. Therefore, it is not possible to make a comparison with contemporaneous NATA estimates.

#### References

USEPA. 2002c. *Health Assessment Document for Diesel Engine Exhaust*. Prepared by the NCEA, Washington, DC for the Office of Transportation and Air Quality. EPA/600/8-90/057F. Available from National Technical Information Service, Springfield, VA; PB 2002-107661, at <u>http://www.epa.gov/ncea</u>.

USEPA 2010 Integrated Risk Information Database, Diesel Engine Exhaust, <u>www.epa.gov/iris</u>

## 12. STAKEHOLDER GROUP

A specific task undertaken as part of the grant effort included development of a community stakeholder group formed to help determine the best strategy for communicating findings of the risk assessment. Recruitment for the stakeholder group began with the list of individuals serving on the original Detroit Air Toxics Initiative workgroup. Some members of the group were available and included in this DATI-2 stakeholder group consisted of 16 members. Four meetings were held to assist with development of the communication strategy. The questions posed to the group at the first meeting were these:

- 1. What is the best media for reaching the public with this information?
- 2. How shall we describe the analyses in a manner that will be most readily understood?
- 3. How shall we describe chemicals for which data was available in the DATI-1 project, but new data is not available for this analysis?
- 4. Shall we include descriptive information about Criteria Pollutants as well as air toxics (that is, data on ozone, particulate matter, sulfur dioxide, nitrogen dioxide, lead and carbon monoxide from our regular fixed site monitors)?

AQD staff presented data in a variety of modes to the group. The group preferred the type of graphs and charts reflected in the present document to a variety of other types (including

notched box and whisker plots). Paper media and the internet were media that were favored by the group. The group suggested the development of a plain language report, simple pamphlet and a technical summary (similar to what was done in DATI-1). Distribution of materials to middle or high schools was suggested as a good media; i.e., student packets could be developed and disseminated via principals. Legislative newsletters, community groups were also suggested. A description (simplified) of how, what and why we are monitoring should be included. A comparison with other State and National Air Toxics levels would be useful. NATA 2005 has not yet been released.

Stakeholders suggested we clearly state the reason why chemicals were not available for analysis in this DATI-2 project although they were available in DATI-1. In Section 3, the description is provided regarding budget cuts which reduced the number of monitors and chemicals available for the DATI-2 analysis. A public summary will be prepared which focuses only on those locations having data for both time periods.

Criteria pollutant data was determined to be outside the scope of this analysis. Criteria pollutant information is compiled and described annually in the DNRE Air Quality Division annual reports, available at <a href="http://www.michigan.gov/deqair">www.michigan.gov/deqair</a> under the heading Air Publications.

As to how to depict the findings – some members of the group stressed that we practice caution when presenting findings as compared to health benchmarks The authors have attempted to follow this suggestion in the present document, as noted in Sections 5 and 10. A relative risk comparison will also be discussed briefly in the technical summary.

#### 13. CONCLUSIONS

#### **Concentrations**

Most chemicals showed overall declines in concentrations between the DATI-1 assessment and the current study. One exception was chloroform, which was also identified in a recent report on National Air Toxics Trends Sites as showing elevated levels in Dearborn. AQD staff is currently investigating the chloroform levels. Concentrations of manganese declined at all monitored locations save for a slight increase at the urban background site of Ypsilanti. Acrylonitrile concentrations declined to non-detection at N. Delray, an appreciable finding since the prior concentrations were the highest found in the country.

#### <u>Risks</u>

Cancer risk estimates for acetaldehyde, arsenic, benzene, formaldehyde, cadmium (slightly above),1,3-butadiene, 1,4-dichlorobenzene, chloroform and carbon tetrachloride continue to have risk levels elevated above the 1 in a million value. Only one chemical – manganese – ranked a hazard quotient greater than the "acceptable" value of 1. Chloroform values must be interpreted carefully and AQD efforts will continue to identify potential sources of chloroform or sources of chemicals that could breakdown in the atmosphere and form chloroform.

Methylene chloride risk estimates showed dramatic declines, reduced from a high risk of 401 in a million at Allen Park to risks below one in a million at all locations sampled in this follow-up analysis. Appreciable declines in risk from formaldehyde were also found at all locations measured for both DATI-1 and DATI-2.

Total cancer risk estimates by monitoring location declined for all metal chemicals with the exception of arsenic at the background locations of Ypsilanti and Houghton Lake. Total cancer risk estimates for carbonyls declined at every location measured for both DATI-1 and DATI-2.

Total cancer risk estimates for VOCs at the two locations sampled declined for all chemicals except chloroform. Most Michigan sites are within National concentrations for metals as per results from Sonoma Technology (Sonoma, 2008). National levels for cancer risks, according to Sonoma included the following:

Pollutants with a majority of sites with risk estimates above the one-in-a-million risk level: ethylene oxide, acrylonitrile, **carbon tetrachloride, benzene, arsenic, 1,3 butadiene, acetaldehyde, 1,4-dichlorobenzene**, tetrachloroethylene, naphthalene, and the larger particulate size fractions of **nickel**.

Those chemicals shown in bold above were also elevated in the Michigan assessment.

#### 14. NEXT STEPS

Technical staff from the Air Quality Evaluation Section of the AQD will continue monitoring for air toxics to the fullest extent that resources allow. Staff will continue to investigate trends in chloroform. Investigations will continue into elevated manganese levels, including identification of potential sources and possible strategies for reduction. As noted in Section 8, the AQD Manganese Workgroup report is due at the end of 2010. Levels of relatively elevated metal concentrations at the background monitoring sites of Houghton Lake and Ypsilanti will be investigated. Education and outreach opportunities for disseminating the information contained in this report will be sought with guidance from the Community Stakeholders.

Term	Definition
μg	microgram
µg/m <sup>3</sup>	micrograms per cubic meter (1000 µg = 1 mg)
μm	micron
ACGIH	American Conference of Governmental Industrial Hygienists
AIRS ID	Aerometric Information System (US EPA database) Identification Number
AQD	Air Quality Division
ATSDR	U.S. Agency for Toxics Substances and Disease Registry
AVG	Average
CA REL	California Reference Exposure Level
CAA	Clean Air Act
Cal EPA	California EPA
CAS	Chemical Abstract Service
CNS	central nervous system
Cr <sup>+6</sup>	Hexavalent Chromium – a carcinogenic valence state of chromium
DATI	Detroit Air Toxic Initiative
DEARS	Detroit Exposure Aerosol Research Study
DL	Detection Limit
DNRE	Michigan Department of Natural Resources and Environment

#### 15. GLOSSARY

Term	Definition
DPM	Diesel Particulate Matter
EC	Elemental Carbon
GC	Gas Chromatograph (analytical instrument)
НАР	Hazardous Air Pollutant
HEC	human equivalent concentration
HEI	Health Effects Institute
Нд	Mercury
H	hazard index (sum of the hazard quotients for a particular effect
	grouping)
HQ	hazard quotient (ratio of predicted ambient impact/initial threshold
br	bour
	Inductively Coupled Pleame/Mass Spectrometer
	Inductively Coupled Plasma/Mass Spectrometer
	initial risk acrossing level
	Kilogiani Loko Mishigan Air Director's Consertium
	Lake Michigan All Director's Consolition
	Lethal Concentration 50% (for innatation dosing)
	Lethal Dose 50% (for oral dosing)
LUAEL	
	Maximum achievable control technology
MATESTI	Multiple Air Toxics Exposure Study II
	Nethed Detection Limit
MDL	Method Detection Limit
MDL/2	Method Detection Limit divided by 2
mg	
mg/m°	milligrams per cubic meter (1000 mg = 1 gram)
MDEQ	Michigan Department of Environmental Quality
MITAMP	Michigan Toxics Air Monitoring Program
MRL	Minimal Risk Level (derived by the ATSDR)
MSA	Metropolitan Statistical Area
N. Delray	Detroit's West Fort Street monitoring site (also called "Southwestern High School")
N F. Detroit	Northeast Detroit's East Seven Mile Road monitoring site
NAAOS	National Ambient Air Quality Standard
ΝΑΤΑ	National Air Toxics Assessment LISEPA
NATTS	National Air Toxics Trend Site
	National Center for Environmental Assessment
	Non-detect (i.e., lower than the MDL)
ng/m <sup>3</sup>	nanograms per cubic meter
	National Institute of Health (ILS, Dont, of Health & Human Services)
NIOSH	National Institute of Occupational Safety and Health
NAAQS NATA NATTS NCEA ND ng/m <sup>3</sup> NIH NIOSH	National Ambient Air Quality Standard         National Air Toxics Assessment, USEPA         National Air Toxics Trend Site         National Center for Environmental Assessment         Non-detect (i.e., lower than the MDL)         nanograms per cubic meter         National Institute of Health (U.S. Dept. of Health & Human Services)         National Institute of Occupational Safety and Health

Term	Definition
nm	nanometer
NOAEL	no-observed-adverse-effect level
NOAEL <sub>ADJ</sub>	NOAEL adjusted to continuous exposure duration from an
	intermittent regimen by hour/day and days/7 days.
NOAEL <sub>HEC</sub>	NOAEL adjusted for dosimetric differences across species to a HEC.
NTP	National Toxicology Program
Num Obs	Number of observations during the sampling period
Obs > MDL	number of observations greater than the method detection limit
OAQPS	Office of Air Quality Planning and Standards (USEPA)
OC	organic carbon
OEHHA	Office of Environmental Health Hazard Assessment
OEL	Occupational Exposure Limit
ORD	Office of Research and Development (USEPA)
PAH	Polycyclic Aromatic Hydrocarbon
PAMS	Photochemical Assessment Monitoring Stations
PBT	persistent bioaccumulative toxics
PCE	perchloroethylene
PDF	Portable Document Format (Adobe Acrobat)
pg	picogram
pg/m <sup>3</sup>	picograms per cubic meter
PM	particulate matter
PM <sub>10</sub>	particulate matter less than 10 µm in diameter
PM <sub>2.5</sub>	particulate matter less than 2.5 µm in diameter
PMF	Positive Matrix Factorization (model)
ppbV	parts per billion in volume
ppm	parts per million (air concentration)
ppt	parts per trillion
REL	Recommended Reference Level
RfC	Reference Concentration
RfD	Reference Dose
River Rouge	River Rouge monitoring site location
RTP	Research Triangle Park
S. Delray	Detroit's West Jefferson monitoring site
SCAQMD	South Coast Air Quality Management District
Southfield	I-696/Lodge Freeway monitoring site location
SQL	sample quantitation limit
St Dev	Standard Deviation
STI	Sonoma Technology Incorporated
SVOC	Semi-volatile organic compound
TCDD	2,3,7,8-tetrachlorodibenzo-p-dioxin
TCE	trichloroethylene
TEQ	Toxic equivalent concentration
TLV	Threshold Limit Value (used by the ACGIH)
TOSHI	Target Organ Specific Hazard Index

Term	Definition
Total HI	Total Hazardous Index
TSP	Total suspended particulate
TTD	Target Organ Toxicity Dose
TTN	Technology Transfer Network (USEPA internet based information)
TWA	time-weighted average
UCL	Upper Confidence Limit
UF	uncertainty factor
URE	Unit Risk Estimate
U.S.	United States
USEPA	U.S. Environmental Protection Agency
VOC	volatile organic compound
w/ND	with non-detect

#### APPENDIX A

Summary of DATI-1 study

Data derived from Detroit Pilot Monitoring project:

- Duration of Project: April 19, 2001–April 19, 2002
- 8 Monitoring Sites
- Pollutants Measured: VOCs, Carbonyls, Semi-volatiles (including PAHs), Metals (TSP), Cr+6, Mercury
- Other Measurements: PM<sub>2.5</sub> Speciation, meteorology (wind speed and direction, temp, humidity, pressure)
- **Sampling Frequency:** Varies depending on site and pollutant. Examples include: 1 sample per 6 days, 1 per 12 days, and at the Dearborn site, samples were collected every day for one year.
- Measurement: 24-hour average concentrations
- 2 Laboratories: DNRE and Eastern Research Group (ERG) in North Carolina



# **Monitoring Sites**

- Monitored for over 200 compounds.
- Most pollutants do not pose health risk.
- 16 compounds of concern identified.
  - 13 compounds with cancer risk estimates greater than 1 in 1 million.
  - 3 compounds with monitored levels greater than health protective levels for noncancer effects.

Thirteen pollutants had risk greater than 1 in one million at least one site:

- Acetaldehyde
- Acrylonitrile
- Arsenic
- Benzene
- 1,3-Butadiene
- Cadmium
- Carbon tetrachloride
- Diesel Particulate Matter
- 1,4-Dichlorobenzene
- Formaldehyde
- Methylene chloride
- Naphthalene
- Nickel

Increased Lifetime Cancer Risk	Pollutant
100 to 400 in one million	methylene chloride naphthalene benzene
10 to 100 in one million	acrylonitrile formaldehyde 1,4-dichlorobenzene arsenic
1 to 10 in one million	carbon tetrachloride 1,3-butadiene acetaldehyde cadmium nickel

Total Cancer Risk by Site	
Monitoring Site	Total Cancer Risk (per million)
South Delray	525
Allen Park	473
North Delray	236
River Rouge	130
Southfield	111
Dearborn	101
Ypsilanti	35 *
Northeast Detroit	52 *
Houghton Lake	27 *

Non-cancer risks: •

- Monitored levels for three pollutants were greater than health protective values.
- Acrolein\*
- ManganeseNaphthalene

\*Based on preliminary data from DEARS

#### APPENDIX B

## **APPENDIX B: Chemical Information with Benchmarks**

CHEMICAL NAME	CAS NO	MOLECULAR WEIGHT	CAR- BONYL	voc	METAL	CR <sup>+6</sup>	PAH	AQD ITSL	ITSL AVG TIME	AQD IRSL	BASIS ITSL	BASIS IRSL
1,1,1-Trichloroethane	71556	133.4		Х				1000	24 hr		EPA	
1,1,2,2-Tetrachloroethane	79345	167.84		Х						0.02		EPA
1,1,2-Trichloroethane	79005	133.4		Х						0.06		EPA
1,1-Dichloroethane	75343	98.96		Х				500	24 hr		EPA	
1,1-Dichloroethene	75354	96.94		Х				200	24 hr	0.02	EPA	EPA
1,2,4-Trichlorobenzene	120821	181.44		Х				370	1 hr		TLV	
1,2-Dibromoethane	106934	187.88		Х						0.005		EPA
1,2-Dichloroethane	107062	98.96		Х						0.04		EPA
1,2-Dichloropropane	78875	112.99		Х				4	24 hr		EPA	
1,3-Butadiene	106990	54.1		Х				2	24 hr	0.03	EPA	EPA
1,4-Dichlorobenzene	106467	147		Х				800	24 hr	0.14	EPA	AQD
2,2,4-Trimethylpentane	540841	114.26		Х								
2-Chloro-1,3-Butadiene	126998	88.54		Х						0.001		AQD
Acetaldehyde	75070	44.06	Х					9	24 hr	0.5	EPA	EPA
Acetonitrile	75058	41.06		Х				60	24 hr		EPA	
Acetylene	74862	26.04		Х								
Acrylonitrile	107131	53.07		Х				2	24 hr	0.01	EPA	EPA
Acrolein												
Arsenic (TSP)	7440382	74.92			Х					0.0002		EPA
Barium												
Benzene	71432	78.12		Х				30	24 hr	0.1	EPA	EPA
Benzidine	92875	184.24					Х			0.00002		EPA
Benzyl alcohol	100516	108.14					Х	5000	24 hr		AQD	
Beryllium (TSP)	7440417	9.01			Х			0.02	24 hr	0.0004	EPA	EPA
bis (2-Chloroethyl)ether	111444	143.02					Х			0.003		EPA
bis(2-												
Chloroethoxy)methane	111911	173.04					Х					<b></b>
bis(2-Chloroisopropyl)ether	108601	171.07					Х					

#### **APPENDIX B: Chemical Information with Benchmarks**

CHEMICAL NAME	CAS NO	MOLECULAR WEIGHT	CAR- BONYL	voc	METAL	CR <sup>+6</sup>	PAH	AQD ITSL	ITSL AVG TIME	AQD IRSL	BASIS ITSL	BASIS IRSL
bis(2-Ethylhexyl)phthalate	117817	390.62					Х			0.2		AQD
Bromochloromethane	74975	129.39		Х				10600	8 hr		TLV	
Bromodichloromethane	75274	163.83		Х						0.027		
Bromoform	75252	252.75		Х						0.9		EPA
Bromomethane	74839	94.95		Х				5	24 hr		EPA	
Butyl benzyl phthalate	85687	312.36					Х	700	24 hr		EPA	
Butyr/Isobutyraldehyde		72.12	Х									
Cadmium (TSP)	7440439	112.4			Х					0.0006		EPA
Carbazole	86748	167.21					Х					
Carbon Tetrachloride	56235	153.81		Х						0.07		EPA
Chlorobenzene	108907	112.56		Х				70	24 hr		AQD	
Chlorobenzilate	510156	325.19					Х					
Chloroethane	75003	64.52		Х				10000	24 hr		EPA	
Chloroform	67663	119.37		Х						0.4		AQD
Chloromethane	74873	50.49		Х				90	24 hr	1.6	EPA	AQD
Chloromethyl Benzene	100447	126.59		Х						0.02		
Chromium (TSP)	7440473	52			Х							
Chromium VI (TSP)	18540300	52				Х		0.1	24 hr	0.000083	EPA	EPA
Chrysene	218019	228.3					Х					
cis-1,2-Dichloroethene	156592	96.94		Х				35	24 hr		EPA	
cis-1,3-Dichloropropene	10061020	110.97		Х								
Crotonaldehyde		70.1	Х					9	1 hr		TLV	
Diallate	1303164	270.22					Х					
Dibenzo(ah)anthracene	53703	278.36					Х					
Dibenzofuran	132649	168.19					Х	0.1	annual		AQD	
Dibromochloromethane	124481	208.29		Х						0.04		AQD
Dichlorodiflouromethane	75718	120.91		Х				49500	8 hr		TLV	
Dichlorotetrafluoroethane	76142	170.92		Х				69000	8 hr		AQD	
Diethyl phthalate	84662	222.24					Х	50	8 hr		TLV	

APPENDIX B:	Chemical	Information	with	Benchmarks
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CHEMICAL NAME	CAS NO	MOLECULAR WEIGHT	CAR- BONYL	voc	METAL	CR <sup>+6</sup>	PAH	AQD ITSL	ITSL AVG TIME	AQD IRSL	BASIS ITSL	BASIS IRSL
Dimethyl phthalate	131113	194.186					Х	50	8 hr		TLV	
Di-n-butyl phthalate	84742	278.347					Х	50	8 hr		TLV	
Di-n-octyl phthalate	117840	390.56					Х					
Dinoseb	88857	240.22					Х	4	24 hr		EPA	
Diphenylamine	122394	169.22					Х	100	8 hr		TLV	
Ethyl Acrylate	140885	100.13		Х						0.07		AQD
Ethyl methanesulfonate	62500	124.15					Х					
Ethyl Tert-Butyl Ether	637923	102.2		Х				373	24 hr		AQD	
Ethylbenzene	100414	106.18		Х				1000	24 hr	3	EPA	AQD
Fluoranthene	206440	202.26					Х	140	24 hr		EPA	
Fluorene	86737	166.23					Х	140	24 hr		EPA	
Formaldehyde	50000	30.03	Х							0.08		EPA
Halocarbon 113	76131	187.37		Х				76700	8 hr		TLV	
Halocarbon 114	76142	170.92		Х				69000	8 hr		AQD	
Hexachloro-1,3-Butadiene	87683	260.74		Х						0.05		EPA
Hexachloro-1,3-Butadiene	87683	260.74					Х			0.05		EPA
Hexachlorobenzene	118741	284.78					Х			0.002		EPA
Hexachlorocyclopentadiene	77474	272.77					Х	0.2	24 hr		EPA	
Hexachloroethane	67721	236.74					Х	3.5	24 hr	0.3	EPA	EPA
Hexachloropropene	1888717	248.75					Х					
Hexanaldehyde	66251	100.18	Х									
Indeno(123-cd)pyrene	193395	276.34					Х					
Isodrin	465736	364.91					Х					
Isophorone	78591	138.21					Х	280	1 hr	3.7	TLV	EPA
Isosafrole	120581	162.19					Х					
Isovaleraldehyde	590863	86.15	Х					800	annual		AQD	
	7400004	007.40			X				3			
Lead (ISP)	/439921	207.19			Х			1.5	months		NAAQS	
m,p-Tolualdehyde	1334787	120.16	Х									

<b>APPENDIX B:</b>	Chemical	Information	with	Benchmarks
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CHEMICAL NAME	CAS NO	MOLECULAR WEIGHT	CAR- BONYL	voc	METAL	CR <sup>+6</sup>	PAH	AQD ITSL	ITSL AVG TIME	AQD IRSL	BASIS ITSL	BASIS IRSL
m/p -Xylene	1330207	106.18		Х				100	24 hr		EPA	
Manganese (TSP)	7439965	54.94			Х			0.05	24 hr		EPA	
Methyl Ethyl Ketone	78933	72.12		Х				5000	24 hr		EPA	
Methyl Isobutyl Ketone	108101	100.18		Х				3000	24 hr		EPA	
Methyl Methacrylate	80626	100.13		Х				700	24 hr		EPA	
Methyl methanesulfonate	66273	110.13					Х					
Methyl Tert-Butyl Ether	1634044	88.17		Х				3000	24 hr		EPA	
Methylene Chloride	75092	84.93		Х						2		EPA
Naphthalene	91203	128.18					Х	3	24 hr	0.3	EPA	AQD
n-Butyraldehyde	123728	72.12	Х					7	24 hr		AQD	
n-Hexane	110543	86.18		Х				200	24 hr		EPA	
Nickel (TSP)	7440020	58.71			Х					0.0042		EPA
Nitrobenzene	98953	123.11					Х	0.7	24 hr	0.05	AQD	AQD
N-Nitrosodibutylamine	924163	158.24					Х					
N-Nitrosodiethylamine	55185	102.14					Х					
N-Nitrosodimethylamine	62759	74.08					Х					
N-Nitrosodipropylamine	621647	130.19					Х			0.0005		AQD
N-Nitrosomethylethylamine	10595960	88.11					Х					
N-Nitrosopiperidine	100754	114.15					Х					
N-Nitrosopyrrolidine	930552	100.12					Х					
n-Octane	111659	114.26		Х								
o-Tolualdehyde	529204	120.16	Х									
o-Toluidine	95534	107.15					Х			0.07		AQD
o-xylene	95476	106.18		Х				100	24 hr		EPA	
Pentachlorobenzene	608935	250.34					Х					
Pentachloroethane	76017	202.29					Х					
Pentachloronitrobenzene	82688	295.34					Х	5	8 hr		TLV	
Pentachlorophenol	87865	266.34					Х	100	24 hr	0.03	AQD	AQD
Phenacetin	62442	179.22					Х					
<b>APPENDIX B:</b>	Chemical	Information	with	<b>Benchmarks</b>								
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CHEMICAL NAME	CAS NO	MOLECULAR WEIGHT	CAR- BONYL	voc	METAL	CR <sup>+6</sup>	PAH	AQD ITSL	ITSL AVG TIME	AQD IRSL	BASIS ITSL	BASIS IRSL
Phenanthrene	85018	178.24					Х	0.1	annual		AQD	
Phenol	108952	94.11					Х	600	1 hr		NIOSH	
Pronamide	23950580	256.13					Х					
Propionaldehyde	318989	58.09	Х					4	annual		AQD	
Propylene	115071	42.09		Х				1500	24 hr		AQD	
Pyrene	129000	202.26					Х	100	24 hr		EPA	
Pyridine	110861	79.1					Х	3.5	24 hr		EPA	
Safrole	94597	162.19					Х					
Styrene	100425	104.16		Х				1000	24 hr	1.7	EPA	EPA
Tert-Amyl Methyl Ether	994058	102.2		Х				62	24 hr		AQD	
Tetrachloroethene	127184	165.82		Х						1.7		AQD
Tolualdehydes	1334787	120.16	Х									
Toluene	108883	92.15		Х				400	24 hr		EPA	
trans-1,2-Dichloroethene	156605	96.94		Х				70	24 hr		EPA	
trans-1,3-Dichloropropene	10061030	110.97		Х								
Trichloroethene	79016	131.38		Х						0.6		AQD
Trichloroflouromethane	75694	137.36		Х				56200	1 hr		TLV	
Trichlorotrifluoroethane	76131	187.376		Х				76700	8 hr		TLV	
Valeraldehyde	110623	86.15	Х					1760	8 hr		TLV	
Vinyl Chloride	75014	62.5		Х				100	24 hr	0.11	EPA	EPA

#### APPENDIX C Comparison with Other State Air Toxics Studies

<u>The studies listed below are based on the reports produced by the individual state</u> <u>environmental agencies and presented to give details to the data listed in chapter 9. Since the</u> <u>information below were pulled directly from the reports generated for each city, further</u> <u>information regarding these studies should be referred to the references at the end of the</u> <u>section and the authors for any specific details for the following cities.</u>

#### The Addyston, Ohio Case Study

In Ohio, the U.S. EPA had delegated its authority over air quality to the Ohio EPA, which in turn delegated authority for Cincinnati and its environs to the Hamilton County Department of Environmental Services (HCDOES). The air was sampled at five monitoring stations, located in the Village of Addyston, the City of Reading, and the Cincinnati neighborhoods of Carthage, Lower Price Hill, and Winton Place. These locations were selected due to their proximity to area, industrial, and mobile air pollution sources. The monitors were installed on the roofs of public buildings or schools.

Samples were collected for all sites (except Addyston) every 12 days over a 24-hour period, for a total of 28 to 30 samples in one year. The samples were collected into a SUMMA canister, which is a stainless steel vessel with an inert surface that will not react with other chemicals. At the request of the Ohio EPA, the Addyston station samples were collected every six days, for a total of approximately 60 samples per year. The samples were analyzed for approximately 60 different VOCs using standard U.S. EPA laboratory methods. VOCs are chemicals that evaporate quickly in air. The chemicals can be reliably detected by laboratory analysis at very low (parts per billion) concentrations (Hamilton County, 2007).

Cincinnati has several major industries including industrial agricultural food production; food processing and brewing industry; machine manufacturing; automotive parts manufacturing; converters; aerospace industries; product manufacturing; multimedia industry; chemical industry; personal care products industry; pharmaceuticals; plastics manufacturing; commercial item transport and distribution facilities; a large railroad hub; port for barges, and an international airport; oil and coal transport and storage facilities; large landfill; disposal and recycling industry, and waste treatment facilities.

Risk characterization was performed for both carcinogenic compounds and non-carcinogens. The equation used to calculate carcinogenic compounds is:

#### Air Concentration x Unit Risk = Probability of Developing Cancer

This study also used a cancer risk of 1 in 100,000 people, which Hamilton County, Ohio considers to confer an acceptable margin of safety. For chemicals that do not cause cancer, but cause other health effects, the following equation was used:

 $\frac{Air...Concentration}{"Safe"...Concentration} = Hazard...Quotient$ 

If the Hazard Quotient (HQ) is less than 1, then it is unlikely that people will develop harmful health effects from breathing that concentration of the chemical. When more than one chemical is present, the HQs from each of the chemicals present are added together to better understand the combined hazard posed by exposure to multiple chemicals. The total of all HQs at each monitoring station is called the hazard index. Because each chemical may cause different effects in humans (for example lung or liver effects), the hazard index may overestimate the risk, but can provide an indication of whether further analysis is needed. Hamilton County, Ohio considers a chemical of potential concern as any chemical whose HQ is 1 or more or whose cancer risk is greater than 1 excess cancer in 100,000 people. The information ("safe" concentration for non-cancer effects and "unit risk" for cancer effects) used to develop the list of chemicals of potential concern came from the EPA's Integrated Risk Information System (IRIS).

Air toxics in Hamilton County are produced by three main sources: area, industrial, and mobile. As part of this study, the monitoring data were analyzed and compared to the EPA's health guidelines to estimate the potential for health risks. This analysis identified chemicals of potential concern, which are those most likely to result in cancer and non-cancer health risks. The chemicals of potential concern for Hamilton County are as follows: acrylonitrile, benzene, 1,3-butadiene, carbon tetrachloride, and chloroform. Acrylonitrile is an industrial process chemical and is a driver for total non-cancer and total cancer risks at Addyston. Benzene was detected at all five air monitoring stations in Hamilton County, and 1,3-butadiene was detected at every station except one. Both chemicals are mostly attributed to mobile sources and are commonly found in the air of large urban areas across the U.S. Benzene is a component in gasoline, and 1,3-butadiene is formed during the combustion of gasoline. 1,3-butadiene is also used as an industrial process chemical. 1,3-butadiene is a driver for total cancer risk at the Addyston station. Carbon tetrachloride was also detected at all five air monitoring stations. Carbon tetrachloride was heavily used as an industrial solvent until the 1980s, when it was phased out due to its potential to cause cancer. Its slow breakdown in the environment contributes to its persistent concentration. Carbon tetrachloride is common in air across the U.S., but at very low concentrations. Chloroform was detected at the Addyston. Chloroform is mainly a disinfection byproduct of chlorinated drinking water, swimming pools, and wastewater treatment plants. As a result, it is commonly found in the air of most major cities. With the exception of acrylonitrile, the chemicals of potential concern identified for Hamilton County are similar to the chemicals found in the air of other major industrial cities across the U.S., as reported in U.S. EPA's National-Scale Air Toxics Assessment (NATA). Around the nation, these same chemicals are also emitted from motor vehicles, are persistent in the environment as a result of past industrial uses, and are released from industrial processes. The total excess cancer risk in Hamilton County (based on all detected chemicals for the 2007 monitoring year) is estimated to range form 3 to 44 additional cancers per 100,000 people, depending on the monitoring site.

Addyston is a small residential village on the western side of Cincinnati, near the Ohio river, with approximately 1,000 inhabitants with several large facilities nearby. The facilities along this portion of the Ohio river include: a steel manufacturing plant, chemical companies, and a plastics manufacturer. One company produces ABS plastic pellets which are shipped and used as raw material by other companies. The three basic chemicals used are acrylonitrile, 1,3-butadiene, and styrene. The high levels of acrylonitrile and 1,3-butadiene were found to coincide with several incidents reported by the company; an isolation damper malfunction, a batch was over pressurized and released, and a valve failure. Concentrations of 1,3-butadiene were still higher than anticipated. After further investigation it was determined that a steam-assisted flare was not working properly. The company installed new computer controls and 1,3-butadiene emissions markedly decreased. Acrylonitrile concentrations were also higher than

expected. Work is ongoing to reduce these emissions which include covering settling and aeration tanks and adding a biofilter to the venting system.

Differences Bet	Differences Between Addyston, Ohio Risk Assessment Values with Michigan Risk Assessment Values							
Addyston, Ohio	Air Concentration for Addyston, Ohio (µg/m <sup>3</sup> )	Hamilton County (Addyston), Ohio Risk Assessment Values	Comparison using State of Michigan Risk Assessment Equations	Reference:				
Risk Drivers		Hazard Quotient	Hazard Quotient					
Non-cancer								
Acrylonitrile	3.0	1.5	N/A	IRIS database				
Cancer		Cancer Risk (# of cancers per 100,000)	Cancer Risk (# of cancers per 1,000,000)					
Acrylonitrile	3.0	21	30	IRIS database				
Benzene	1.2	0.9	12	IRIS database				
1,3-Butadiene	5.5	17	180	IRIS database				
Carbon tetrachloride	1.1	1.6	15	IRIS database				
Chloroform	0.14	1.5	1.7	IRIS database				

#### The Austin-Round Rock Case Study

The Austin-Round Rock Metropolitan Statistical Area, which is comprised of Bastrop, Caldwell, Hays, Travis, and Williamson Counties, had a 2005 estimated population of over 1.4 million. Its two largest counties, Travis and Williamson (which composed 85 percent of the total area population) ranked 85<sup>th</sup> and 376<sup>th</sup>, respectively, in total Hazardous Air Pollution (HAP) emissions out of the 1,207 U.S. urban counties according to the 1999 National Emission Inventory. About half the estimated HAP emissions were from on road mobile sources. Only one percent of the 1999 estimated HAP emissions in Travis and Williamson Counties were from major industrial sources. The Austin-Round Rock Toxin Study (ARTS) is an exploratory study of air toxics levels in the Austin-Round Rock area to identify any chemicals in the air that might pose an appreciable health risk, either regionally or at a particular location. The study is also intended to establish a baseline for measuring future air toxics trends brought about by VOC control measures, cleaner burning vehicles, or other factors including those that might counteract air pollution controls such as increased vehicular traffic and congestion. Measurements were made at five fixed sites over a 12-month period to estimate the annual average concentrations of 83 hazardous air pollutants, including 19 core air toxics that are measured at National Air Toxics Trends Sites (NATTS) throughout the U.S. The monitoring sites were oriented north to

south from Round Rock to south Austin, near areas of relatively high population density. All the measurements were performed using standard EPA sampling and analytical methods.

The Austin-Round Rock area has several major industries including: electronics industries; equipment manufacturing; converters; materials manufacturing; semiconductor industry; energy industry; consumer electronics manufacturing; computer equipment manufacturing; product manufacturing; disposal and recycling; environmental industries; aerospace industries; pharmaceutical industries; energy industry, and a municipal utility operating three natural gas power plants in the Austin area.

Risk characterization was performed for both carcinogenic compounds and non-carcinogens. A comparative analysis of non-cancer effects were performed using target compounds ranked by the likelihood of producing non-cancer adverse health effects. The rankings were based on each compound's average HQ which, for a particular compound, is equal to the average concentration divided by the compound's RfC. HQ values less than one indicate no adverse health affects are expected while HQ values greater than one indicate that adverse health effects are possible. Acrolein is the only ARTS target compound with a hazard quotient greater than one. The acrolein measurements are of particular interest and concern because of the high HQ and because they are among the highest annual average acrolein levels reported in the EPA AQS database for 2005 and 2006. The highest acrolein levels were measured in samples collected during July-November 2005 and during May-June 2006. The measurement precision appears reasonably good, based on analyses of collocated samples; however, the data are guestionable because no known sources of acrolein account for the differences in the measured levels relative to the average concentrations reported for most other areas and because potential positive biases in the measurement approach using in ARTS have been observed elsewhere. Acrolein was measured in ARTS using EPA Compendium Method TO-15, after extensive performance tests in 2005, because method TO-11A, which was the basis for much of the earlier measurement data throughout U.S., had been shown to underestimate the true levels (ERG, 2005). However, research conducted by the Rhode Island Department of Health shows that TO-15 can produce unrealistically high measurement values for acrolein under some conditions, perhaps by production of acrolein from the decay of other sample constituents inside the TO-15 canisters (Heaton, 2006).

For the comparative analysis of excess cancer risks, the average excess risk estimate for each compound was calculated by taking the average concentration from all the ARTS monitoring sites and multiplying that value by the particular compound's upper-bound excess risk estimate (URE). The URE is the upper-bound excess risk estimated to result from a lifetime of continuous exposure to a carcinogenic air pollutant at a concentration of 1.0  $\mu$ g/m<sup>3</sup>. Values of URE for each ARTS target compound was obtained from the EPA Integrated Risk Information System (IRIS), which is accessible on the Internet at <u>http://www.epa.gov/iris</u>. The average concentrations and cancer risk estimates are based on substituting ½ DL for non-detected values. Note that several of the compounds having comparatively high cancer risks were rarely detected and only appear in the table below because of the data reporting convention. The actual risks posed by exposure to these compounds might not be so high if ½ DL is not a good estimate for the average of the non-detected concentrations. An alternate approach using zero  $\mu$ g/m<sup>3</sup> for non-detected values give lower risk estimates for infrequently detected compounds.

With one exception, the levels of the 19 core air toxics averaged over all ARTS monitoring sites were comparable to or less than the average levels in most other U.S. cities where similar measurements have been made. Acrolein is the one core compound that was found at appreciably higher concentrations in ARTS compared with most other U.S. cities. Acrolein was

found to have the greatest potential for producing non-cancer health effects of all ARTS target compounds and it is also the most appreciable non-cancer risk driver on a national scale, according to the EPA 1999 National Air Toxics Assessment. Acrolein is emitted by motor vehicles, electricity generating units, wildfires, and other combustion processes including smoking cigarettes; however, no known sources account for the differences between the ARTS data and measurements collected elsewhere. The greatest risks of contracting cancer from inhalation exposure to measured HAPs in the Austin-Round Rock area come from carbon tetrachloride and benzene. Carbon tetrachloride exists primarily as a background air pollutant resulting from prior widespread uses including in fire extinguishers, as a propellant for aerosol spray cans, as a cleaning fluid, and in the production of Freon refrigerants. Carbon tetrachloride production and use for consumer products has been phased out over concern for its toxicity and harm to the Earth's ozone layer but it remains a background constituent of outdoor air because of its long half-life of 30-100 years. The average level of carbon tetrachloride measured in ARTS varied by less then 10 percent from the lowest to highest site. Benzene is a constituent of motor vehicle emissions and is also found in emissions from burning coal and oil, evaporative emissions from gasoline refueling, and in industrial solvents. About half the benzene in ARTS study appears to come from motor vehicles. The average benzene levels were within  $\pm 13$ percent of the 2005 national median for ARTS sites but were almost twice the national median at Webberville Road where the highest levels of other motor vehicle emissions constituents were also measured. After carbon tetrachloride and benzene, the next greatest risk of contracting cancer form inhalation exposure to HAPs come from 1,3-butadiene and acetaldehyde, which along with benzene are classified by EPA as priority mobile source air toxics. The ARTS measurement results agreed remarkably well with results of the 1999 National Air Toxics Assessment (NATA), based on its identification of key air pollutants, estimations of air toxics levels, and estimations of total risks due to inhalation exposure to toxic air pollutants. The NATA modeled estimate of total cancer risk for Travis County, 41 in a million, is equal to the total cancer risk estimated from ARTS measurement data. The NATA estimate for Williamson County, 28 in a million, differs by less than 20 percent from the 34 in a million estimated from the ARTS monitoring data collected in Round Rock. To place these risk estimates in perspective, note that one out of every three Americans (330,000 in one million) will contract cancer during a lifetime, when all causes are taken into account.

Differences Between Austin, TX Risk Assessment Values with Michigan Risk Assessment Values

Assessment Values							
Austin, TX	Air Concentration for Austin, TX (μg/m <sup>3</sup> )	Austin-Round Rock, TX Risk Assessment Values	Comparison using State of Michigan Risk Assessment Equations	Reference:			
Risk Drivers		Hazard Quotient	Hazard Quotient				
Non-cancer							
Acrolein	3.77	172	N/A	IRIS database			
Cancer		Cancer Risk (# of cancers per 1,000,000)	Cancer Risk (# of cancers per 1,000,000)				
Acetaldehyde	1.62	3.1	3.2	IRIS database			
Acrylonitrile	0.18	5.9	18	IRIS database			
Arsenic	0.0011	3.0	5.5	IRIS database			
Benzene	1.88	8.9	19	IRIS database			
1,3-Butadiene	0.33	4.1	11	IRIS database			
Carbon tetrachloride	0.67	9.9	9.6	IRIS database			
Chloroform	0.09	2.4	0.23	IRIS database			
Chloromethylbenzene	0.05	2.6	N/A	IRIS database			
1,2-Dibromoethane	0.10	22.7	N/A	IRIS database			
Hexachloro-1,3- butadiene	0.80	17.9	N/A	IRIS database			
1,3-Dichlorobenzene	0.35	2.9	2.5	IRIS database			
1,2-Dichloroethane	0.05	1.4	N/A	IRIS database			
1,2-Dichloropropane	0.08	1.6	N/A	IRIS database			
1,1,2,2- Tetrachloroethane	0.09	5.6	N/A	IRIS database			
Tetrachloroethylene	0.19	1.1	N/A	IRIS database			

#### The Burbank, California Case Study

The South Coast Air Quality Management District staff conducted a sub-regional air toxics monitoring program in the Sun Valley region as a complement to the Multiple Air Toxics Exposure Study III (MATES III). The Sun Valley region (located in the northwestern portion of the South Coast Air Basin) contains several sources of potential air toxic emissions, including a landfill, as well as recycling and industrial facilities, and is located downwind from a commercial airport. The monitoring locations were selected to characterize air toxic impacts in the community. The study monitored toxic metals, particulate matter size 10 microns or smaller (PM<sub>10</sub>), and some VOCs.

A total of six locations are reported in this study. Three portable sampling platforms were utilized: two of the platforms were deployed to two locations (LA County Fire Station and Los Angeles Unified School District [LAUSD]) for the duration of the project. The third sampling platform, based on prevailing winds, was moved to one of two locations determined by season to be downwind of the major emission sources (Stonehurst and Poly High). A MATES III Micro scale site located at Fernangeles Elementary School was in operation throughout the study period as was its nearest paired fixed MATES III site at Burbank. The monitoring locations were selected to best determine the air toxic exposure of the residents within the Sun Valley area with specific interest and focus on the Bradley landfill. The PM<sub>10</sub> filters were analyzed for elemental and organic carbon concentrations. Total carbon is the sum of these two measured components. The total carbon content of the site filters closely follows the PM<sub>10</sub> concentrations.

Burbank has several major industries including: the motion picture industry; metals manufacturing; aerospace industry; metal manufacturing; and consumer products manufacturing. The risk assessment was not published in the Burbank, CA study, but was published in the much larger Multiple Air Toxics Exposure Study (MATES II) which focused on the South Coast Air Basin. Computer modeling was performed to determine a more complete picture of toxics risks. The determination of risk values for each compound are derived from animal or epidemiological studies of exposed workers or other populations. Uncertainty occurs from the application of individual results to the general population. When risk factors for specific compounds are determined, levels are usually established conservatively. There is an estimated uncertainty level of ± 25 percent associated with laboratory measurements of many toxic compounds. Part of this uncertainly is attributed to the fact that many of the toxic compounds measured are at extremely low concentration levels, at parts per billion (ppb) levels, and often near detection limits of the instrumentation. A number of compounds cannot be detected at all. When non-detections occur, it is assumed that the actual levels are not zero, but are half of the instrument detection limit. In other words, if the detection limit is 1 ppb, and a compound is not detected at that level, it is assumed that the actual concentration is one-half of 1 ppb. This convention allows the vast majority of the data users to statistically manage the data. Other methods of handling non-detects are often difficult to implement or offer no practical advantage. The method is a conservative one that protects the public when analytical shortcomings cannot address real emissions that are known to exist. Although this convention is not in regulation form, it is considered at this time to be the best available tool for addressing concentrations of pollutants where current laboratory technologies cannot yet detect such low levels, and at the same time treating public safety concerns. As a sensitivity test, it was assumed that non-detect values were zero for those pollutants which had a predominance of non-detections. Under such an assumption, the overall risk values would have been lowered by 4.6%.

To assess the potential for noncancer health risks, the monitored average levels were compared to the Chronic Reference Exposure Levels (RELs) established by OEHHA. The chronic REL is the air concentration at or below which adverse noncancer health effects would not be expected in the general population with exposure for at least an appreciable fraction of a lifetime. In general, the measured concentrations of air toxics were below the RELs. The exception is formaldehyde. The chronic REL is 3  $\mu$ g/m<sup>3</sup> (2 ppb). Formaldehyde effects include eye irritation, injury to nasal tissue, and respiratory discomfort. OEHHA, however, is proposing revisions to the RELs for several toxic air contaminants. For formaldehyde, the proposed chronic REL is 9  $\mu$ g/m<sup>3</sup> (7 ppb). If the proposed level is promulgated, then all sites would be under the chronic REL.

The intent of a cancer risk assessment aims to characterize the relationship between an applied dose of a carcinogen and the risk of tumor appearance in a human. This is usually expressed as a cancer slope factor ["potency" - in units of reciprocal dose - usually (mg/kg-body weight.day)<sup>-1</sup> or "unit risk" – reciprocal air concentration - usually  $(\mu g/m^3)^{-1}$  for the lifetime tumor risk associated with lifetime continuous exposure to the carcinogen at low doses. Cancer potency factors may also be referred to as "cancer slope factors". The procedures used to extrapolate low-dose human cancer risk from epidemiological or animal carcinogenicity data are generally health-protective in that they determine an upper confidence bound on the risk experienced by an exposed population. As statistical estimates they cannot be regarded as definite predictions of the risk faced by any one specific individual, who might for a variety of reasons, including individual exposure and susceptibility, experience a risk different from the estimate. The risk assessment procedures used aim to include the majority of variability in the general human population with the confidence bounds of the estimate, although the possibility that some individuals might experience either lower or even no risk, or a considerably higher risk, cannot be excluded. The models used fall into three main classes: mechanistically based models, empirical models, and (where data are lacking to support a true data-based model) default assumptions. The factors affecting the dose-response relationships for carcinogens may also be divided into those relating to absorption, distribution, metabolism, and excretion on the one hand (i.e. toxicokinetics), and those relating to the underlying dose-response characteristics of carcinogenesis at the tissue or cellular level (*i.e.* toxicodynamics). In this sense the problem of dose response assessment for carcinogens is similar to that for non-cancer toxic effects. The toxicokinetic models used may in fact be similar for both situations, but the toxicodynamic models are generally different.

Cancer unit risk factors [in units of  $(\mu g/m^3)^{-1}$ ] have been calculated from cancer potency factors [in units of  $(mg/kg-day)^{-1}$ ] using the following relationship:

 $UR = \frac{CPF \times 20m^3}{70kg \times CV}$ 

Where: UR = the cancer unit risk CPF = the cancer potency factor 70kg is the reference human body weight 20 m<sup>3</sup> is the reference human inspiration rate/day CV = the conversion factor from mg to  $\mu$ g (=1,000)

The cancer unit risk describes the excess cancer risk associated with an inhalation exposure to a concentration of  $1 \mu g/m^3$  of a given chemical; the cancer potency factor describes the excess

cancer risk associated with exposure to 1 mg of a given chemical per kilogram of body weight. The risk is considered "excess" in that it is above what background cancer risks would be expected to occur.

There are uncertainties in the risk potency values used to estimate lifetime risk of cancer. This study used the unit risks for cancer potency established by OEHHA and the annual average concentration measured or modeled to calculate risk. This methodology has long been used to estimate the relative risks from exposure to air toxics in California and is useful as a yardstick to compare potential risks from varied sources and emissions and to assess any changes in risks over time that may be associated with changing air quality. The estimates of health risks are based on the state of current knowledge, and the process has undergone extensive scientific and public review. However, there is uncertainty associated with the processes of risk assessment. This uncertainty stems from the lack of data in many areas necessitating the use of assumptions. The assumptions are consistent with current scientific knowledge, but are often designed to be conservative and on the side of health protection in order to avoid underestimation of public health risks. As noted in the OEHHA risk assessment guidelines, sources of uncertainty, which may either overestimate or underestimate risk, include: (1) extrapolation of toxicity data in animals to humans, (2) uncertainty in the estimation of emissions, (3) uncertainty in the air dispersion models, and (4) uncertainty in the exposure estimates. Uncertainty may be defined as what is not known and may be reduced with further scientific studies. In addition to uncertainty, there is a natural range or variability in the human population in such properties as height, weight, and susceptibility to chemical toxicants. Thus, the risk estimates should not be interpreted as actual rates of disease in the exposed population, but rather as estimates of potential risk, based on current knowledge and a number of assumptions. However, a consistent approach to risk assessment is useful to compare different sources and different substances to prioritize public health concerns.

The key findings of this study showed, with the exception of hexavalent chromium, measured levels of toxic air contaminants were similar across the Sun Valley region. The average concentrations of toxic metals and toxic gaseous compounds entering Sun Valley on the predominant winds were changed slightly in traversing the valley. Any influence of the landfill on toxic compound concentrations could not be discerned at the sites chosen for this study. The hexavalent chromium analysis shows that immediately downwind of a stationary source (a plating company) measureable hexavalent chromium concentration levels were detected. However, at short distances away from the source, levels decline and approach concentration levels similar to background levels. The plating company ceased operations in November 2006, four months after the end of this study. PM<sub>10</sub> concentrations are indicative of predominant wind patterns within the sub-region of Sun Valley. Local disturbances to this homogeneity could be ascribed to an abundance of crustal elements. Compared to previous studies of air toxics in the Basin, this study found a decreasing risk for air toxics exposure, with the estimated Basin-wide population-weighted risk down by 8% from the analysis done for the MATES II time period. The ambient air toxics data from the fixed monitoring locations also demonstrated a reduction in air toxic levels and risks. The results from this study underscore that a continued focus on reduction of toxic emissions, particularly from diesel engines, is needed to reduce air toxics exposure.

#### The Elizabeth, New Jersey Case Study

The New Jersey Department of Environmental Protection established four air toxics monitoring sites located in Camden, Elizabeth, New Brunswick, and Chester. These sites mainly measured VOCs. Each 24-hour sampling event was collected approximately every six days

with a total of approximately 57 VOC samples and 58 carbonyl samples collected from each site in 2006.

Elizabeth has several major industries including: consumer products manufacturing; plastics industry; petroleum refineries; disposal and recycling industries; and is a major transportation hub for commercial transport and distribution facilities including trucking companies and a large trail station, a large shipping port, and an international airport.

A way to determine whether the ambient concentration of an air toxic could pose a potential human health risk is to compare the air concentration to its health benchmark. The risk ratio is the number produced when the air concentration is divided by the benchmark. If the ratio is less than one, the air concentration should not pose a health risk. If it is greater than one, it may be of concern. The risk ratio also indicates how much higher or lower the estimated air concentration is than the health benchmark. Risk characterization in human risk assessment includes some consideration of uncertainty, scientific judgment, and the major assumptions that were made regarding exposure. Human health risk estimates for inhalation of carcinogens are based on the following calculation:

Cancer Risk = C x URF

Where:

C = maximum annual average ambient air concentration of a pollutant,  $\mu g/m^3$  URF = pollutant-specific inhalation unit risk factor, ( $\mu g/m^3$ )<sup>-1</sup>

Human health risk estimates for inhalation of noncarcinogens are based on the following calculation:

Hazard Quotient = C/RfC

Where:

C = maximum ambient air concentration,  $\mu g/m^3$ RfC = pollutant-specific reference concentration,  $\mu g/m^3$ 

The toxic air pollutants that exceeded their health benchmarks for Elizabeth, NJ include: acetaldehyde, benzene, carbon tetrachloride, chloroform, chloromethane, formaldehyde, 1,3-butadiene, and tetrachloroethylene.

On-road mobile sources (cars and trucks) account for 36% of the air toxics emissions, and nonroad mobile sources (airplanes, trains, construction equipment, lawnmowers, boats, dirt bikes, etc.) contribute 25%. Area sources (residential, commercial, and small industrial sources) represent 27% of the inventory, and major point sources (such as factories and power plants) account for the remaining 12%. Air toxics come from many different sources, not only manufacturing, but also other kinds of human activity. When New Jersey's emissions estimates are broken down by county, it is evident that the areas with the largest air toxic emissions are generally those with the largest populations. This is directly related to high levels of vehicle use, solvent use, heating, and other population-related activities in those counties.

#### Differences Between Elizabeth, NJ Risk Assessment Values with Michigan Risk Assessment Values

Assessment Values							
Elizabeth, NJ	Air Concentration for Elizabeth, NJ (µg/m <sup>3</sup> )	Elizabeth, NJ Risk Assessment Values	Comparison using State of Michigan Risk Assessment Equations	Reference:			
Risk Drivers							
Cancer		Cancer Risk (# of cancers per 1,000,000)	Cancer Risk (# of cancers per 1,000,000)				
Acetaldehyde	5.7	13	11.0	IRIS database			
Benzene	1.3	10	13.0	IRIS database			
1,3-Butadiene	0.16	5	5.3	IRIS database			
Carbon tetrachloride	0.59	9	8.4	IRIS database			
Chloroform	0.13	2.9	0.33	IRIS database			
Chloromethane	1.14	2.0	N/A	IRIS database			
Formaldehyde	4.6	59	57.0	IRIS database			
Tetrachloroethylene	0.36	2.1	N/A	Cal EPA 09a			

#### The Indianapolis, Indiana Case Study

Between October 2006 and October 2008, Indiana Department of Environmental Management (IDEM), the EPA, the city of Indianapolis, and a diverse group of stakeholders conducted a study of HAPs and other air toxics in a 10 square mile area of southwestern Indianapolis, Indiana. In the 1999 NATA, the EPA identified census tracts in this area as being of potential concern for exposure to air toxics. In addition, there was considerable concern by residents in this part of the city, as documented by articles in the Indianapolis Star (February 22-23, 2004). IDEM conducted ambient air monitoring in two residential neighborhoods: the Harding Street location and Stout Field. The monitoring sites were strategically located based on proximity to major sources for emissions, and in locations where the general public lives and congregates. Both sites were operated consistent with procedures established for the EPA's National Air Toxics Trends Station (NATTS) Network. IDEM monitored VOCs, carbonyls, and toxic metals. IDEM monitored a total of 95 air pollutants. The goal of this study was to gather more information about air toxics in an area where little information was available. Currently, Marion County is designated as not meeting the federal health standard set by the EPA for particulate matter. However, current monitoring results demonstrate that Marion County meets federal particulate matter health standards. IDEM has petitioned the EPA to redesignate the area from nonattainment to attainment.

Monitoring results were analyzed using the EPA approved statistical methods. IDEM used a statistical analysis tool called Kaplan-Meier to evaluate the data. During sampling, it is not uncommon to have pollutant concentrations below the detection limits. Even with the very low detection limits that IDEM is able to achieve (parts per billion). Instead of ignoring readings that were below the detection limit, assuming that the concentration is always zero, or assuming that the concentration is always at the detection limit for that chemical, IDEM applied a more complex and robust statistical analysis. The EPA recommends that, if possible, the Kaplan-Meier Product Limit Estimate (Kaplan-Meier) method be used. Kaplan-Meier was used to evaluate the data so that a 95 percent upper confidence limit of the mean (UCL) could be determined. This is the standard methodology recommended by the EPA for estimating the concentration to which people are exposed. Kaplan-Meier is a non-parametric method that allows the calculation of a less biased mean and standard error (and by extension, many other statistical values) from a dataset that contains non-detects. Kaplan-Meier has many advantages over other methods for dealing with non-detects; it is a non-parametric method, and as such does not require that the distribution of the data be known, it can be used with datasets that contain many non-detects, and is more accurate than substitution methods such as using half the detection limit. There are at least two different variations of the Kaplan-Meier method. The main difference in these methods appears to be where censoring occurs in the dataset. The dataset can be censored either at the lowest detection in the dataset or at the lowest detection limit. Censoring the lowest detection limit will introduce less bias into your results, where censoring at the lowest detection limit will provide results that are slightly more conservative. To be consistent with the EPA's ProUCL software, this analysis chose to censor at the lowest detection, rather than the lowest detection limit.

Indianapolis is home to several major industries including: metals manufacturing; aerospace industry; automotive industry; metal working industry; plastics industry; marine manufacturing industry; media industry; disposal and recycling industries; consumer products manufacturing; pharmaceutical industry; health care product manufacturing; chemical manufacturing; and commercial item transportation facilities including an international airport and a large railway facility.

The risk characterization focuses on two toxic endpoints for each pollutant, cancer and noncancer health effects from inhalation exposure over a lifetime (70 years) and uses health protective assumptions and inputs. The primary function of the risk characterization is to put into context the concentration of each of the pollutants to which the public is exposed by taking into account the toxicity of the different pollutants. Risk characterization, while a useful tool, is not a statement of "actual risk" that people face but rather a reasonable estimate of upperbound potential risk. The "actual risk" that individuals face is a complex combination of many factors, including genetic predisposition, diet, lifestyle choices, and environmental contribution. Risk values should not be considered to represent actual predicted cases of cancer. IDEM used risk characterization methodology based on U.S. EPA's Air Toxics Risk Assessment Reference Library Volumes 1, 2, and 3. Methods were reviewed by a Technical Advisory Group during the course of the study. The U.S. EPA uses a range between one in a million to one hundred in a million  $(1.0 \times 10^{-6} \text{ to } 1.0 \times 10^{-4})$  when evaluating whether the estimated risk is at a level where action should be taken. Generally, U.S. EPA considers risk estimates over one hundred in a million  $(1.0 \times 10^{-4})$  to be at levels where action or more investigation is required. Risks that fall between one in a million and 100 in a million  $(1.0 \times 10^{-6} \text{ to } 1.0 \times 10^{-4})$  level generate decisions and actions taking into account the assumptions used to determine the estimate. Risk estimates below one in a million  $(1.0 \times 10^{-6})$  are usually considered as not requiring further action.

IDEM evaluates non-cancer hazard assuming a threshold for each pollutant under which no adverse effect is expected. IDEM uses health protective assumptions by taking into account people who might be more sensitive to the pollutants. A hazard quotient (HQ) is a ratio that divides an exposure concentration by a reference value. A HQ under 1.0 is commonly recognized to be below the health protective level. HQs over 1.0 indicate that further investigation may be necessary and does not mean that health effects are expected. Given the many health protective assumptions used in the evaluation, most HQs over 1.0 are still not at levels where health effects may be observed.

IDEM modeled a total of 464 sources of emissions within the study area. This included major industry sources, trucking companies, gas stations/truck stops, auto body shops, and dry cleaning facilities. IDEM also modeled major and secondary roadways for emissions and impacts from cars and trucks. IDEM split the roads into segments and used traffic count data from the Indiana Department of Transportation to aid in the determination of the volume of emissions deriving from each segment.

Concentrations of most pollutants in southwest Indianapolis were similar to concentrations observed in other areas of Indiana and other metropolitan areas. One pollutant, p-dichorobenzene, was observed to be higher at the Stout Field location than other monitoring locations in the state. A majority of the time 1,3-dichlorobenzene was monitored at low concentration at both monitors. However, during a two-month period, 1,3-dichlorobenzene concentrations were higher than normal at Stout Field. This episode of higher 1,3-dichlorobenzene concentrations coincided with other pollutants also at levels not normally observed. IDEM investigated possible sources of the 1,3-dichlorobenzene, but was unable to identify the likely source. An event like this was not observed again during the two-year monitoring period and concentrations during the event were not above acute health protective levels. All pollutants were monitored at concentrations below the one hundred in a million  $(1.0 \times 10^{-4})$  risk level. Only benzene was monitored above the ten in a million  $(1.0 \times 10^{-5})$  risk level. Risk estimates for 1,3-butadiene, acetaldehyde, arsenic, carbon tetrachloride, chloroform, 1,3-dichlorobenzene, 1,4-dioxane, ethylbenzene, and tetrachloroethene were over one in a million (1.0 x 10<sup>-6</sup>) risk. Benzene can come from many sources, most commonly cars and trucks. The benzene concentrations observed at the Southwest Indianapolis monitors are consistent with the concentrations observed at monitors in other cities around Indiana and the U.S. The only pollutant with a monitored HQ over 1.0 is acrolein. Acrolein concentrations were well above the health protective benchmark at both monitoring locations. Acrolein is a common pollutant found in many urban areas. It is most commonly associated with the burning of organic materials and from motor vehicles. It can also be formed in the air when pollutants reach with the sun and other chemicals. Animal studies have shown that breathing acrolein may cause irritation to the nasal cavity and can damage the lining of the lungs. The results indicate that acrolein concentrations in southwest Indianapolis are comparable to concentrations observed in other urban areas of the state. The study results indicate that inhalation risk from potential air toxics exposure in the southwest Indianapolis area is comparable to other cities around Indiana and the U.S. The larges contributors to air toxics in the study area are background and mobile sources (i.e., cars, trucks, etc.). Industrial source contributions to air toxics and risk were small when compared to the risk from background and mobile sources. However, IDEM has indentified a few industrial sources in the area that, while not significant sources of risk, could warrant further evaluation for potential pollution prevention opportunities. A new mobile source air toxics rule along with new emission regulations on new cars and trucks are expected to reduce mobile source impacts. These new federal standards combined with the replacement of older, less efficient cars with new cleaner, more efficient cars is expected to reduce mobile source air toxics emissions by up to 45 percent over the next 15 years.

Differences Between Indianapolis, IN Risk Assessment Values with Michigan Risk Assessment Values

Assessment values				
Indianapolis, IN	Air Concentration for Indianapolis, IN (µg/m <sup>3</sup> )	Indianapolis, IN Risk Assessment Values	Comparison using State of Michigan Risk Assessment Equations	Reference:
Risk Drivers		Hazard Quotient	Hazard Quotient	
Non-cancer				
Acrolein	1.7	84	N/A	IRIS database
Cancer		Cancer Risk (# of cancers per 1,000,000)	Cancer Risk (# of cancers per 1,000,000)	
Acetaldehyde	0.70	1.5	1.4	IRIS database
Arsenic	0.0012	5.3	6.0	IRIS database
Benzene	1.9	15	19	IRIS database
1,3-Butadiene	0.12	3.5	4.0	IRIS database
Carbon tetrachloride	0.28	4.2	4.0	IRIS database
Chloroform	0.063	1.5	0.16	IRIS database
1,3-Dichlorobenzene	0.72	8.0	5.1	IRIS database
1,4-Dioxane	0.13	1.0	N/A	IRIS database
Ethylbenzene	0.48	1.2	N/A	IRIS database
Formaldehyde	2.4	0.010	30.0	IRIS database
Tetrachloroethene (PCE)	0.27	1.6	N/A	IRIS database

#### The Pittsburgh, Pennsylvania Case Study

The Alleghany County Health Department in collaboration with Carnegie Mellon University embarked on a project to investigate air toxics in Allegheny County. The project involved both baseline and intensive sampling a suite of gas-phase organic air toxics. Measurements were made at multiple sites that represent different source/exposure regimes. The study sites were chosen to compare air toxics concentrations and health risks among areas dominated by different sources. Air toxics concentrations were measured at six monitoring sites in and around Pittsburgh, Pennsylvania. Two of the sites (Avalon and Stowe) were in residential areas adjacent (about 0.8 km) to Neville Island, which is heavily industrialized. Sites were also located in downtown Pittsburgh (Flag Plaza site, Diamond Building, and at the Carnegie Mellon University Campus), which has substantial mobile source emissions. A final site (South Fayette) was located to measure regional background air toxic concentrations.

The Allegheny County Health Department measured 24-hour averaged concentrations at each site on a 1 in six day schedule. Intensives were conducted at Avalon, Diamond Building, and Carnegie Mellon University, which featured hourly measurements of gas-phase organic air toxics. Approximately 57 organic air toxics were measured using SUMMA canisters and the TO-15 method and approximately seven organic air toxics were measured using a cartridge and the TO-11a method.

Allegheny County has historically been the home of heavy industry. Though Pittsburgh's steel days are over, there are still 186 point sources in the county, 87 of which are large enough to be required to report air toxic emissions. There are still several large clusters of industrial activity, potentially creating concerns with environmental inequality. Neville Island is home to many chemical and manufacturing facilities including a large metallurgical coke production plant; many of these facilities are old and poorly controlled. Pittsburgh has several major industries including: metals manufacturing; chemical manufacturing; consumer products manufacturing; food and beverage processing; pharmaceuticals manufacturing; and energy production including coal mining, oil and natural gas extraction, timber, and electric power; and consumer item transport and distribution facilities including a large railway hub and port.

Although air toxic concentration data are useful for identifying hot spots, the variations in human health risks are ultimately a more important concern. In fact, since the toxicity of air toxics varies widely, one can draw misleading conclusions if one only considers the concentration data. Chronic health risks were calculated using estimated annual average concentrations. Since measurements were taken on a one-in-six day schedule, the sample mean is not necessarily the same as the annual average concentration. Therefore, it is assumed that the concentrations were normally distributed and the confidence interval for the annual mean concentration was estimated for each pollutant. To be conservative, the concentrations used in the chronic risk analysis were the upper limit of the 95% confidence interval of the mean. This study measured outdoor concentrations and the risk analysis was performed directly on these data.

A linear no-threshold model was used to assess the lifetime cancer risk for 50 pollutants. To be conservative, the 95<sup>th</sup> upper confidence level of the mean annual concentration was used to calculate total risks. The lifetime cancer risk, LIR, for individual air toxics was determined by

 $LIR = URE \times C$ 

Where C is the 95<sup>th</sup> upper confidence level of the mean annual concentration and URE is the unit risk estimate for the target species. A LIR of  $1 \times 10^{-6}$  or less is considered acceptable according to the 1990 Clean Air Act. Compounds with LIR greater than this represent an elevated risk. If URE data were not available, an estimate was calculated from the oral carcinogenic potency slope factor.

$$URE = \frac{OSF \times IR}{BW}$$

Where OSF is the oral carcinogenic slope factor (mg/kg-day), IR is the inhalation rate (20  $m^{3}$ /day) and BW is the assumed body weight (70 kg).

The pollutants that pose the most cancer risks across the county, from largest to smallest, are formaldehyde, benzene, carbon tetrachloride, acetaldehyde, and 1,3-butadiene. Formaldehyde and carbon tetrachloride are both regional toxics. Carbon tetrachloride is no longer widely used, but it has a long atmospheric lifetime. Formaldehyde is formed in the atmosphere from the oxidation of hydrocarbons. The other toxics that post substantial risk throughout the county (benzene, carbon tetrachloride, and 1,3-butadiene) are associated with mobile and industrial source emissions.

To quantify non-cancer health risk, the hazard quotient, HQ, was determined for the compounds measured

$$HQ = \frac{C}{RFC}$$

By dividing the 95th percentile upper confidence limit of the study average concentration by the reference concentration, RFC, for each species. The hazard index was also determined for each site by adding all of the HQ values for species at the same location. The hazard quotient is thought to be proportional to risk, but is not a direct measure of the probability of disease like the LIR. Therefore HQ provides a binary indication of risk: values less than 1 are considered non-hazardous, while values of 1 or greater indicate that there is potential for an elevated non-cancer risk. It also indicates how much ambient concentrations must be reduced to achieve a "safe" level. The only air toxic that poses a non-cancer risk is acrolein. The HQ for acrolein exceeds one at all of the sites. The maximum value from the hourly measurements were used to assess acute health risks. There were no acute health risks found at any of the sites.

Traditional risk analysis does not account for interaction of pollutants. The EPA model modifies each pollutant's individual HQ according to its interaction with each other pollutant in the mixture to define the total interactive hazard for target system/organ *p* as:

$$HI_{\text{int},p} = \sum_{j=1}^{n} HQ_{pj} \left( \sum_{k \neq j}^{n} f_{pjk} \left( M_{jk} \right)^{Bjk \times gpjk} \right)$$

Where:

 $HQ_{pj}$  = hazard quotient for pollutant *j* for system *p*.

- $f_{pjk} =$  hazard of the  $k^{th}$  pollutant relative to the total additive hazard of all of the chemicals interacting with pollutant *j*.
- $M_{jk}$  = interaction magnitude, the EPA has suggested a default of  $M_{jk}$  = 5, but  $M_{jk}$  has been shown to be up to 10 for low dose mixtures.
- $B_{jk}$  = weight of evidence that chemical k will effect chemical j's toxicity.  $B_{jk}$  ranges from -1 to 0 for antagonistic effects and from 0 to 1 for synergistic effects.
- $G_{pjk}$  = the degree to which *j* and *k* are present in equi-toxic amounts.

The main assumptions of the model are that interactions between pairs of chemicals contribute the majority of the mixture effect, that synergistic/antagonistic effects are maximized when two pollutants are present in equal toxicity, the equation reduces to the additive model when interactions are minimized, and adverse health effects of chemical mixtures are limited to the effects of the individual pollutants. This model also allows for non-symmetric interactions between compounds. For instance, chemical A may have a synergistic effect on chemical B's toxicity, but chemical B may have an antagonistic or additive effect on chemical A's toxicity.

The Allegheny County Health Department used lifetime cancer risks and non-cancer hazard quotients determinations for each compound. They also performed a mixture-interactions model as a screening tool to prioritize pollutant pairs for further study based on their plausible synergistic/antagonistic impacts on the toxicity of mixtures of gas phase air toxics for both cancer and non-cancer risks. The time series at each site were characterized by relatively stable background concentrations with short periods of higher concentrations. These shortduration, high-concentration event were likely associated with plumes from local sources influencing the site. The frequency and magnitude of these events varied from site to site and as a function of wind direction. Preliminary source apportionment analysis has been performed using Positive Matrix Factorization (PMF). The goal of the analysis is to identify the sources of the air toxics posing the greatest health risk. The analysis indicates the importance of emissions from metallurgical coke production to benzene concentrations at the residential sites adjacent to Neville Island. Concentrations of 1,4-dichlorobenzene and trichloroethene were 12 and 26 times higher downtown compared to the regional background. This indicates an important local source(s) of these compounds, but the nature of these sources is not known. Only minor sources of these chlorinated toxics are contained in the Allegheny County Point Source Emissions Inventory and they are not emitted by mobile sources.

Differences Between Pittsburgh, PA Risk Assessment Values with Michigan Ris	ik 🛛
Assessment Values	

Pittsburgh, PA	Air Concentration for Pittsburgh, PA (μg/m <sup>3</sup> )	Pittsburgh, PA Risk Assessment Values	Comparison using State of Michigan Risk Assessment Equations	Reference:
Risk Drivers		Hazard Quotient	Hazard Quotient	
Non-cancer				
Acrolein	0.11	9	N/A	IRIS database
Cancer		Cancer Risk (# of cancers per 1,000,000)	Cancer Risk (# of cancers per 1,000,000)	
Acetaldehyde	1.8	2.2	3.6	IRIS database
Benzene	1.3	7.8	13	Cal EPA
1,3-Butadiene	0.16	30	5.2	IRIS database
Carbon tetrachloride	0.5	15	7.2	Cal EPA
Chloroform	0.15	2.4	0.37	IRIS database
1,4-Dichlorobenzene	0.78	11	5.6	Cal EPA
Formaldehyde	2.1	13	26	IRIS database
Trichloroethane	0.11	16	N/A	IRIS database

#### The Portland, Oregon Case Study

The State of Oregon Department of Environmental Quality (DEQ) Air Quality Surveillance Network collects data throughout the state for a number of pollutants and meteorological parameters. The DEQ uses air sampling methods designated by the EPA as Federal Reference Methods to judge attainment with the NAAQS. The following air quality data summaries for particulate and gaseous pollutants are summarized for comparison to the federal standards. Some PM<sub>10</sub> samples were collected with high volume samples which draw air through a size-separating inlet then a pre-weighed quartz filter at about 40 cubic feet per minute. After 24 hours of sampling, the filter is removed and reweighed. The difference between the starting and ending weight is expressed as micrograms of fine particulate per cubic meter sampled. This is an EPA Federal Reference Method. Some PM<sub>10</sub> samples are collected with DEQ designed medium volume samplers that draw air through size-separating inlets at four cubic feet per minute. The samplers collect particles on two separate filters simultaneously (quartz and Teflon), allowing for chemical analysis. The difference between the starting and the ending weight is expressed as micrograms of fine particulate per cubic meter of air sampled. This is an EPA Federal Equivalency Method. PM<sub>10</sub> and PM<sub>2.5</sub> samples are collected with the FRM samplers that draw air through a size separating inlet then a pre-weighted filter at about 16.7 liters per minute. After 24 hours of sampling the filter is removed and reweighed. The difference between the starting and ending weight is expressed as micrograms of fine particulate per cubic meter of air sampled. This is an EPA Federal Reference Method. For 2006 particulates ( $PM_{10}$ ) nonattainment areas are sampled every sixth day and the annual average is determined by averaging the quarterly means. The PM<sub>10</sub> maximum daily sample is determined by taking the highest 24-hour sample for the year. The PM<sub>10</sub> second highest daily sample is determined by taking the second highest value for the year. Light scattering is used as a PM<sub>2.5</sub> concentration surrogate and is used for the Air Quality Index, the Wildfire Air Quality Rating, EPA AIRNow (EPA's air quality current conditions webpage), Portland PM<sub>2.5</sub> forecast, woodstove advisories, air stagnation health alerts, field burning calls, forest health (prescribed burning) call, and forest fire smoke health alerts. The nephelometer measures a common property of small particles in the air; the ability to scatter light and cause visibility reduction. The instrument measures the scatter coefficient (BScat) of the sample by drawing air into the detection chamber where it is illuminated by a pulse-flash lamp. The scattered light is measured over a range of angles by means of a photomultiplier tube. This signal is averaged, amplified, and recorded. The amount of light scattered is roughly proportional to the fine particle mass concentration and to observed visibility. The annual average is determined by taking the arithmetic mean of all the one hour averages. The one hour max is determined by taking the highest one hour average for the year. The PM<sub>2.5</sub> maximum daily sample is determined by taking the highest 24 hour sample for the year. The PM<sub>2.5</sub> 98<sup>th</sup> percentile is determined by multiplying the number of days sampled by 0.98.

Most sites sample carbon monoxide from October 1 to March 31 with Portland, Eugene, and Medford having year round sampling. Infrared energy from a lamp is passed through a cell containing the gas sample to be analyzed and simultaneously through a reference cell containing a non-absorbing gas. Carbon monoxide in the sample absorbs some of the energy, creating an out-of-balance condition in the detector. The imbalance is proportional to the amount of carbon monoxide in the sample air and is electronically amplified and recorded. This is an EPA Federal Reference Method. The maximum one hour CO is determined by taking the highest one hour average for the year. The max. 8-hour CO average is determined by calculating a rolling average (across midnight) and the second highest 8-hour average CO is determined from this data as well. Only one max per CO episode is used to count to the second highest. For ozone all sites are sampled from May 1 to September 30. The air sample enters a chamber with an ultraviolet lamp at one end and detector at the other. The ozone in the sample stream absorbs the ultraviolet light at a specific wavelength. The amount absorbed is proportional to the amount of ozone in the air stream. The detector then sends an amplified signal to the recorder. This is an EPA Federal Reference Method. The maximum 1-hour average ozone value is determined by taking the highest 1-hour average for the year. The max. 8-hour ozone average is determined by calculating a rolling average (across midnight) and the fourth highest 8-hour average is also determined from this data (only one max per day is used to count to the fourth highest). For oxides of nitrogen  $(NO_x)$  and hydrocarbons (HC) sampling occurs from mid-May to September 30. Only NO<sub>2</sub> has a NAAQS standard. The air sample is continuously pumped into two paths within the analyzer, one leading through a converter to reduce nitrogen dioxide (NO2) to nitric oxide (NO); the other bypasses the converter. Both samples reach the reaction chambers where the nitric oxide is detected by its chemiluminescent (light emitting) reaction with ozone. The light emissions are detected by photomultiplier tubes, amplified, and recorded. This is an EPA Federal Reference Method. The maximum 1-hour average NO<sub>2</sub> and NO is determined by taking the highest one average for the year. Sulfur dioxide (SO<sub>2</sub>) sampling started in December 2004 and sampling is done year around. The UV fluorescence method operates on the principle that when the SO<sub>2</sub> molecules contained in the sample gas are excited by ultraviolet radiation they emit a characteristic fluorescence in the range of 220-240 nm. This fluorescence is measured and the SO<sub>2</sub> concentration is obtained from changes in the intensity of the fluorescence. The maximum 3-hour average is calculated (must have three consecutive hours). The max 24-hour daily average is calculated (must have  $\geq$  18 hours/day). The annual average is calculated.

Ambient air toxic levels are compared to bench mark level of one in a million chance of cancer. The EPA has pared the 188 HAPS down to 32 National Air Toxics Assessment (NATA) air toxics that are most common and hazardous in urban areas. Oregon has been identified as having levels above the benchmark for 14 NATA compounds. The NATA toxics DEQ monitors are averaged. The annual averages are determined by taking the arithmetic mean of all the one hour averages. Where the values are below the minimum detection limit (MDL), the MDL is halved prior to inclusion in the average. For aldehydes and ketones, ambient air is drawn through a carbonyl cartridge at one liter/minute for 24 hours, then solid phase extracted and analyzed by high pressure liquid chromatography. For VOCs, ambient air is drawn into an evacuated canister during preprogram cycle times at about 50 cc/minute for 24 hours. The sample is analyzed using Gas Chromatography/Mass Spectrometry (GC/MS). For poly organic carbons, ambient air is drawn through a quartz filter then through polyurethane foam at eight cubic feet per minute for 24 hours. The sample is soxhlet extracted from the filter and foam and analyzed using GC/MS. For metals, a TSP, PM<sub>10</sub> or PM<sub>2.5</sub> sample is collected on a quartz or Teflon filter for 24 hours then the filter is analyzed using inductively coupled plasma mass spectrometry (ICP-MS). For diesel particulate, ambient air is drawn through a glass filter tape and measured with an ultraviolet/visible lamp and photodiode detector every five minutes. The five minute measurements are compiled for an hourly average. Black carbon is measured and used as a surrogate for diesel particulate. These are EPA Federal Reference Methods.

Portland has several major industries including: automotive industry; transportation equipment manufacturing; machinery manufacturing; mining and construction equipment manufacturing; aerospace industry; marine manufacturing; consumer products manufacturing; computer manufacturing; food and beverage industry; commercial item transport and distribution facilities including a large shipyard; and energy production facilities for natural gas and electric generation.

The potential for adverse effects from exposure to a carcinogenic air toxic was estimated using two different methods: (1) the benchmark quotient and (2) the unit risk estimate. The benchmark quotient method does not estimate the probability of an adverse outcome, only whether exposure is above or below a toxicity reference point. Here, the benchmark quotient (BQ) is defined as the ratio between the estimated exposure (at both the 50<sup>th</sup> and 90<sup>th</sup> percentiles) to an individual and the ambient benchmark concentration for a carcinogen endpoint,

$$BQ_C = \frac{EC_{50}orEC_{90}}{ABC_C}$$

Where:  $BQ_{C}$  = Carcinogen benchmark quotient (unit less)  $EC_{50}$  = Exposure concentration, 50<sup>th</sup> percentile (µg/m<sup>3</sup>)  $EC_{90}$  = Exposure concentration, 90<sup>th</sup> percentile (µg/m<sup>3</sup>) ABC<sub>C</sub> = Ambient benchmark concentration, carcinogen (µg/m<sup>3</sup>)

Although a quotient does not express risk, for a given air toxic, exposures at or below the benchmark (BQ <1) are not likely to be associated with adverse health effects. At exposures increasingly greater than the benchmark (BQ  $\geq$ 1), the potential for adverse effects increases but is not possible with this method to estimate the actual probability of an adverse outcome.

Method 2 unit risk estimate) estimates the probability of contracting cancer from a lifetime of continuous exposure (70 year lifespan) to a constant air concentration of that air toxic.

$$LCR = (EC_{50}orEC_{90}) \times URE$$

Where: LCR = Excess lifetime cancer risk estimate (unit less) EC<sub>50</sub> = Exposure concentration, 50<sup>th</sup> percentile ( $\mu$ g/m<sup>3</sup>) EC<sub>90</sub> = Exposure concentration, 90<sup>th</sup> percentile ( $\mu$ g/m<sup>3</sup>) URE = Inhalation unit risk estimate ([ $\mu$ g/m<sup>3</sup>]<sup>-1</sup>)

This method allows cancer risk to be expressed as the probability of an individual developing cancer during their lifetime risk of contracting cancer of 1 chance in 1,000,000 (or one additional person in 1,000,000) is written as  $1 \times 10^{-6}$ .

The potential for adverse effects from exposure to a non-carcinogenic air toxic was estimated using only the benchmark quotient method, where the benchmark quotient (BQ) is defined as the ratio between the estimated exposure to an individual and the ambient benchmark concentration for a non-carcinogenic endpoint,

$$BQ_{NC} = \frac{EC_{50}orEC_{90}}{ABC_{NC}}$$

Where:

 $\begin{array}{l} BQ_{NC} = \text{Non-carcinogen benchmark quotient (unit less)} \\ EC_{50} = Exposure concentration, 50^{th} percentile (\mu g/m^3) \\ EC_{90} = Exposure concentration, 90^{th} percentile (\mu g/m^3) \\ ABC_{NC} = Ambient benchmark concentration, non-carcinogen (\mu g/m^3) \end{array}$ 

Here again, for a given air toxic, exposures at or below the benchmark (BQ  $\leq$ 1) are not likely to be associated with adverse health effects. At exposures increasingly greater than the benchmark (BQ >1), the potential for adverse effects increases but it is not possible with this method to estimate the actual probability of an adverse outcome.

When multiple non-carcinogens were present simultaneously, the individual benchmark quotients were summed to create a non-cancer benchmark index ( $BI_{NC}$ ), defined as:

$$BI_{NC} = \sum_{i=1}^{n} BQ_{NCi}$$

Where:

 $BI_{NC}$  = Non-carcinogen benchmark index (unit less)  $BQ_{NCi}$  = Non-carcinogen benchmark quotient for the ith air toxic (unit less) n = Number of air toxics present simultaneously (unit less)

The BINC is a measure of the potential for non-cancer adverse health effect from all air toxics in the Portland area combined. Different pollutants, however, may cause completely different non-cancer adverse health effects or act via completely different mechanisms of action, so it is often inappropriate to sum benchmark quotients associated with different endpoints. This difficulty can be overcome by adding individual benchmark quotients for air toxics that act by a similar mechanism of action or target the same organ for the critical effect. However, as information regarding mechanisms and target organs is not always available, the benchmark indices presented here are the sum of all benchmark quotients for the air toxics in the Portland area, an approach which expeditiously (but conservatively) assumes that all of these air toxics have similarities in the mechanism of action or the target organ for the critical effect.

The air pollutants of greatest concern in Oregon are: ground level ozone, commonly known as smog; fine particulate matter (mostly from wood smoke, other combustion sources, cars, and dust) known as PM<sub>10</sub> (10 micrometers and smaller diameter) and PM<sub>2.5</sub> (2.5 micrometers and smaller diameter); hazardous air pollutants (also called air toxics); and carbon monoxide (mostly from motor vehicles). Oregon's air quality is influenced by the weather. The weather not only impacts ground level air quality by trapping pollutants during inversions, it also influences some pollutant emitting activities (e.g., cold days cause more woodstove burning). The dryer, cool conditions in March 2006, lead to some elevated PM<sub>2.5</sub> levels in the state. The summer heat wave had exceptionally high dew point temperatures, leading to uncharacteristically elevated night time temperatures. The elevated temperatures contributed to a smog event that exceeded the 8-hour average. The first week of December 2006 was cold and dry with stagnant conditions. The cold stagnant weather resulted in elevated PM<sub>2.5</sub> levels. For criteria pollutants (PM<sub>2.5</sub>, PM<sub>10</sub>, NO2, SO<sub>2</sub>, lead, VOC, and CO), although industry is a source of some air pollution in Oregon, it accounts for less than 15 percent of most types of criteria pollutants. Motor vehicles are now the primary source of air pollution in Oregon. Although each individual car or truck contributes relatively small amounts of pollution, the sheer number of vehicles makes their total contribution larger than any other single source. Emissions from cars contribute to ground level ozone pollution (smog) especially on hot summer days. Smog is a problem in the Portland, Eugene, Salem, and Medford areas. Other major sources of pollution are from individual actions such as using wood stoves, gas-powered lawn motors, motor boats, paints, solvents, aerosol products like hairspray and air fresheners, charcoal barbeques, and outdoor burning.

#### The Tonawanda, New York Case Study

In July 2007, the New York State Department of Environmental Conservation (NYSDEC) initiated a year-long community air quality monitoring study in the town of Tonawanda (Erie County) to measure the concentration of air contaminants within the community and to evaluate the potential risk to public health. Tonawanda is an industrialized, urban community located in the western part of New York State in Erie County, just north of the city of Buffalo. The Tonawanda Community Air Quality Study was conducted to determine the ambient concentrations for selected air toxics and criteria pollutants at four locations was motivated by a number of critical factors; first and foremost, complaints received by NYSDEC from the community regarding odors and an overall compromised quality of life; second, the elevated ambient benzene concentrations sampled by a local community group and the NYSDEC; and third, the Tonawanda industrial area represents an excellent opportunity to assess the effectiveness of the current federal and state hazardous air pollution reduction strategies. The air quality monitoring study was designed to identify inhalation exposure risks to the community. identify risk reduction efforts in the community and to generate data that can be used to evaluate air quality models and other risk assessment tools. To address these issues, NYSDEC conducted monitoring, modeling, and an inhalation risk assessment to estimate the risk posed by ambient concentrations of hazardous air pollutants (HAPs). The study design allowed for the identification of results which could be used for risk management decisions and selection of options to reduce exposure to HAPs in the Tonawanda community.

Four air quality monitors were installed in and around the community in reference to the prevailing wind direction from the southwest. One monitor at Beaver Island State Park (BISP) was sited to establish background measurements of air toxics upwind of the industrial sources. Three monitors were placed downwind of the industrial sources in the study area: Grand Island Boulevard Industrial (GIBI), Brookside Terrace Residential Site (BTRS), and Sheridan Park Water Tower (SPWT). The monitors collected 24-hour average ambient air concentrations of 56 air toxic pollutants on a one-in-six day schedule. All four monitors collected hourly average concentrations of sulfur dioxide (SO<sub>2</sub>) and carbon monoxide (CO). A meteorological station was placed at the BISP site to assess the local meteorology for this study area and for use in assessing the sources influencing the air monitoring concentrations.

Tonawanda has several major industries including: chemical manufacturing; consumer product manufacturing; machinery manufacturing; military product industry; aerospace industry; scientific product manufacturing; raw material extraction including coal processing and foundry coke processing; and waste disposal and recycling industry.

The GIBI monitoring site found significantly elevated concentrations of benzene and formaldehyde when compared to other areas of New York. The evaluation for benzene indicated higher daily concentrations of benzene when the wind originated from the direction of the largest known point source, a foundry coke processing operation. The BTRS monitor, downwind from the industrial sources, also indicated more of an influence from the industrial sources than contributions from mobile sources in the area. The results for benzene at the other two ambient air quality monitors were similar to ambient air levels found in large urban areas such as New York City. The formaldehyde evaluation indicated that the measured concentrations were influenced by local sources and mobile sources. The GIBI monitor reported the highest concentrations, much higher than the other study monitors and other monitors in the statewide network. The formaldehyde concentrations also appear to be influenced both by temperature and wind speed fluctuations with direct temperature correlations

and an inverse wind speeds correlation. A public health evaluation was conducted using NYSDEC derived health-based guideline concentrations and the results from the ambient air quality monitoring. The annual average concentration for five air toxics (1,3-butadiene, acetaldehyde, benzene, carbon tetrachloride, formaldehyde) exceeded the cancer risk screening level of one-in-one-million and one air toxic (acrolein) exceeded the non-cancer health-based comparison value. The predicted concentrations of the HAPs were modeled for the entire study area and the results were compared to the monitored data and predictions from the 2002 National-scale Air Toxics Assessment (NATA). The comparisons of the monitoring data to the 2002 NATA predictions indicated that the 2002 National Emission Inventory (NEI) used in the NATA model was fairly accurate for a number of HAPs. However, the NEI emissions inventory under reported acrolein emissions for the entire Tonawanda area and under reported 1,3-butadiene, benzene, ethylbenzene, formaldehyde, and propionaldehyde emissions for sources near the GIBI monitor. The study measured air quality in close proximity to the foundry coke processing operation to fill a data gap identified in the USEPA Residual Risk Assessment for Coke Ovens, which identified the lack of ambient monitoring information. Some HAPs known to be released from the facility were measured and elevated concentration of benzene was observed at the study area monitors. Based on the assessment of the monitored and modeled data, the maximum individual cancer risk and population cancer risk associated with facility-wide emissions from the foundry coke processing operation exceeds an excess lifetime cancer risk of 10 in one million for the nine census tract study area. Specific neighborhoods exceeded a 100 in-one-million cancer risk level. The findings from the study have already resulted in a number of actions by NSYDEC and the EPA to evaluate and address potential sources of benzene emissions in the study area.

#### The Warwick, Rhode Island Case Study

The main impetus for the study was concerns of Warwick residents and the Warwick City government about the impact of airport operations on local air quality. This concern was heightened by plans for an extension of the main runway and by an analysis of cancer incidence data released by Rhode Island Department of Health in early 2004 that showed elevated lung cancer rates in several census tracts that are frequently downwind of the Airport. Due to the long latency period associated with lung cancer, measurements of air quality cannot be directly linked to recently occurring cancers. However, the study was designed to address local concerns by providing data to characterize current health risks from inhalation of air toxics in Warwick and, to the extent possible, to identify the contribution of the airport and other stationary and mobile sources to those risks. Rhode Island Department of Environmental Management (RI DEM) measured air toxics levels at five locations in Warwick during a 17 month period from April 2005 through August 2006. Concurrent samples were collected at four permanent monitoring sites in Rhode Island: an urban site in Providence, a suburban site in East Providence that is often downwind of the metropolitan Providence area, a site in a residential area adjacent to Interstate Route 95 in Pawtucket, and a rural site in W. Greenwich.

Sampling included a combination of 24-hour time-integrated samples, short-duration samples during peak emissions periods and real-time measurements using continuous instrumentation. RI DEM measured Polycyclic aromatic hydrocarbons (PAHs), VOCs, carbonyls, diesel particulate and fine particles (PM<sub>2.5</sub>). EPA Method TO-15 was used to measure VOC concentrations. In this method, air samples are collected in Summa canisters and are analyzed using a gas chromatograph/mass spectrometer. Carbonyls (acetaldehyde, formaldehyde, and acetone) were measured using EPA Method TO-11a, which involves collection on DNPH-treated absorbent material and analysis with High Pressure Liquid Chromatography. Aethalometers were used to measure black carbon as an indicator of diesel/jet engine

particulate matter. RI DEM also operated beta attenuation monitors (BAMs) at two of the sites to continuously measure  $PM_{2.5}$  concentrations.

Warwick has several major industries including: chemical industry; computer manufacturing; plastics manufacturing; consumer products manufacturing; and commercial item transport and distribution facilities including a large airport.

Levels of formaldehyde at the Field View site, of tetrachloroethylene at the Lydick site and of trichloroethylene at the Fire Station site were higher than those at the other Warwick sites and at the comparison sites. Monitored concentrations were compared to concentrations predicted by an EPA modeling study and will establish a baseline that can be used in the future to evaluate the air quality impacts of changes at the airport over time. RI DEM was less successful in definitively identifying the sources of elevated levels of air toxics. It was possible to definitely demonstrate that the airport significantly impacted level of black carbon at the four sites near the airport. There will be follow-up activities aimed at further characterizing air quality and health impacts around the airport and more definitely identifying significant emissions sources.

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#### APPENDIX D Other Air Quality and Health Studies in Michigan

#### Criteria Air Pollutants and Asthma Hospitalizations

As part of a CDC grant-funded asthma initiative, researchers from MSU, U of M and the State of Michigan investigated spatio-temporal relationships between hospitalizations due to asthma and monitored air pollutant levels in the greater Detroit area. Investigators looked at all hospitalizations in the Michigan Inpatient Database coded for asthma between 1990 and 2001. Monitored levels of ozone, sulfur dioxide, nitrogen dioxide and fine particulate matter were also analyzed for three locations in the greater Detroit area with Lansing included as a background site. PM<sub>2.5</sub> data was only available for two locations in Detroit during the years 1999-2000 due to the change in the EPA standard. Sulfur dioxide levels were positively associated with increased hospitalizations for asthma when allowance was made for a four-day lag period between exposure and admission dates.

#### Adverse birth outcomes and criteria air pollutants

A grant from ATSDR provided funding for research investigating associations with monitored levels of criteria air pollutants and measurements of low birth weight, pre-term birth and small for gestational age infants. Researchers from the U of M, MSU and the State of Michigan analyzed levels of NO<sub>2</sub>,CO, SO<sub>2</sub> and PM from fixed site monitoring stations in four locations in and around Detroit. After controlling for trends and covariates, consistent patterns of increase were observed in the odds of SGA for CO, NO<sub>2</sub> and PM<sub>10</sub> exposures, and of PTB for SO<sub>2</sub> exposures. After accounting for long-term trends, however, the statistical significance of CO-PTB and SO<sub>2</sub>-SGA associations was removed.

#### Asthma and Air Toxics

Another study conducted in Michigan concerning risks from air toxics was performed under a grant from the Mickey Leland Center for Urban Air Toxics. The overall objective of the project was to assess the relationships between exposure to ambient levels of urban air toxics and utilization of urgent care facilities for asthma and respiratory disease by children enrolled in Medicaid in the Dearborn area of Southeast Michigan. The analysis showed that exposure to fuel combustion and gasoline exhaust and evaporated gasoline sources was associated with increased risk for emergency department (ED) visits for respiratory disease among children. This project was important because the exposure assessment techniques used in this project had only been used in a few previous studies to investigate relationships between air toxic exposures and asthma and respiratory disease. However, these results were viewed cautiously due to problems with the precision and accuracy of some of the air toxics exposure data.

#### APPENDIX E

#### AIR MONITOR DATA AVAILABLE FOR DATI-2 ANALYSIS

		Average	Num	Ohe	0/	Priority
Site Name	Chemical Name	(µg/III <sup>e</sup> ) wND=1/2MDL	Obs	>MDL	<sup>70</sup> Detected	Chemical?
Allen Park	Arsenic (TSP)	0.00139	59	59	100%	x
Allen Park	Barium (TSP)	0.0369	58	58	100%	
Allen Park	Beryllium (TSP)	0.0000212	58	56	97%	
Allen Park	Cadmium (TSP)	0.000257	59	59	100%	x
Allen Park	Chromium (TSP)	0.00295	58	58	100%	
Allen Park	Cobalt (TSP)	0.000155	58	58	100%	
Allen Park	Copper (TSP)	0.319	58	58	100%	
Allen Park	Iron (TSP)	0.535	58	58	100%	
Allen Park	Lead (TSP)	0.00684	58	58	100%	
Allen Park	Manganese (TSP)	0.0248	59	59	100%	x
Allen Park	Molybdenum (TSP)	0.000796	58	58	100%	
Allen Park	Nickel (TSP)	0.00143	59	59	100%	x
Allen Park	Vanadium (TSP)	0.00192	58	58	100%	
Allen Park	Zinc (TSP)	0.0591	58	58	100%	
Dearborn	1,1,1-Trichloroethane	0.112	59	58	98%	
	1,1,2,2-					
Dearborn	Tetrachloroethane	0.118	59	0	0%	
Dearborn	1,1,2-Trichloroethane	0.0484	59	0	0%	
Dearborn	1,1-Dichloroethane	0.0241	59	0	0%	
Dearborn	1,1-Dichloroethene	0.0485	59	0	0%	
Dearborn	1,2,4-Trichlorobenzene	0.161	59	3	5%	
Dearborn	1,2-Dibromoethane	0.0998	59	0	0%	
Dearborn	1,2-Dichloroethane	0.106	59	2	3%	
Dearborn	1,2-Dichloropropane	0.0783	59	0	0%	
Dearborn	1,3-Butadiene	0.105	59	54	92%	x
Dearborn	1,4-Dichlorobenzene	0.104	59	51	86%	x
Dearborn	2,2,4-Trimethylpentane	0.377	20	17	85%	
Dearborn	2-Chloro-1,3-Butadiene	0.0424	59	1	2%	
Dearborn	Acetaldehyde	1.75	59	59	100%	x
Dearborn	Acetonitrile	5.02	59	54	92%	
Dearborn	Acrolein	0.388	59	49	83%	
Dearborn	Acrylonitrile	0.0786	59	2	3%	x
Dearborn	Arsenic (PM-10)	0.00186	61	61	100%	
Dearborn	Arsenic (TSP)	0.00187	61	60	98%	x
Dearborn	Barium (TSP)	0.0457	61	60	98%	
Dearborn	Benzene	1.09	59	59	100%	x
Dearborn	Beryllium (PM-10)	0.0000529	61	60	98%	
Dearborn	Beryllium (TSP)	0.000133	61	60	98%	
Dearborn	Bromoform	0.132	59	0	0%	
Dearborn	Bromomethane	0.0415	59	50	85%	

		Average	Num	Obs	%	Priority
Site Name	Chemical Name	wND=1/2MDL	Obs	>MDL	Detected	Chemical?
Dearborn	Cadmium (PM-10)	0.000556	61	61	100%	
Dearborn	Cadmium (TSP)	0.000553	61	60	98%	x
Dearborn	Carbon Disulfide	0.121	59	38	64%	
Dearborn	Carbon Tetrachloride	0.566	59	59	100%	x
Dearborn	Chlorobenzene	0.158	59	47	80%	
Dearborn	Chloroethane	0.0522	59	50	85%	
Dearborn	Chloroform	0.762	59	58	98%	х
Dearborn	Chloromethane	1.06	59	59	100%	
Dearborn	Chloromethyl Benzene	0.0675	59	0	0%	
Dearborn	Chromium (PM-10)	0.00465	61	61	100%	
Dearborn	Chromium (TSP)	0.0054	61	61	100%	
Dearborn	Chromium VI (TSP)	0.0000612	59	54	92%	
Dearborn	Cobalt (TSP)	0.000274	61	61	100%	
Dearborn	Copper (TSP)	0.307	61	60	98%	
Dearborn	Ethyl Acrylate	0.0274	59	0	0%	
Dearborn	Ethylbenzene	0.33	59	59	100%	
Dearborn	Formaldehyde	2.68	59	59	100%	x
	Hexachloro-1,3-					
Dearborn	Butadiene	0.225	59	3	5%	
Dearborn	Iron (TSP)	2.02	61	61	100%	
Dearborn	Lead (PM-10)	0.0181	61	61	100%	
Dearborn	Lead (TSP)	0.0213	61	61	100%	
Dearborn	Manganese (PM-10)	0.0638	61	61	100%	
Dearborn	Manganese (TSP)	0.128	61	61	100%	х
Dearborn	Methyl Ethyl Ketone	0.826	59	58	98%	
Dearborn	Methyl Isobutyl Ketone	0.207	59	52	88%	
Dearborn	Methyl Methacrylate	0.0181	59	0	0%	
Dearborn	Methyl Tert-Butyl Ether	0.037	59	1	2%	
Dearborn	Methylene Chloride	0.523	59	58	98%	x
Dearborn	Molybdenum (TSP)	0.00129	61	60	98%	
Dearborn	n-Hexane	1.3	20	16	80%	
Dearborn	Nickel (PM-10)	0.00249	61	61	100%	
Dearborn	Nickel (TSP)	0.00295	61	61	100%	х
Dearborn	o-xylene	0.308	59	59	100%	
Dearborn	Propionaldehyde	0.384	59	59	100%	
Dearborn	Styrene	0.084	59	47	80%	
Dearborn	Tetrachloroethene	0.722	59	56	95%	
Dearborn	Toluene	1.94	59	59	100%	
Dearborn	Trichloroethene	0.133	59	21	36%	
Dearborn	Vanadium (TSP)	0.00435	61	60	98%	
Dearborn	Vinyl Chloride	0.0522	59	4	7%	
Dearborn	Zinc (TSP)	0.312	61	60	98%	
N.E. Detroit	Barium (TSP)	0.0392	61	61	100%	

		Average		<u>.</u>	0/	D-1 14
Site Name	Chemical Name	(µg/m³) wND=1/2MDL	Num Obs	Obs >MDL	% Detected	Priority Chemical?
N.E. Detroit	Bervllium (TSP)	0.0000283	61	60	98%	
N.E. Detroit	Chromium (TSP)	0.00274	61	61	100%	
N.E. Detroit	Cobalt (TSP)	0.000174	61	61	100%	
N.E. Detroit	Copper (TSP)	0.135	61	61	100%	
N.E. Detroit	Iron (TSP)	0.506	61	61	100%	
N.E. Detroit	Lead (TSP)	0.00782	61	61	100%	
N.E. Detroit	Molybdenum (TSP)	0.000756	61	61	100%	
N.E. Detroit	Vanadium (TSP)	0.00252	61	61	100%	
N.E. Detroit	Zinc (TSP)	0.164	61	61	100%	
Houghton Lk	1,1,1-Trichloroethane	0.123	52	8	15%	
	1,1,2,2-					
Houghton Lk	Tetrachloroethane	0.564	52	0	0%	
Houghton Lk	1,1,2-Trichloroethane	0.254	52	0	0%	
Houghton Lk	1,1-Dichloroethane	0.076	52	0	0%	
Houghton Lk	1,1-Dichloroethene	0.136	52	0	0%	
Houghton Lk	1,2,4-Trichlorobenzene	0.692	53	0	0%	
Houghton Lk	1,2-Dibromoethane	0.365	52	0	0%	
Houghton Lk	1,2-Dichloroethane	0.123	52	0	0%	
Houghton Lk	1,2-Dichloropropane	0.124	52	0	0%	
Houghton Lk	1,3-Butadiene	0.092	52	1	2%	х
Houghton Lk	1,4-Dichlorobenzene	0.379	52	1	2%	х
Houghton Lk	2,2,4-Trimethylpentane	0.077	44	3	7%	
Houghton Lk	2-Chloro-1,3-Butadiene	0.0522	52	0	0%	
Houghton Lk	Acetaldehyde	0.822	29	29	100%	х
Houghton Lk	Acetonitrile	0.621	52	29	56%	
Houghton Lk	Acrolein	0.182	8	1	13%	
Houghton Lk	Acrylonitrile	0.154	52	0	0%	х
Houghton Lk	Arsenic (TSP)	0.000514	60	60	100%	х
Houghton Lk	Barium (TSP)	0.016	60	60	100%	
Houghton Lk	Benzene	0.375	52	51	98%	х
Houghton Lk	Beryllium (TSP)	0.0000156	60	52	87%	
Houghton Lk	Bromoform	0.537	52	0	0%	
Houghton Lk	Bromomethane	0.153	52	6	12%	
Houghton Lk	Cadmium (TSP)	0.00011	60	57	95%	х
Houghton Lk	Carbon Disulfide	0.014	8	0	0%	
Houghton Lk	Carbon Tetrachloride	0.518	52	51	98%	х
Houghton Lk	Chlorobenzene	0.208	52	0	0%	
Houghton Lk	Chloroethane	0.112	52	5	10%	
Houghton Lk	Chloroform	0.819	52	50	96%	x
Houghton Lk	Chloromethane	1.23	52	52	100%	
Houghton Lk	Chloromethyl Benzene	0.438	52	0	0%	
Houghton Lk	Chromium (TSP)	0.00154	60	60	100%	
Houghton Lk	Cobalt (TSP)	0.0000691	60	57	95%	

		Average	Num	Obe	%	Priority
Site Name	Chemical Name	wND=1/2MDL	Obs	>MDL	<sup>70</sup> Detected	Chemical?
Houghton Lk	Copper (TSP)	0.468	60	60	100%	
Houghton Lk	Ethyl Acrylate	0.0225	8	0	0%	
Houghton Lk	Ethylbenzene	0.199	52	8	15%	
Houghton Lk	Formaldehyde	1.38	29	29	100%	x
	Hexachloro-1,3-					
Houghton Lk	Butadiene	0.995	52	0	0%	
Houghton Lk	Iron (TSP)	0.106	60	60	100%	
Houghton Lk	Lead (TSP)	0.00285	60	60	100%	
Houghton Lk	Manganese (TSP)	0.00521	60	60	100%	x
Houghton Lk	Methyl Ethyl Ketone	0.936	52	48	92%	
Houghton Lk	Methyl Isobutyl Ketone	0.268	52	3	6%	
Houghton Lk	Methyl Methacrylate	0.0123	8	0	0%	
Houghton Lk	Methyl Tert-Butyl Ether	0.18	52	0	0%	
Houghton Lk	Methylene Chloride	0.422	52	10	19%	x
Houghton Lk	Molybdenum (TSP)	0.000201	60	54	90%	
Houghton Lk	n-Hexane	0.397	44	13	30%	
Houghton Lk	Nickel (TSP)	0.000592	60	58	97%	х
Houghton Lk	o-xylene	0.187	52	5	10%	
Houghton Lk	Propionaldehyde	0.0562	29	3	10%	
Houghton Lk	Styrene	0.252	52	5	10%	
Houghton Lk	Tetrachloroethene	0.241	52	1	2%	
Houghton Lk	Toluene	0.397	52	30	58%	
Houghton Lk	Trichloroethene	0.145	52	0	0%	
Houghton Lk	Vanadium (TSP)	0.000397	60	58	97%	
Houghton Lk	Vinyl Chloride	0.0745	52	0	0%	
Houghton Lk	Zinc (TSP)	0.0304	60	60	100%	
N. Delray	1,1,1-Trichloroethane	0.118	28	4	14%	
	1,1,2,2-					
N. Delray	Tetrachloroethane	0.547	28	0	0%	
N. Delray	1,1,2-Trichloroethane	0.265	28	0	0%	
N. Delray	1,1-Dichloroethane	0.078	28	0	0%	
N. Delray	1,1-Dichloroethene	0.124	28	0	0%	
N. Delray	1,2,4-Trichlorobenzene	0.685	28	0	0%	
N. Delray	1,2-Dibromoethane	0.386	28	0	0%	
N. Delray	1,2-Dichloroethane	0.171	28	2	7%	
N. Delray	1,2-Dichloropropane	0.135	28	1	4%	
N. Delray	1,3-Butadiene	0.139	28	5	18%	x
N. Delray	1,4-Dichlorobenzene	0.383	28	3	11%	x
N. Delray	2,2,4-Trimethylpentane	0.317	24	21	88%	
N. Delray	2-Chloro-1,3-Butadiene	0.0555	28	0	0%	
N. Delray	Acetaldehyde	1.77	30	30	100%	x
N. Delray	Acetonitrile	1.02	28	20	71%	
N. Delray	Acrolein	0.31	4	1	25%	

		Average (ug/m <sup>3</sup> )	Num	Obs	%	Priority
Site Name	Chemical Name	wND=1/2MDL	Obs	>MDL	Detected	Chemical?
N. Delray	Acrylonitrile	0.157	28	0	0%	x
N. Delray	Arsenic (TSP)	0.00187	60	60	100%	x
N. Delray	Barium (TSP)	0.052	60	60	100%	
N. Delray	Benzene	1.39	28	28	100%	x
N. Delray	Beryllium (TSP)	0.0000655	60	60	100%	
N. Delray	Bromoform	0.577	28	0	0%	
N. Delray	Bromomethane	0.142	28	1	4%	
N. Delray	Cadmium (TSP)	0.000619	60	60	100%	х
N. Delray	Carbon Disulfide	0.221	4	1	25%	
N. Delray	Carbon Tetrachloride	0.521	28	28	100%	x
N. Delray	Chlorobenzene	0.232	28	3	11%	
N. Delray	Chloroethane	0.129	28	3	11%	
N. Delray	Chloroform	0.21	28	4	14%	x
N. Delray	Chloromethane	1.17	28	28	100%	
N. Delray	Chloromethyl Benzene	0.457	28	0	0%	
N. Delray	Chromium (TSP)	0.00551	60	60	100%	
N. Delray	Cobalt (TSP)	0.000316	60	59	98%	
N. Delray	Copper (TSP)	0.213	60	60	100%	
N. Delray	Ethyl Acrylate	0.0225	4	0	0%	
N. Delray	Ethylbenzene	0.508	28	15	54%	
N. Delray	Formaldehyde	2.58	30	30	100%	x
	Hexachloro-1,3-					
N. Delray	Butadiene	0.953	28	0	0%	
N. Delray	Iron (TSP)	1.89	60	60	100%	
N. Delray	Lead (TSP)	0.0376	60	60	100%	
N. Delray	Manganese (TSP)	0.0669	60	60	100%	x
N. Delray	Methyl Ethyl Ketone	2.68	28	25	89%	
N. Delray	Methyl Isobutyl Ketone	1.22	28	10	36%	
N. Delray	Methyl Methacrylate	0.0123	4	0	0%	
N. Delray	Methyl Tert-Butyl Ether	0.159	28	0	0%	
N. Delray	Methylene Chloride	0.514	28	6	21%	x
N. Delray	Molybdenum (TSP)	0.00157	60	60	100%	
N. Delray	n-Hexane	1.16	24	18	75%	
N. Delray	Nickel (TSP)	0.00413	60	59	98%	x
N. Delray	o-xylene	0.52	28	15	54%	
N. Delray	Propionaldehyde	0.36	30	20	67%	
N. Delray	Styrene	0.218	28	3	11%	
N. Delray	Tetrachloroethene	0.365	28	5	18%	
N. Delray	Toluene	2.37	28	28	100%	
N. Delray	Trichloroethene	0.208	28	2	7%	
N. Delray	Vanadium (TSP)	0.00403	60	60	100%	
N. Delray	Vinyl Chloride	0.0942	28	2	7%	
N. Delray	Zinc (TSP)	0.124	60	60	100%	

		Average	Num	Obs	0/_	Priority
Site Name	Chemical Name	(µg/III <sup>2</sup> ) wND=1/2MDL	Obs	>MDL	<sup>70</sup> Detected	Chemical?
N.E. Detroit	Arsenic (TSP)	0.00124	61	61	100%	x
N.E. Detroit	Cadmium (TSP)	0.000282	61	61	100%	x
N.E. Detroit	Manganese (TSP)	0.0225	61	61	100%	x
N.E. Detroit	Nickel (TSP)	0.00173	61	61	100%	x
Rouge	Acetaldehyde	1.86	59	59	100%	X
Rouge	Arsenic (TSP)	0.00169	60	60	100%	x
Rouge	Barium (TSP)	0.0336	59	59	100%	
Rouge	Beryllium (TSP)	0.0000399	59	58	98%	
Rouge	Cadmium (TSP)	0.000722	60	60	100%	х
Rouge	Chromium (TSP)	0.0051	59	59	100%	
Rouge	Cobalt (TSP)	0.000271	59	59	100%	
Rouge	Copper (TSP)	0.474	59	59	100%	
Rouge	Formaldehyde	3.65	59	59	100%	x
Rouge	Iron (TSP)	1.19	59	59	100%	
Rouge	Lead (TSP)	0.012	59	59	100%	
Rouge	Manganese (TSP)	0.0609	60	60	100%	x
Rouge	Molybdenum (TSP)	0.000906	59	59	100%	
Rouge	Nickel (TSP)	0.00257	60	60	100%	х
Rouge	Propionaldehyde	0.375	59	40	68%	
Rouge	Vanadium (TSP)	0.00428	59	59	100%	
Rouge	Zinc (TSP)	0.112	59	59	100%	
S. Delray	Arsenic (TSP)	0.002	58	58	100%	x
S. Delray	Barium (TSP)	0.0483	57	57	100%	
S. Delray	Beryllium (TSP)	0.000228	57	57	100%	
S. Delray	Cadmium (TSP)	0.000798	58	58	100%	x
S. Delray	Chromium (TSP)	0.00782	57	57	100%	
S. Delray	Cobalt (TSP)	0.000379	57	57	100%	
S. Delray	Copper (TSP)	0.21	57	57	100%	
S. Delray	Iron (TSP)	2.27	57	57	100%	
S. Delray	Lead (TSP)	0.0179	57	57	100%	
S. Delray	Manganese (TSP)	0.159	58	58	100%	x
S. Delray	Molybdenum (TSP)	0.00142	57	57	100%	
S. Delray	Nickel (TSP)	0.0041	58	58	100%	x
S. Delray	Vanadium (TSP)	0.00697	57	57	100%	
S. Delray	Zinc (TSP)	0.15	57	57	100%	
Ypsilanti	1,1,1-Trichloroethane	0.125	30	4	13%	
	1,1,2,2-	0.500		•	00/	
Ypsilanti	I etrachloroethane	0.568	30	0	0%	
Ypsilanti	1,1,2-Trichloroethane	0.263	30	0	0%	
Ypsilanti	1,1-Dichloroethane	0.0781	30	0	0%	
Ypsilanti	1,1-Dichloroethene	0.134	30	0	0%	
Ypsilanti	1,2,4-Trichlorobenzene	0.702	30	0	0%	
Ypsilanti	1,2-Dibromoethane	0.378	30	0	0%	

Site Name	Chamical Name	Average (µg/m <sup>3</sup> )	Num	Obs	% Detected	Priority
Site Name	1.2 Dichloroothono		20			Chemical?
Ypsilanti	1,2-Dichloroethane	0.17	30	1	3% 00/	
Ypsilanti	1,2-Dichloropropane	0.127	30	0 E	0% 170/	
Ypsilanti		0.128	30	5	70/	X
Ypsilanti	1,4-Dichlorobenzene	0.387	30	2	7%	X
Ypsilanti	2,2,4-IIImethylpentarie	0.342	20	24	92%	
Ypsilanti	2-Chioro-1,3-Butadiene	0.0538	30	0	0%	
Ypsilanti	Acetaidenyde	1.25	23	23	100%	X
Ypsilanti	Acetonitrile	0.813	30	20	67%	
Ypsilanti	Acrolein	0.144	4	1	25%	
Ypsilanti		0.215	30	1	3%	X
Ypsilanti		0.000963	30	30	100%	X
Ypsilanti	Barium (TSP)	0.0207	30	30	100%	
Ypsilanti	Benzene	0.973	30	30	100%	X
Ypsilanti	Beryllium (TSP)	0.0000158	30	28	93%	
Ypsilanti	Bromotorm	0.562	30	0	0%	
Ypsilanti	Bromomethane	0.158	30	4	13%	
Ypsilanti	Cadmium (TSP)	0.000118	30	29	97%	X
Ypsilanti	Carbon Disulfide	0.014	4	0	0%	
Ypsilanti	Carbon Tetrachloride	0.519	30	30	100%	X
Ypsilanti	Chlorobenzene	0.218	30	1	3%	
Ypsilanti	Chloroethane	0.127	30	4	13%	
Ypsilanti	Chloroform	0.169	30	5	17%	X
Ypsilanti	Chloromethane	1.24	30	30	100%	
Ypsilanti	Chloromethyl Benzene	0.454	30	0	0%	
Ypsilanti	Chromium (TSP)	0.0022	30	30	100%	
Ypsilanti	Cobalt (TSP)	0.000204	30	30	100%	
Ypsilanti	Copper (TSP)	0.311	30	30	100%	
Ypsilanti	Ethyl Acrylate	0.0225	4	0	0%	
Ypsilanti	Ethylbenzene	0.299	30	10	33%	
Ypsilanti	Formaldehyde	2.24	23	23	100%	x
Ypsilanti	Hexachloro-1,3- Butadiene	0.996	30	0	0%	
Ypsilanti	Iron (TSP)	0.335	30	30	100%	
Ypsilanti	Lead (TSP)	0.00436	30	30	100%	
Ypsilanti	Manganese (TSP)	0.0114	30	30	100%	x
Ypsilanti	Methyl Ethyl Ketone	0.805	30	27	90%	
Ypsilanti	Methyl Isobutyl Ketone	0.265	30	2	7%	
Ypsilanti	Methyl Methacrylate	0.0123	4	0	0%	
Ypsilanti	Methyl Tert-Butyl Ether	0.178	30	1	3%	
Ypsilanti	Methylene Chloride	0.834	30	9	30%	x
Ypsilanti	Molybdenum (TSP)	0.000532	30	30	100%	
Ypsilanti	n-Hexane	1.09	26	17	65%	
Ypsilanti	Nickel (TSP)	0.0011	30	30	100%	x

Site Name	Chemical Name	Average (µg/m <sup>3</sup> ) wND=1/2MDL	Num Obs	Obs >MDL	% Detected	Priority Chemical?
Ypsilanti	o-xylene	0.325	30	11	37%	
Ypsilanti	Propionaldehyde	0.183	23	10	43%	
Ypsilanti	Styrene	0.268	30	8	27%	
Ypsilanti	Tetrachloroethene	0.44	30	7	23%	
Ypsilanti	Toluene	2.21	30	28	93%	
Ypsilanti	Trichloroethene	0.209	30	1	3%	
Ypsilanti	Vanadium (TSP)	0.00121	30	30	100%	
Ypsilanti	Vinyl Chloride	0.0784	30	1	3%	
Ypsilanti	Zinc (TSP)	0.0418	30	30	100%	

#### APPENDIX F. Additional Information on Relative Risks for DATI-2

The following estimates were made for compounds analyzed in DATI-2. The data is included in this Appendix rather than the main document as comparisons with DATI-1 are not appropriate due to the fact that fewer chemicals were measured in the DATI-2 time frame as a result of budget reductions. Therefore, it is not appropriate to compare total risk from each site in DATI-1 and compare it to the data in **Figure 2** below. It is, however, useful for general overview and comparison to risk drivers in other areas.

Wherever formaldehyde was monitored, including Houghton Lake, it comprised a significant portion of total cancer risk as shown in **Figure 2** below. This agrees with the EPA's nationwide studies indicating that some carcinogenic air toxics are present virtually everywhere, at levels well above a 1 in one million risk level. Benzene levels at all four sites that monitored for VOCs during DATI-2 also showed that it is a major risk driver. Carbon tetrachloride showed very little variation between sites and sampling times (DATI-1 and DATI-2). Estimated nickel cancer risks were elevated in the more industrialized areas of Detroit and lower at Allen Park, NE Detroit and Ypsilanti, at their lowest at the rural background site of Houghton Lake.




Chemical	Allen	Dearborn	N.E.	Houghton	N. Delray	Rouge	S. Delray	Ypsilanti
	Park		Detroit	Lake				
1,3-Butadiene	ns	3.5	ns	>85% ND	4.6	ns	ns	4.3
1,4-	ns	0.7	ns	>85% ND	>85% ND	ns	ns	>85% ND
Dichlorobenzene								
Acetaldehyde	ns	3.5	ns	1.6	3.5	3.7	ns	2.5
Acrylonitrile	ns	>85% ND	ns	>85% ND	>85% ND	ns	ns	>85% ND
Arsenic (TSP)	6.9	9.3	6.2	2.6	9.3	8.5	10.0	4.8
Benzene	ns	10.9	ns	3.7	13.9	ns	ns	9.7
Cadmium (TSP)	0.4	0.9	0.5	0.2	1.0	1.2	1.3	0.2
Carbon	ns	8.1	ns	7.4	7.4	ns	ns	7.4
Tetrachloride								
Chloroform	ns	1.9	ns	2.0	>85% ND	ns	ns	0.4
Formaldehyde	ns	33.4	ns	17.2	32.3	45.6	ns	28.0
Methylene Chloride	ns	0.3	ns	0.2	0.3	ns	ns	0.4
Nickel (TSP)	0.3	0.7	0.4	0.1	1.0	0.6	1.0	0.3

## Data for Figure 2. Total Cancer Risk During DATI-2:

ND = Data not used since minimum criteria for monitoring data inclusion not met

ns = Not Sampled

For the chemicals noted above, it may be informative to look at risks relative to health benchmarks other than those used in AQD risk assessment procedures. The relative risks of formaldehyde, benzene and manganese are depicted in the graphs below. Note the relative health benchmarks are the Immediately dangerous to life and health (IDLH) occupational level at which concentrations should never be exceeded in the workplace; the Occupational Exposure level is the concentration determined to be acceptable for exposures by workers allowable for an 8 hour shift and the IRSL is the Initial Risk Screening level used by AQD (See Section 5):



## Formaldehyde

Highest 24-hr level of formaldehyde from DATI-2 = 0.0036 mg/m3 at Rouge



Manganese relative risk levels are shown in the schematic above. Note that the highest average level is  $0.16 \,\mu g/m^3$  in S. Delray.