Tonawanda Community Air Quality Study

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**New York State
Department of Environmental Conservation**

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Preface

The Tonawanda Community Air Quality Study was conducted to determine the ambient concentrations for selected air toxics and criteria pollutants at four locations in Tonawanda, New York. 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 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.

Disclaimer

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Beaver Island State Park
- William Huntoon, Park Manager and John McGinty, Maintenance Crew Chief for permission to site Beaver Island State Park monitor

Clean Air Coalition of Western N.Y.
- Jackie James-Creedon
- Adele Henderson

Erie County Legislature
- Michele Iannello

National Grid Real Property
- Mark Agle, Supervisor Real Property Section for permission to site Grand Island Boulevard Industrial and Brookside Terrace Residential Site monitors

New York State Senate
- Antoine M. Thompson

New York State Assembly
- Robin Schimminger

Town of Tonawanda

Town of Tonawanda Water Resources
- John Camilleri, Director for permission to site Sheridan Park Water Tower monitor

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List of Acronyms and Abbreviations

AerMOD	American Meteorological Society/Environmental Protection Agency Regulatory Model
AFS	Air Facility System
AGC	Annual Guideline Concentration
AIRS	Aerometric Information Retrieval System
ANSI	American National Standard Institute
AQS	Air Quality System
ASTM	American Society for Testing and Materials
BAQAR	Bureau of Air Quality Analysis & Research
BAQS	Bureau of Air Quality Surveillance
BISP	Beaver Island State Park
BLP	Buoyant Line Plume
BSO	Benzene Soluble Organics
BTEX	Benzene, toluene, ethylbenzene and xylene
BTRS	Brookside Terrace Residential Site
BQA	Bureau of Quality Assurance
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CAAC	Clean Air Act Advisory Committee
CACWNY	Clean Air Coalition Western New York
CAS	Chemical Abstracts Service
CL	Confidence Limit
CO	Carbon monoxide
CPS	Citizen Participation Specialist
CRM	Certified Reference Material
CSATAM	Community-Scale Air Toxics Ambient Monitoring
DAR	Division of Air Resources
DBMS	Database Management System
DNPH	2,2-Dinitro-phenyl hydrazine
DQA	Data Quality Assessment
DQI	Data Quality Indicators
DQO	Data Quality Objectives
EJ	Environmental Justice
ELAP	Environmental Laboratory Approval Program
EPA	Environmental Protection Agency
EPCRA	Emergency Planning and Community Right-to-Know Act
FIPS	Federal Information Processing Standards
FOSTTA	Forum on State and Tribal Toxics Actions
FRM	Federal Reference Method

GC/MS	Gas Chromatography/Mass Spectrometry
GIBI	Grand Island Boulevard Industrial
GIS	Geographic Information System
HAP	Hazardous Air Pollutant
HEM	Human Exposure Modeling
HI	Hazard Index
HPLC	High Performance Liquid Chromatography
HQ	Hazard Quotient
HVAC	Heating, Ventilation, Air Conditioning system
IRIS	Integrated Risk Information System
ISCST3	Industrial Source Complex Short-Term 3
ISO	International Organization for Standardization
IUPAC	International Union for Pure and Applied Chemistry
IUR	Inhalation unit risk
LC	Liquid Chromatograph
LCD	Liquid Crystal Display
MACT	Maximum Achievable Control Technology
MDL	Method Detection Limit
MQO	Measurement Quality Objectives
MSR	Management System Review
NAAQS	National Ambient Air Quality Standards
NATA	National-scale Air Toxics Assessment
NATTS	National Air Toxics Trends Stations
NEI	National Emissions Inventory
NESHAP	National Emission Standards for Hazardous Air Pollutant
NIST	National Institute of Standards and Technology
NSPS	New Source Performance Standards
NYC	New York City
NYSDEC	New York State Department of Environmental Conservation
NYSDOH	New York State Department of Health
OAQPS	Office of Air Quality Planning and Standards
OSHA	Occupational Safety and Health Administration
PAH	Polycyclic aromatic hydrocarbons
PAMS	Photochemical Assessment Monitoring Stations
PBS	Petroleum Bulk Storage
PC	Personal Computer
PE	Performance Evaluation
$PM_{2.5}$	Particulate matter aerodynamic diameter of 2.5 microns or less
POM	Polycyclic Organic Matter
POTW	Publicly Owned Treatment Works

ppb	Part Per Billion
ppbv	Part Per Billion by Volume
QA	Quality Assurance
QA/QC	Quality Assurance / Quality Control
QAD	Quality Assurance Division
QAPP	Quality Assurance Project Plan
QASA	Quality Assurance System Audit
QC	Quality Control
RAIMI	Regional Air Impact Modeling Initiative
RAPCE	Regional Air Pollution Control Engineer
SGC	Short-term Guideline Concentration
SO_2	Sulfur dioxide
SOP	Standard Operating Procedure
SPWT	Sheridan Park Water Tower
SUNY	State University of New York
TEOM	Tapered Element Oscillating Microbalance
TPY	Tons per year
TRI	Toxics Release Inventory
TWA	Time-Weighted Average
UATMP	Urban Air Toxics Monitoring Program
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VOC	Volatile Organic Compound

1. Executive Summary

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.   The Tonawanda Community Air Quality Study (hereinafter referred to as Study) 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.

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. The Study design and findings were presented through a series of public meetings within the community to seek input, hear concerns and answer questions from the public and all interested parties in attendance. The findings from the Study have already resulted in a number of actions by NYSDEC and USEPA to evaluate and address potential sources of benzene emissions in the Study area.

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 fine particulate matter (PM$_{2.5}$). Monitors placed at the BTRS site collected hourly average concentrations of sulfur dioxide (SO$_2$) and carbon monoxide (CO). A meteorological station was placed at the BISP site to assess the local meteorology for the Study area and for use in assessing the sources influencing the air monitoring concentrations.

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, Tonawanda Coke Corporation. 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 area 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.

A comprehensive inventory of sources for the Study area was prepared for use with two air dispersion models (Regional Air Impact Modeling Initiative (RAIMI) and AerMod) that are used by NYSDEC to evaluate the inhalation risk of exposure to HAPs from stationary and mobile sources. 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 average ratios for ten air pollutants selected for the comparison of the RAIMI modeled predictions to the monitored concentrations were in close agreement (ranged from 0.58 to 1.25) across all four monitoring sites. However, an analysis of the site by site comparisons for benzene and formaldehyde revealed very poor agreement between the modeled and measured concentrations at the GIBI site.

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. As a risk assessment screening tool designed to identify areas for further air pollution investigations, it would be preferable for the NATA modeled ambient concentrations to be similar to measured ambient concentrations for those air toxics that are identified as risk drivers.

The Study measured air quality in close proximity to the Tonawanda Coke Corporation in order to fill a data gap identified in the USEPA's 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 an elevated concentration of benzene was observed at the Study area monitors. When compared to the USEPA's residual risk assessment, NYSDEC's modeling assessment, using a revised facility emissions inventory, resulted in larger predicted impacts within the community. 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 Tonawanda Coke Corporation exceeds an excess lifetime cancer risk of 10 in-one-million for the nine census tract Study area. Specific neighborhoods exceed a 100 in-one-million cancer risk

level. Further work will be conducted on this issue by NYSDEC prior to USEPA's 2011 scheduled completion of a final residual risk assessment for the Coke Oven source category.

The Study design had several noteworthy strengths. The source attribution conclusions were derived from a weight-of-evidence approach rather than relying on a single result to achieve a conclusion. The source attribution assessment included evaluating meteorological information, emission releases through dispersion modeling and an in depth evaluation of the USEPA's residual risk assessment that included a site specific risk assessment for the Tonawanda Coke Corporation. A comprehensive emissions inventory was developed to further elucidate source contributions and emission reduction strategies for sources identified as contributing to elevated risk levels in the community. This information, coupled with the results between the upwind and downwind inhalation cancer risk values, provides a strong basis for further compliance monitoring and regulatory actions to reduce the inhalation cancer risk in the Tonawanda community.

In conclusion, the results of the Tonawanda Community Air Quality Study indicate that further work can be done to improve air quality in the community. Follow-up activities (e.g. increased compliance inspections and community observations) already have been implemented by the NYSDEC and the USEPA in an effort to improve air quality in the community. NYSDEC is continuing to monitor hourly benzene concentrations at the GIBI site to further evaluate the high levels of benzene measured at this monitoring site with a higher degree of temporal resolution.

2. Background

2.1 Why Tonawanda, New York was Selected for a Community Air Monitoring Study

Tonawanda, NY was selected based on a number of critical factors: first, complaints by the community regarding odors and an overall compromised quality of life; second, the elevated ambient benzene results sampled by a local community group and the New York State Department of Conservation (NYSDEC); and third, the Tonawanda industrial area represents an excellent area to assess the effectiveness of the current federal and state hazardous air pollution reduction strategies. In addition, elevated inhalation cancer risk estimates from the 1999 National-Scale Air Toxics Assessment (NATA) and the federal residual risk assessment conducted for coke ovens under §112(f) of the Clean Air Act Amendments indicated the potential for an additional inhalation cancer risk associated with emissions from the Tonawanda Coke Corporation. All these factors provided a strong impetus for an in-depth community air quality study.

2.2 Community Concerns

The residents of the Town of Tonawanda have been concerned about air quality issues for many years. The Tonawanda community has a large active industrial base that is surrounded by residential neighborhoods. The citizen complaints in the neighborhoods that are in or surround the area zoned as a general industrial district have primarily involved odors, particulate deposition and events associated with eye and upper respiratory tract irritation. Additionally, citizens expressed concerns about other possible long-term health effects associated with exposure to the industrial emissions. A group of concerned citizens organized to form the Clean Air Coalition of Western New York (CACWNY) in an effort to identify, monitor and reduce emissions in the Town of Tonawanda. Their concerns were summarized succinctly in a recent community newsletter, "These emissions impact our quality of life on a daily basis and make us worry for the health of our loved ones."

The CACWNY has been constructively working with the NYSDEC and their federal, state and local government officials to address and find solutions to the quality of life issues in their community. The Tonawanda Community Air Quality Study was developed to define the air quality within the community over a period of one year to assist the Department in the development a focused air quality management strategy.

2.3 Results from Short-term Air Monitoring

In February 2005, the CACWNY presented results of their short-term ambient air monitoring study to NYSDEC Region 9 staff. CACWNY used a "Bucket" air collection method which is advertised as an easy to use and inexpensive method and consists of a sampling device housed inside a five gallon plastic bucket. The Bucket was developed 1995 by an environmental engineering firm Northern California. Sampling is conducted

over a short time frame, generally 5-15 minutes. After collection, the sample is sent to an USEPA certified laboratory for analysis.

Bucket sampling can provide useful information but the results must be interpreted carefully. For example, certain chemicals are associated with the Bucket sampling media (Tedlar™) and this makes interpretation of those chemicals very difficult.   Additionally, for sources with intermittent releases, it may be very difficult to associate a short-term collected sample with releases from a particular source. Finally, in the absence of relevant meteorological data (e.g., wind direction data) and "upwind" air measurements, information may not be sufficient to relate the measurements to a particular source of air contaminants.

CACWNY collected fifteen minute air samples from two locations in the town of Tonawanda. On July 20, 2004, at 11:00 pm CACWNY collected a sample across from the 3M facility at 340 Sawyer Avenue. The sample was analyzed and carbon disulfide was found at a concentration of 100 ppbv (320 $\mu g/m^3$). CACWNY compared their short-term monitoring results with NYSDEC's Annual Guideline Concentrations (AGC)[1]. Comparison of short-term monitoring results with long-term health-based comparison values is generally, not considered an acceptable approach. This value was below NYSDEC's Short-term Guideline Concentration (SGC) of 6200 $\mu g/m^3$ and AGC of 700 $\mu g/m^3$ for carbon disulfide.

On August 16, 2004, at 10:55 pm, CACWNY collected a second fifteen minute bucket sample across from the NOCO Energy Facility at 700 Grand Island Boulevard. The sample was analyzed and a concentration of 50 $\mu g/m^3$ was found for benzene. This value was approximately ten times higher than other statewide data reported by NYSDEC for the years of 1990 through 2000. NYSDEC's SGC for benzene is 1300 $\mu g/m^3$ and the AGC is 0.13 $\mu g/m^3$. This area of Tonawanda has three significant point sources of benzene, a coke plant and two gasoline distribution terminals (NOCO Energy and Sunoco Transfer Station). This prompted NYSDEC to investigate a long-term monitoring approach which would allow for comparisons to NYSDEC's AGC.

NYSDEC investigated the results obtained by CACWNY with consideration for the limitations of this type of sampling media. NYSDEC conducted a modeling evaluation to identify locations of maximum impact to assist staff in selecting the best locations for short-term ambient air monitoring. Benzene emissions from three facilities were modeled: Tonawanda Coke, NOCO Energy, and Sunoco Transfer Station. Next, NYSDEC Region 9 staff collected four one-hour ambient air samples using a Summa Canister. In the final phase, a monitor-to-model comparison was performed to confirm the selection of the sampling location.

The results of the limited ambient air collection on June 21, and June 23, 2005 at four locations indicated no acute health exposure concerns for benzene in the area but

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[1] AGC's are discussed in Section 7 – Public health interpretation of measured air concentrations.

suggested the need to assess chronic exposure through a long-term sampling and analysis effort. The results can be found in Table 2.1.

Staff in the NYSDEC Region 9 office have been working with the CACWNY and the Town of Tonawanda Commission for Conservation and Environment (Commission), since the initial bucket results were presented to the Department. These two groups have expressed their concerns about odors in the area and the potential health effects associated with air toxics emissions from facilities in the area. The Department concluded that a long-term monitoring study would help to assess potential health risks to people living in the Tonawanda area. The results of this effort could identify a need to further reduce facility emissions.

2.4 Results of USEPA's Residual Risk Assessment for Coke Ovens

In 2005, the USEPA released the Coke Oven Residual Risk Assessment (USEPA, 2005a). The Tonawanda Coke Corporation was one of four coke oven facilities included in this assessment which concluded that "The results of the more refined level of analysis of this assessment showed that the emissions from these four facilities are not considered to cause a potential concern for adverse noncancer health impacts but do pose potential cancer risks to the individual most exposed living within 50 km of these facilities." Cancer risk isopleths around Tonawanda Coke showed a greater than one-in-one-million potential cancer risk for individuals living within 5 km from the facility. However, the risk assessment documentation stated "For this risk analysis, no monitoring data exist. Therefore, it was not possible to evaluate the ambient concentrations estimated by the modeling using monitoring data."

The Department concluded that information from a community-based monitoring study in the vicinity of the coke oven may help verify the conclusions of the residual risk assessment.

2.5 Results of the USEPA's 1999 National-Scale Air Toxics Assessment

The results of the 1999 NATA indicated that Erie County, in comparison to other counties in New York State, had a higher cancer and respiratory non-cancer risk associated with inhalation exposure to hazardous air pollutants. One of the primary objectives of NATA is to help state and local air pollution agencies identify areas for further data gathering (e.g. monitoring), investigate the underlying data (e.g. accuracy of emissions inventory) and facilitate further assessment (e.g. where to focus local-scale assessments). A more refined analysis of local-scale ambient air quality and spatial variability of air toxic contaminants through the establishment of an ambient air monitoring study may verify the applicability of such modeled ambient concentration data and risk characterization.

3. Introduction

3.1 New York State and Federal Air Pollution Control Programs

In the early 1960's, The New York State Legislature passed the Air Pollution Control Act, Article 12-A of the Public Health Law in recognition of the need to safeguard the air resources of the State from pollution by controlling or abating air pollutant releases from existing sources and preventing new source releases for the public good. The State's policy was then and remains:

> "It is declared to be the public policy of the state of New York to maintain a reasonable degree of purity of the air resources of the state, which shall be consistent with public health and welfare and the public enjoyment thereof, the industrial development of the state, the propagation and protection of flora and fauna, and the protection of physical property and resources, and to that end to require the use of all practical and reasonable methods to prevent and control air pollution in the State of New York….This can be done most effectively by focusing on goals to be achieved by a maximum of cooperation of all parties and that codes, rules and regulations established under the provisions of this article should clearly be premised upon scientific knowledge of causes as well as effects." (Environmental Conservation Law Section 19-0103).

This policy statement was used to develop a state air pollution control program in 1962 to control emissions from industrial processes and the combustion of fuels. The state program was designed to protect the public from adverse effects of air contamination and to further protect and conserve the natural resources and environment. The goal of the program was to promote maximum comfort and enjoyment and use of property consistent with the economic and social well-being of the community. The state program continued to evolve over the decades as our knowledge about the adverse public health and environmental impacts of air pollution grew, coupled with advances in our ability to assess the impacts of air pollution and technological advances in air pollution control. This allowed New York to implement numerous air pollution abatement strategies over the years to improve air quality and better ensure the protection of public health and the environment. One of these strategies was the development of a state program to control emissions of toxic ambient air contaminants (air toxics) from stationary sources (Cashman 1982, NYSDEC, 1991). The state program covered numerous sources of air toxics and required control of an emission source based on its impacts on public health and the environment.

In 1990, extensive revisions of the federal Clean Air Act (CAA) resulted in the development of a national program to control hazardous air pollutant (HAP) emissions from industrial and mobile sources. The 1990 amendments required the federal government to develop National Emission Standards for Hazardous Air Pollutants (NESHAPs) for 187 listed pollutants referred to as HAPs. Prior to the 1990 CAA, only eight substances were identified and listed as HAPs (asbestos, beryllium, mercury, vinyl chloride, radionuclides, inorganic arsenic, benzene and coke oven emissions). NESHAPs

only were promulgated for sources of seven of these eight HAPs. One of the main goals of the 1990 CAA was to ensure that the requirements to reduce HAPs were national, with no facility being allowed a competitive edge by having to meet less stringent control requirements.

The 1990 CAA established a number of milestones or regulatory deadlines to improve air quality. The goal of the NESHAP program was to reduce air toxics emissions by over 75% from industrial source categories within 10 years. This goal was to be accomplished by enacting a two stage regulatory process. First, the development and implementation of technology based standards (NESHAPS) for 174 categories of industrial sources, followed by an assessment of the risk to public health and the environment after the source is in compliance with the NESHAP. Other goals established by the USEPA to measure progress in the reduction of air pollution under the CAA are briefly discussed below. In summary, the goals of the federal and state air pollution control programs are consistent and promote the economic and social well-being of the community.

3.2 USEPA's Urban Air Toxics Monitoring Program

The Clean Air Act Amendments (CAAA) of 1990 requires USEPA to regulate source categories to substantially reduce the public health risk due to exposure to HAPs. Recognizing that HAPs pose unique threats in urban areas and that industrial and mobile sources contribute to the public health risk, USEPA supplemented their existing air toxics regulatory program with an Integrated Urban Air Toxics Strategy. In the Strategy, USEPA presents a framework for addressing air toxics in urban areas, looking collectively at large and small industrial and commercial sources. Goals for the Strategy reflect both statutory requirements stated in section 112(k) and the goals of the overall air toxics program. The overall goal is to attain a 75% reduction in incidence of cancer attributable to exposure to HAPs emitted by air pollution sources. To achieve this goal, the Integrated Urban Air Toxics Strategy selected a primary focus of reducing 33 priority HAPs in urban areas from both the stationary and mobile source sectors, rather than the full suite of 187 HAPs.

USEPA developed as a component of the Integrated Urban Air Toxics Strategy, the Urban Air Toxics Monitoring Program (UATMP). The goals of this Program are to measure the effectiveness of the national mitigation efforts and establish long-term trends in ambient air toxic levels. Since the inception of UATMP in 1987, many environmental and health agencies have participated in the UATMP to assess the causes and effects of air pollution within their jurisdictions (USEPA 2004a). The program has four key air toxics monitoring objectives. The first is to develop trends in air toxic concentrations to assess the effectiveness of HAP reduction strategies. The second component establishes ambient air monitors in locations of elevated air toxics concentrations ("hot spots"), whereby concentration gradients within communities can be identified through a network of monitors. These types of projects also provide data for the potential identification of personal exposure and health effects associated with air toxics. A third component provides data to support and evaluate dispersion and deposition models used for air quality planning and risk assessment evaluations. Finally, the fourth component provides

data to the scientific community to support studies to reduce uncertainty about the relationships between levels of ambient air toxics, actual human exposure to air toxics, and health effects from such exposures.

In 2004, USEPA began awarding grants to State and local agencies to conduct short-term, local-scale air monitoring projects through the Community-Scale Air Toxics Ambient Monitoring (CSATAM) program. In the first year of funding, USEPA selected 16 local-scale projects and awarded $6.2 million in funding (USEPA, 2005b). NYSDEC applied for CSATAM program funding in the 2005/2006 grant cycle. The Department was awarded approximately $300,000 and matched this with additional in-kind support to conduct a community-based monitoring study in the town of Tonawanda.

3.3 Study Community

The Study community is an industrialized, urban area in the western part of New York State in Erie County, north of the city of Buffalo. Access to waterways and proximity to an international border and the development of railroad lines (Buffalo and Niagara Falls Railroad in 1836 (BHW 2006)) fostered the development of industry over the years.

The Study community includes the western portions of the Town of Tonawanda, the City of Tonawanda, and the Village of Kenmore (collectively called "Tonawanda"). The Study community includes nine census tracts[2] and is framed by the Niagara River to the west and the Erie Canal waterway at the northern edge as shown in Figure 3.1. The general area can be characterized as flat terrain with industry located in the western region and residences and commerce in the north, east and south regions. The Study community area is approximately 9,000 acres and the 2000 census reports a total population size of 38,875. The 2002 Economic Census compiled by the US Census Bureau reports the manufacturing industry as the largest employment sector for the Town of Tonawanda based on the North American Industry Classification System (NAICS) scheme (USCB 2002).

Two major interstate highways bisect the community, I-190[3] and I-290 (Youngmann Memorial Highway). A toll booth is located on I-190 prior to crossing the Grand Island Bridge in the northern direction and traffic congestion is common at this location. Grand Island Boulevard is a major street adjacent to the I-190 between the Grand Island Bridge and Sheridan Drive.

The area is also home to some of New York's largest industrial facilities, located in the western portion, including: a coke production facility, two petroleum distribution terminals, chemical bulk storage terminals, combined-cycle combustion turbine (gas-fired) electric generation facility, a coal-burning electric generation facility, a tire manufacturing plant, chemical manufacturing facilities, a cellulose sponge manufacturing

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[2] Federal Information Processing Standards (FIPS) codes for the tracts included in the study community: 36029008202, 36029008700, 36029008800, 36029007700, 36029007800, 36029008300, 36029008201, 36029008400, 36029005800.

[3] I-190 through Tonawanda is called the NYS Thruway – Niagara section.

facility, and DuPont Corian® (solid surfaces) and Tedlar® (polyvinyl fluoride) manufacturers. Section 6 (Emission Inventory) and Appendix F (Emission Inventory Development) provide a more comprehensive list of facilities and emissions inventory for the area.

3.4 Air Pollutants of Interest in the Study

The air toxics of interest are the 15 priority urban HAPs identified in section 112(k) of the CAAA of 1990. In addition to monitoring for these 15 priority HAPs, the Study also evaluated air concentrations of 41 additional HAPs. Table 3.1 lists the air toxics selected for the study and identifies the 15 priority HAPs and those HAPs reported in the USEPA NATA for 1996 and 1999.

Additionally, fine particulate matter ($PM_{2.5}$ - aerodynamic diameter of 2.5 microns or less), sulfur dioxide (SO_2) and carbon monoxide (CO) were monitored on a continuous basis to identify potential health risks and long-range transport versus local contribution to air quality. Meteorological parameters of wind speed and direction, horizontal wind deviation (sigma theta), temperature and relative humidity also were measured on a continuous basis to assist in the evaluation of source contribution to air quality.

3.5 Potential Environmental Justice Area

Following NYSDEC's Commissioner Policy 29, Environmental Justice and Permitting (Policy), an area is considered to be a potential environmental justice (EJ) area if minority or low-income communities are present. NYSDEC's Policy defines minority communities when a census block group, or continuous area with multiple census block groups, has a minority population (Hispanics, African-Americans or Black persons, Asian Americans and Pacific Islanders, American Indians, Alaskan Natives, and other race or multi-race) equal to or greater than 51.1 percent of the total population. NYSDEC's Policy defines a low-income community to be any census block group, or continuous area with multiple census block groups, having a low income population (i.e., percent living below the poverty threshold) equal to or greater than 23.59 percent of the total population (NYSDEC 2003).

Two potential environmental justice areas have been identified within this community as shown in Figure 3.2. These areas, comprised of four census blocks[4], contain a total population of 3,855. Eighty-seven percent of the total population is white, six percent is Black or African-American, one percent is American Indian, three percent is multi-race and two percent is other race not specified. This area can be described as residential, surrounded by commercial and industrial business and some community services. The percent below the poverty threshold for the four census blocks is 39%, 41%, 43%, and 28%.

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[4] Census block FIPS codes: 360290083001, 360290083003, 360290083005 and 360290058008.

NYSDEC awarded two EJ Community Grants to the CACWNY a community group in the Study area. Details of these two grants are discussed in Section 4 (Community Component).

3.6 Study Objectives

The Study objectives are summarized below:
1. Conduct ambient air monitoring of selected HAPs and criteria pollutants for one year to determine the overall air quality in the Tonawanda area;
2. Use available emissions inventory databases from NYSDEC and USEPA to generate a point, area and mobile source emission estimates for monitored HAPs in the Tonawanda area;
3. Predict ambient air concentrations using the Regional Air Impact Modeling Initiative (RAIMI) software model;
4. Compare the ambient air monitoring results of the selected HAPs to modeled predictions (residual risk assessment for coke ovens, 2002 National-scale Air Toxics Assessment (NATA) and RAIMI) using various statistical analyses;
5. Assess the relative contributions of various air pollution sources in the Tonawanda area using time-weighted pollutant concentration roses and pie charts generated from the emissions inventory data analysis;
6. Hold public meetings to present the ongoing and final results of the Study; and
7. Prepare a final report to summarize the data and explain the results of the various data analyses that were conducted.

4. Community Component

NYSDEC's Office of Environmental Justice awarded two Environmental Justice Grants to a community group in the Tonawanda area. The grant goals and assistance provided by the Department are discussed in this section. One of the project tasks, listed in the Quality Assurance Program Plan (QAPP) (NYSDEC 2007a) was a series of public meetings in the Tonawanda community, presenting ongoing and final results of the study. Those meetings also are discussed in this section. Finally, other outreach efforts initiated by the Department will be detailed.

4.1 Environmental Justice Grant

NYSDEC's Environmental Justice (EJ) program awards grants to community groups for projects that address exposure of communities to multiple environmental harms and risks. NYSDEC began funding projects in 2006, with awards ranging from $2,500 to $50,000. Two awards were given to the Clean Air Coalition of Western New York (CACWNY), a community-based organization that formed to reduce pollution in Tonawanda. Their primary focus has been the reduction of benzene from the Tonawanda Coke Corporation.[5]

4.1.1 2007 Award

During the 2007 funding cycle, the Department awarded an EJ community grant in the amount of $24,000 to the CACWNY to research the potential link between negative health outcomes and air pollution from sources in the Tonawanda area. The CACWNY study placed emphasis on community exposure and health outcomes. The study proposed the use of personal air monitoring badges that would be worn by resident volunteers. Additionally, the study proposed the collection and analysis of bucket samples, and the use of a network of volunteers to track odors and acute health effects of residents. The project was intended to complement the NYSDEC's community air toxics study.

Staff in NYSDEC's Bureau of Air Quality Analysis and Research assisted the CACWNY by providing information to enhance the personal air monitoring portion of their study. Staff researched and summarized best practices used by other researchers and offered recommendations on the following topics: placement of the badges, optimization of the detection limit, assessment of indoor sources, and the assessment of personal activities. Appendix A details the recommendations prepared by staff for CACWNY.

Upon completion of sampling, staff provided meteorological information to CACWNY to aid in their evaluation of potential sources for the concentrations recorded by the sampling badges.

During the course of their EJ project, CACWNY requested an evaluation of the benzene risk using the first six months Study monitoring results collected by the Department.

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[5] To learn more about CACWNY visit their web site at: http://www.cacwny.org/.

Staff conducted this analysis and presented the information shown in Appendix B, which included a description of confidence in the derivation of the unit risk estimate[6]. For comparison purposes, the cancer risk estimate based on the benzene concentration from the 2007 State average (an average of all the monitors recording ambient air benzene concentrations in 2007) and the background monitor in the State for 2006 were included.

CACWNY shared the results of their personal air monitoring with NYSDEC. Detectable levels of the three air toxics evaluated (benzene, naphthalene, and toluene) were not found in any of the personal air monitoring badges evaluated. The detection limit for the personal air monitoring badges was relatively high compared to the ambient concentrations commonly found in the urban environment.

4.1.2 2008 Award
During the 2008 funding cycle, the NYSDEC awarded an EJ community grant of $40,000 to CACWNY. The focus of this grant was to implement benzene reduction strategies, which included working with a facility in the area to reduce benzene emissions (Tonawanda Coke) and educating the community about ways they could reduce personal exposure to benzene. The outline listed below summarizes the project components:
1. Continue air testing for benzene in the affected communities;
2. Create a Good Neighbor Program to encourage local businesses to reduce their benzene emissions;
3. Host various educational events for the affected community. The educational component of the Project will consist of a series of seminars, development and dissemination of educational materials through meetings and canvassing, development of a website, and use of news media;
4. Research the potential for benzene emissions policies and/or guidelines; and
5. Investigate potential tollbooth removal within the research area.

4.2 Community Outreach and Presentations

For each of the community presentations, local media outlets received a press release to inform the community and encourage participation. Additionally, a fact sheet with a study area map was presented at each of the meetings. On the date of the public presentations, key staff met with reporters from local newspaper and television stations to discuss details of the study. In June 2009, a web site was created to provide a platform for presenting information to the community including the posting of community presentations and maps of the study area.

At the release of this report, four presentations have been given to the Tonawanda community, detailing various aspects of the study. The meeting dates were; September 2006, March 2008, November 2008 and June 2009.

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[6] Unit risk estimated is discussed in more detail in Section 7.2 – Public health interpretation of measured air concentrations

4.2.1 September 2006
For this first meeting, NYSDEC representatives met with the CACWNY and introduced the air quality monitoring study design. The location of the monitoring sites and the importance of prevailing wind direction on monitoring concentrations were presented. Additionally, a description of the monitoring methods and equipment was provided. Involving the community prior to implementation of the monitoring network fostered a collaborative and collegial relationship that was apparent in subsequent public meetings. Approximately 25 people attended.

4.2.2 April 2007
The NYSDEC issued a press release which formally announced that funding had been obtained from the State and USEPA to conduct air monitoring of hazardous air pollutants in the Town of Tonawanda for a period of one year (Appendix C).

4.2.3 August 2007
A press conference was held at the Grand Island Boulevard monitoring site to announce the beginning of actual air quality sampling in the community. Individuals from NYSDEC, CACWNY, University of Buffalo and local and state elected officials attended the media event. News stories about the event were carried by local newspapers, television and radio stations (Appendix C). Community residents and staff from the NYSDEC and were interviewed by the press.

4.2.4 March 2008
For the second community meeting, the Department presented the results of the first six months of air monitoring data. The six-month average concentrations for four air toxics were provided and compared to the State average for 2007, if available. Additionally, this meeting was used by the CACWNY to recruit volunteers for their community study funded by a NYSDEC EJ grant.

The presentation generated interest in ambient air benzene concentrations and its sources. Approximately 80 people attended. Provided in Appendix C are news articles written as a result of the March public meeting.

4.2.5 November 2008
At the third community meeting, staff presented 12-month average concentrations and characterized risk for five air toxics with results above the NYSDEC's Annual Guideline Concentrations (AGC)[7]. Study results were compared to the State average for 2007 for each air toxic. Staff used a risk communication tool called a "tox tree" to communicate the fairly conservative margin of safety used when uncertainty factors are applied to derive non-cancer guidance values and the one-in-a-million risk level is selected for cancer guidance values. Two example diagrams (non-cancer and cancer endpoints) are presented in Appendix D. The diagrams presented are not intended to represent a specific pollutant.

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[7] AGCs are discussed in Section 7.2 - Public health interpretation of measured air concentrations.

Because the content of this presentation was technical, staff prepared a number of posters that were displayed in the meeting room. This format allowed individuals to ask specific questions about technical components in the presentation in a more personal and private venue.

Approximately 100 people attended the meeting. The public feedback from this meeting indicated some confusion in understanding the presentation. Appendix C provides ongoing news articles about NYSDEC's study and a factsheet and press releases for the November 2008 meeting.

4.2.6 June 2009
The purpose of the meeting was to discuss analysis of the air monitoring results, recent inspection activities at facilities in the area, and on-going air quality monitoring conducted by NYSDEC, and to address questions from the public. The presentation was structured to provide the conclusions in the beginning followed by technical details related to recent analysis.

Approximately 100 people attended the meeting including many local elected officials. The meeting was well received and staff received two rounds of applause and praise for the presentation's clarity and informational content provided. An hour of questions and answers followed the presentation. Most questions focused on the recent compliance inspections conducted by NYSDEC and other concerns related to Tonawanda Coke.

In June 2009, a web site[8] providing details of the study was created. The web site includes a map of the location and lists facilities in the area and also includes contact information for questions about the project. The November 2008 and June 2009 community presentations have been posted to this site and a link to the CACWNY web site is included.

Appendix C provides ongoing news articles about NYSDEC's study as well as a factsheet, flyer and press releases for the June 2009 meeting.

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[8] Link for the Tonawanda Community Air Quality Study web site available at:
http://www.dec.ny.gov/chemical/55471.html

5. Monitoring Network

5.1 Site Selection and Equipment Installation

The Study's Quality Assurance Project Plan (QAPP) (NYSDEC 2007a) details the measuring of ambient air quality at four monitoring sites. Included in the QAPP, is the site selection process which began with an examination of thirty years of local meteorological data (1973 – 2003), showing the predominant wind direction from southwest to northeast. This information was used to select four small areas of interest for the placement of the air quality monitors with reference to the industrial sources in Tonawanda. By probing local maps and touring the Study area, potential sites with full access for one year and meeting USEPA's siting criteria (USEPA, 2009c), were selected from the areas of interest. The siting criteria are listed below.

1) Access to reliable power and phone service;
2) 24-hour access for monitor operators and low likelihood of vandalism;
3) Allow for the siting of monitors at required height;
4) Absence of trees or other wind obstacles;
5) For criteria pollutant monitor, site must meet specific minimum distance to roadway.

Two types of sites – upwind and perimeter - were implemented for the Study. The upwind site southwest of the industrial sources captured background measurements of air toxics. Three perimeter sites in locations east and northeast of the Study area provided measurements downwind of the industrial sources. The site selection process involved many months of investigation and discussions with property owners. The sites selected for the Study are described below.

1. Upwind Site – The area southwest of the Tonawanda Industrial zone at Beaver Island State Park (BISP) on the southern tip of Grand Island was selected for the upwind site. The monitor, shown in Figure 5.1, was placed near the golf course, south of the park maintenance garage approximately 200 feet west of the Niagara River.
2. Perimeter Industrial Site – A large open field under the high power transmission lines on Grand Island Blvd in the industrial zone was selected. National Grid granted permission to site a temporary monitor, provided specific safety regulations were followed. This site called the Grand Island Boulevard Industrial (GIBI) and shown in Figure 5.2 is located directly northeast of most of the industrial facilities.
3. Perimeter Northern Industrial – National Grid granted permission to site a monitor on their property next to the transmission power lines at the western end of the residential neighborhood of Brookside Terrace West (Brookside Terrace Residential Site (BTRS)), close to the northern portion of the Tonawanda industrial zone. This monitor is shown in Figure 5.3.

4. Perimeter Southern Industrial – A monitor was placed at the Sheridan Park Water Tower (SPWT), by permission of the Town of Tonawanda Water Department. This monitor is shown in Figure 5.4.

Figure 5.5 is a map of all monitor locations, and large industrial facilities.

5.2 Monitoring

All monitoring stations were installed and the instruments were calibrated during the spring of 2007. The continuous monitoring instruments (collecting fine particulate matter, sulfur dioxide, carbon dioxide and meteorological data) were collecting and storing valid data on July 1, 2007. The first volatile organic and carbonyl compound samples were collected on July 5, following USEPA's one-in-six day manual monitoring schedule and samples were collected until June 29, 2008. The laboratory analyses quality assurance can be found in Appendix E.

A summary of the parameters and sampling information is presented in Table 5.1.

5.2.1 Hazardous Air Pollutants - Sampling and Analysis Method

The sampled hazardous air pollutants (HAPs) are divided into two categories, volatile organic compounds (VOCs) and carbonyl compounds (hereinafter referred to as carbonyls) based on molecular structure, with distinct sampling and laboratory analysis methods. VOCs are defined as organic compounds having a vapor pressure greater than 10^{-1} Torr[9] (USEPA 2007a). Carbonyls are a type of VOC with a characteristic molecular arrangement of a carbon atom double bonded to an oxygen atom (aldehydes and ketones). All HAP air monitoring samples were collected over a 24-hour period, on a one-in-six day schedule.

Volatile organic compounds

VOCs were collected by using a RMESI (Xon Tech) 910PC 24-hour sampler to fill an evacuated pre-cleaned 6-liter stainless steel canister (Figure 5.6) at a constant flow rate.

The canisters were sent to NYSDEC's Bureau of Air Quality Surveillance (BAQS) laboratory in Albany, New York for analysis of 42 target compounds consistent with NYS Toxics Air Monitoring Network. Two additional compounds (acrolein and carbon disulfide), not included in the QAPP, were added for a total of 44 compounds. Table 5.2 lists all VOCs with associated method detection limit (MDL), NYSDEC's Annual Guideline Concentration (AGC)[10] (NYSDEC 2007b), chemical abstract service (CAS#) and USEPA's urban HAP designation.

The target maximum holding time from sampling to analysis of 30 days was met for all samples obtained. The canister samples were analyzed using a modified version of USEPA's method TO-15 (NYSDEC 2007a). The analytical process is described as

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[9] At temperature of 25°C and pressure of 760 millimeters of mercury
[10] AGC's are discussed in detail in Section 6 - Public health interpretation of measured air concentrations.

follows: Air samples are taken from the canister at a controlled flow and temperature by an Entech Model 7100A preconcentrator. The sample was injected into a Varian Saturn gas chromatograph/mass spectrometer (GC/MS).

Carbonyl compounds
USEPA Method TO-11a (USEPA 1999) sampling and analytical procedures were followed. The method traps carbonyls by reaction with 2,2-dinitro-phenyl hydrazine (DNPH) coated silica gel contained within a commercially available sampling cartridge (Supelco LpDNPH S10). Figure 5.7 shows a photograph of a carbonyl cartridge. Approximately 1440 liters of ambient air were drawn first through an ozone denuder to remove interfering ozone and then through an assembled DNPH cartridge over a 24-hour period by an ATEC 8000 sampler. When the carbonyls contact the DNPH, they react and are retained within the cartridge as carbonyl-DNPH derivatives. Following sampling, the cartridges were sent to the BAQS laboratory for analysis. During storage and transport, all cartridges were kept cold as required. Table 5.3 lists the carbonyls with associated MDL, AGC, CAS# and USEPA's urban HAP designation.

A Gilson ASPEC XL automated sample processor was used to extract the DNPH derivatives, mix the extract and transfer a portion of the extract into auto-sampler vials for analysis using high performance liquid chromatography (HPLC).

5.2.2 Criteria Pollutants and Instrumentation

Particulate matter ($PM_{2.5}$)
Particulate matter, in the size range of 2.5 microns ($PM_{2.5}$) and below, was monitored with a Thermo Environment Inc. Model 1400ab Tapered Element Oscillating Microbalance (TEOM) with a sharp cut cyclone inlet. While this method for monitoring of $PM_{2.5}$ is not considered a federal reference method (FRM), it is used by federal and state agencies to evaluate $PM_{2.5}$ ambient concentrations in real-time for the purpose of reporting the Air Quality Index[11]. Hourly average measurements of $PM_{2.5}$ were recorded at all four Study monitoring sites. The TEOMs were connected to Environmental Systems Corporation (ESC) data loggers which transmitted the data to the NYSDEC central office in Albany every hour. TEOM instruments use a gravimetric method to measure particulate matter concentration. The instrument is heated to 50°C to remove water vapor collected. An adjustment was made to the TEOM results to account for the loss of volatile organic compounds due to the heating of the sample and this adjustment provides results similar to values obtained using the filter-based FRM for monitoring of particulate matter (Felton, 2005).

Sulfur dioxide (SO_2)
A Thermo Electron Model 43C Sulfur Dioxide (SO_2) analyzer which uses a federally approved method for monitoring of SO_2 was installed at the BTRS site. This instrument is capable of detecting SO_2 at concentrations as low as 0.1 ppb. This instrument continuously recorded SO_2 concentrations and transmitted hourly average values to the NYSDEC central office in Albany.

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[11] For more information about the Air Quality Index see http://www.dec.ny.gov/chemical/34985.html

Carbon monoxide (CO)

A Thermo Electron Model 48C Carbon Monoxide (CO) analyzer which uses a federally approved method for monitoring of CO was installed at the BTRS site. This instrument is capable of detecting CO at concentrations as low as 0.02 ppm. This instrument continuously recorded CO concentrations and transmitted hourly average values to the NYSDEC central office in Albany.

5.2.3 Meteorological Parameters and Instrumentation

The BISP site was selected for a meteorological station since this location had the fewest wind obstructions (few surrounding buildings and trees) and a surrounding, expansive flat terrain. A Met One Wind Sensor was installed on a 10-meter high meteorological tower which records wind speed and direction. Barometric pressure, relative humidity, and temperature probes were installed on the tower at ground-level. The data were stored in an ESC data logger and transmitted hourly to NYSDEC central office in Albany.

5.3 Limitations

The air toxics monitored in this study were selected based on those listed in analysis methods TO-11a and TO-15. These two methods include some irritants released by facilities in the Study area, such as acrolein and acetaldehyde, but does not include others released by facilities such as hydrogen fluoride, hydrogen chloride, ammonia, and sulfuric acid. The modeling portion of the Study (Subsection 7.3.2.2) evaluated potential ambient air concentrations of irritants not monitored in the study

Additionally, the Study did not monitor benzene soluble organics (BSO) which is used to characterize coke oven emissions. Coke Oven Emissions are considered a hazardous air pollutant, identified in the 1990 Clean Air Act Amendments and have been classified by the USEPA as a known human carcinogen.

Finally, the results for acrolein should be interpreted with caution. Obtaining accurate measurements of this air toxic is difficult and the laboratory found many validation comparisons exceeding the acceptance limit.

6. Emission Inventory

An emission inventory was compiled for the facilities occupying the nine census tracts encompassing the Study area and was developed to serve several purposes. First and foremost was to gather data on the combined quantity of air toxic emissions impacting the Study area. Air toxic emissions can come from large and small industrial facilities, fugitive emissions from landfills, construction activity, and automobile, truck, and railroad vehicle emissions. Air toxic emissions are also released by residential activities such as lawn mowing, pesticide use, and home repair activities. The mass emissions, in conjunction with the toxicological characteristics making up these emissions, need to be quantified and compared to accepted health based standards or recognized guidance limits. Second, the mass emission data gathered for the Study area were used as input data entered into an air dispersion model. Air dispersion models are used to predict ambient concentrations from the source categories noted above. Air dispersion models are needed to predict ambient concentrations of air toxic emissions which were not or are unable to be monitored. As part of the Study design, the predicted concentrations of air toxics which were modeled were compared to monitored concentrations to quantitatively determine how well the air dispersion model was performing.

The emission inventory for the non-residential sector is comprised of three source categories; major, area and mobile. The distinction between major and area sources is based upon regulatory emission cutoffs defined by the USEPA for a single pollutant or class of pollutants. Major sources describe the facilities with the most significant amount of mass emissions. Area sources describe facilities which are either small stand-alone facilities (i.e. gas stations) or locations with fugitive emission releases, such as landfills or sewage treatment plants. Major and area size facilities with individual emission points are also referred to as point sources or stationary sources. Mobile sources represent passenger car traffic and off-road vehicle traffic. Off-road vehicles generally are described as construction equipment. The emissions of off-road vehicles were not included in this section due to the absence of specific emissions information for the Study area. When a model to monitor comparison was performed, non-road emission estimates were obtained from the National Air Toxic Assessment (NATA2002) data. Other source categories such as railroad yard emissions (thought to be contributors to $PM_{2.5}$) also lacked the emissions information necessary to make a quantitative evaluation.

A list of emission quantities for all HAPs and non-HAPs emitted from major and area point sources can be found in Figures F1 and F2 of Appendix F. Pie charts for the air emissions with the greatest mass can also be found in Figures F1 and F2, as well as those emissions from Mobile sources (Figure F3) of Appendix F.

6.1 Major Sources

A facility emitting criteria pollutants and/or hazardous air pollutants greater than a federally defined mass emission rate is classified as a major source. Depending on the geographical location within New York State, all criteria pollutants have defined mass emission cutoff amounts signifying the major source level. For example, the Niagara

Frontier area, consisting of Niagara and Erie Counties, has a major source cutoff level set at 50 tons per year or greater for any single facility's emissions of volatile organic compounds. The federally defined mass emission rate for HAPs is the same state-wide and is set at 10 tons per year for individual HAPs and 25 tons per year for a combination of HAPs. For the Study location, the classification of major was used as a starting point to identify facilities of concern and was not limited to only HAPs when identifying toxic air contaminants. Facilities whose emissions are greater than the federally defined mass emission rate for major facilities are required to obtain a Title V permit.

Title V sources are the most rigorously regulated sources in the NYSDEC's air permitting system and are required to submit yearly emission statements of actual emissions to the Department. For the purpose of this study, the combined emission statements of 2002, 2005 and 2006 were chosen and the highest reported emission of an individual air contaminant was selected. These years were selected because 2002 and 2005 are classified as periodic inventory years. Periodic inventory years are when a more robust collection of data is required from the regulated facilities. The additional year of 2006 was added as a check and was the latest complete inventory year at the time the data gathering effort began. All of the Title V facilities are also required to submit Toxic Release Inventory[12] (TRI) data to the USEPA under the under Emergency Planning and Community Right-to-Know Act (EPCRA). Emission statement data was compared and verified with all Toxic Release Inventory data. The USEPA releases the National Emission Inventory (NEI) each year after it is complied. The emissions statements filed with NYSDEC are verified and used to populate the NEI.

To remain below major source classification, source owners can obtain a State Facility permit limiting the emissions from the facility to below major size status. Of the State Facility Permit holders, FMC Corporation has a cap of 98 tons per year of sulfur dioxide and Gibraltar Steel Corporation limits its potential emissions below all major source emission levels.

Sources included in the major source category account for the greatest amount of point source emissions. Within the inventory development process, the emission estimates for the major source categories would be qualitatively determined to be of high quality. Source types within the major source category generally have the most robust data for emission factor estimation and are more likely to have been stack tested to verify emissions and compliance with emission limits.

Facilities with Title V and State Facility permits limiting emissions can be found in Table F1 of Appendix F

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[12] To learn more about the Toxic Release Inventory visit: http://www.epa.gov/tri/triprogram/whatis.htm

6.2 Area Sources

Traditionally, area sources have been described as emission sources that are numerous, relatively small stand-alone facilities or locations with fugitive emission releases. For the purpose of this study, the definition of area sources will include NYSDEC regulated Registration sources, petroleum bulk storage facilities, trucking depots, sewage treatment plants, and landfills.

6.2.1 Registration Facilities

There are 22 facilities in the Study area eligible for a Registration certificate. A Registration certificate is issued to sources limiting their actual facility wide emissions below 50 percent of the major source limits. An additional Registration Certificate is held by the Tonawanda sewage treatment plant and its emissions will be addressed separately due to its unique source characteristics. There are an additional three facility owners, who retained permits from our previous permitting system, and are not required to update the permits at this time. The emissions from these facilities are considered negligible and not a significant impact to the Tonawanda area. The Niagara Landfill holds a Registration Certificate but will also be addressed in its own subsection.

A listing of Regulated Air Pollutants for Registration facilities can be found in Table F2 of Appendix F.

6.2.2 Petroleum Bulk Storage

Petroleum Bulk Storage (PBS) facilities include the large petroleum storage facilities, such as NOCO Energy and Tonawanda Sunoco, identified under the Major sources category list. The major facilities are in the business of unloading petroleum products to tanker trucks for further distribution. PBS facilities can also be smaller storage facilities designed to load fleet vehicles and finally PBS facilities can be gasoline retail stations. Petroleum products such as gasoline are a mixture of various hydrocarbons (e.g. toluene, xylene, cyclohexane, ethylbenzene, n-hexane, naphthalene, 1,2,4- trimethylbenzene, benzene and cumene). Five of these chemicals were sampled by the monitoring network. They are considered to be representative of emissions from PBS facilities.

Staff from the Division of Environmental Remediation maintains NYSDEC's Petroleum Bulk Storage database. This database lists all active and inactive PBS sites, including last inspections, liquid stored, tank size, number of tanks and age. This database was used to locate the gasoline fleet and retail sites in the study area. Sixteen retail gasoline stations were located in the nine census block study area.

A listing of Regulated Air Pollutants for Petroleum Bulk Storage facilities can be found in Table 2.0 of Appendix F.

6.2.3 Trucking Depots

The mobile emission sector within the nine census tract Study area is extensive. Although, the emissions of air toxics from mobile sources will be addressed under section 6.3 of this report, another potential contribution of air toxic emissions in the Study area is from the daily operation of trucking depots. The potential for air toxic emissions is from truck idling and traffic including shuttle trucks used to move trailers, and, to a lesser degree, diesel storage.

The air toxics of concern from trucking depots are fine particulate, ultra-fine particulate and black carbon, a surrogate for diesel particulate. The current Study monitored for $PM_{2.5}$ and did not specifically target black carbon. The TEOM monitors measured all particulate matter less than 2.5 microns.

The Study area has thirty-three active trucking depots and one bus terminal recorded in the Petroleum Bulk Storage database. The estimation of VOC and diesel PM emissions from the trucking depot source category is unknown. Low confidence is assigned to this emission estimates for this source category until better verification of truck activity can be established.

A listing of Regulated Air Pollutants for Trucking Depots facilities can be found in Table F2 of Appendix F.

6.2.4 Sewage Treatment Plant

Industrial and residential waste water sent to publicly owned treatment works (POTW) may be treated or untreated prior to release from industrial facilities. POTWs may treat waste water from residential, institutional, and commercial facilities and/or storm water runoff. A POTW will consist of a primary settling tank or tanks, biotreatment, secondary settling, and disinfection.

One sewage treatment plant is located within the nine census block Study area, the Tonawanda SD #2 facility. This facility holds a Registration Certificate from NYSDEC indicating that the potential of volatile organic compound and nitrogen dioxides emissions from this facility are below 50 and 100 tons per year, respectively and actual emissions are below 25 and 50 tons per year respectively. Tonawanda SD #2 has a three stage aqueous packed tower odor scrubbing system. Foul air from a thermal conditioning sludge treatment process, containing low molecular weight volatile compounds, passes first through a water scrubber, second through an oxidative scrubber, and third through an alkaline scrubber. It is then discharged to the atmosphere through a roof exhaust stack.

Listed in Table F3 of Appendix F are the total VOCs estimated for this source category and the five Category C contaminants determined to be above the Annual Guideline Concentration.

6.2.5 Landfills

The Study area encompasses three landfills in close proximity to two of NYSDEC's air monitoring stations. One landfill, Huntley flyash landfill, located between Grand Island Blvd and the Tonawanda Coke Corporation is an actively used landfill; the other two landfills are municipal solid waste landfills no longer in operation. The Niagara Landfill located north of the Highway 290, adjacent to the toll booths and River Road has been closed since the middle 1990's. The Niagara landfill size is below the thresholds for the New Source Performance Standards, Subpart Cc, requiring a flare or 98% control on captured gas emissions. Even though the landfill was below the NSPS threshold, this site was equipped with a flare at the time of final capping. The flare is no longer in use due to issues with gas production and ceased operation. The other municipal landfill adjacent to Highway 290, between two mile creek and the Conrail railroad tracks is the Town of Tonawanda's landfill. This landfill was the site of a municipal waste incinerator and the bottom ash was disposed on-site. Also, some solid waste was disposed on-site and radioactive waste from the Manhattan project is located at this site. The incinerator and landfill shut down in the early 1980's but the site was recently reopened for waste relocation work. Most of the current activity is along Hackett Road. As of this report, a final cover is not on the site.

Listed in Table F3 of Appendix F are the total VOCs estimated for this source category and the five Category C contaminants determined to be above the AGC.

6.3 Mobile Sources

For this study, the mobile source inventory was restricted to on-road diesel and gasoline engines of all size weight classes.

To generate emission factors for various types of light-duty and heavy-duty vehicles, the Division of Air Resources used MOBILE6[13]. MOBILE6 is a computer-based model used to analyze air pollutant impacts from gasoline-fueled and diesel on-road mobile sources. The software program is capable of generating mobile emission profiles for various road types. The software program also provides the user with a flexible analytical tool that can be applied in a wide variety of air quality planning functions. Among the many conditions that can be altered are roadway type, ambient temperature, weekday/weekend, and gasoline formulation.

Using emission factors and the daily vehicle miles traveled for the Study area, the emissions were calculated for the mobile source contribution in the Study area in tons per year and listed in Figure F3 of Appendix F.

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[13] Mobile6 software and documentation are available at http://www.epa.gov/otaq/mobile

6.4 Limitations

The use of modeling to predict ambient air concentrations has inherent uncertainty and limitations. Limitations with models will be discussed in Section 7. Modeling begins with the development of an accurate emission inventory. Although this Study used a number of data sources (NYSDEC facility permits and national derived emissions from TRI and NEI) to develop an emissions profile for each facility in the Study area, there are inherent limitations with these data sources. In most cases, emissions estimates are both variable and uncertain[14]. When measured values are available, they are based on a single day sampling which does not reflect operational variability. Uncertainty for each source category will be further discussed below.

Major facilities: The emission derived for the larger facilities in the Study area have the highest degree of confidence in the estimation since emissions information for these facilities can be verified by multiple data sources. Within this source category the confidence in specific emission profiles varies by source type. For example, emissions from electrical generating facilities are better characterized than emissions from unique source categories such as a coke production facility.

Minor facilities: This source category includes smaller stationary sources such as truck depots, gas stations, sewage treatment plants, and landfills. While many of these facilities hold some type of permit or registration with NYSDEC, less information is included in these applications compared to the major facilities. Additionally, for small sources not required to obtain permits or Registrations, an inventory was developed by using a commercial database compiled from public records (e.g., U.S. Census, yellow page listings, etc.). The reliability of this data source is dependent on the frequency of updates and an accurate listing of facilities. This data were used to determine if a source or group of sources was not previously identified.

Mobile sources: NYSDEC staff model on-road emissions from mobile sources on a routine basis as part of development of the State Implementation Plan to assess criteria pollutant reduction strategies. Therefore, NYSDEC staff has a higher level of confidence in the emission estimates for this category although day-to-day variability may be difficult to characterize accurately. Non-road sources were not modeled due to the lack of a sufficient local inventory.

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[14] Variability refers to differences over time and/or location, whereas uncertainty arises because of lack of perfect knowledge regarding the true value of a quantity (e.g., emission rate) at a given place or time.

7. Air Monitoring Analysis

7.1 Air Monitoring Concentrations in Perspective

Many of the air toxics monitored were at concentrations below the level of detection. Criteria were developed to assess the adequacy of deriving annual average concentrations from these data. For those air toxics that met the criteria, summary statistics were developed and the results were compared among all four monitoring sites and also with the ambient air concentrations obtained at other monitoring sites in the State and in the U.S. Additionally, the annual average concentrations were compared to health-based comparison values in Subsection 7.2.2.

The criteria pollutants were detected frequently and the results were compared to the National Ambient Air Quality Standards (NAAQS) in Subsection 7.2.2.

It was found that the measured pollutant concentrations were not normally distributed, and therefore appropriate approaches (parametric and non-parametric) were used for all statistical comparisons conducted in this Section. Additionally, appropriate statistical tests indicated negligible autocorrelation for the air toxics monitoring data.

7.1.1 Suitability of the Measured Air Concentrations for Data Analysis and Health Risk Evaluation[15]

Air Toxics

Monitored air concentrations must be present at levels that can be measured accurately and detected with sufficient frequency to characterize an annual average concentration. Accurately detecting ambient levels of air toxics is dependent on the lowest reliable monitored level (i.e., MDL[16]) which varies by pollutant and by monitoring method. The MDL and NYSDEC's Annual Guideline Concentrations (AGC) (NYSDEC 2007b) were used to develop a decision matrix for evaluating the level of confidence in deriving annual average concentrations primarily to assess potential adverse health risk. The outcome from the application of the decision matrix categorized air toxics for use in other data analysis components of this Study.

There is low confidence in the ability to derive an annual average concentration if the air toxic was detected in less than 50% of the monitored samples and those air toxics are listed in Categories A1 and A2 of Table 7.1. Air toxics have been placed in one of these two categories based on whether the health-based comparison value (AGC) is above or

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[15] Sonoma Technology's approach presented at the Toxics Data Analysis Workshop, Rosemont, IL on October 4, 2007 was adopted (available online at: http://www.epa.gov/ttn/amtic/files/ambient/airtox/2007-workshop/03_100407_hafner_mccarthy.pdf). The threshold for inclusion in the risk characterization analysis is 50% rather than the 15% threshold presented by Sonoma Technology.

[16] MDL = method detection limit. It is defined in the *Code of Federal Regulations* (Title 40, Part 136, Appendix B, Revision 1.11) as the lowest value at which it can be 99% confident that the true concentration is nonzero.

below the MDL, because a determination about risk can only be made if the MDL is below the AGC. For category A1, NYSDEC's AGC is below the MDL. A risk evaluation for these air toxics will not be conducted because there is low confidence in the ambient air concentrations measured and it cannot be determined whether the air concentrations are above or below the health-based comparison values. For category A2, the AGC is above the MDL therefore, the risk will be qualitatively discussed.

Category B represents the air toxics that were detected above the MDL 50% to less than 75% of the monitoring period. A daily average for those days when the air concentration was less than the MDL was estimated by using the measurement reported by the laboratory. Although there is less reliability in those measurements reported below the MDL, USEPA's Science Advisory Board (USEPA 2001) has stated that these values may be recognized as measurable results. There is less confidence in the annual average for the air toxics in this category because the use of values below the MDL introduces uncertainty in the estimates. A risk evaluation will be estimated, but the results should be interpreted with caution.

There is high confidence in the annual average concentration for those air toxics that were detected above the MDL with a frequency of 75% or greater. For this category, the values below the MDL as reported by the laboratory were used for less than 25% of the days. A risk evaluation will be conducted for all air toxics in this category, labeled as C.

A decision matrix, as shown in Figure 7.1, was developed to summarize the approach for evaluating the suitability of the data for health risk evaluations. Additional analyses presented in this section will be conducted on the air toxics in categories B and C.

Criteria Pollutants
Continuous monitoring was used for the criteria pollutants and MDL is not as much of an issue with these pollutants as compared to the air toxic pollutants. Additionally, the health-based standards used to compare ambient air concentrations for criteria pollutants are much higher than the MDLs. Therefore, the suitability of using the criteria pollutant data was evaluated based on data capture percentages. All four monitor locations report a high data capture (93% or greater) for the $PM_{2.5}$. Carbon monoxide (CO) and sulfur dioxide (SO_2) were monitored at only one site, the BTRS monitor. The data capture for CO was 98% and for SO_2 it was 97%. CO and SO_2 monitoring data will be compared to the appropriate NAAQS with high degree of confidence in this comparison. $PM_{2.5}$ data will be compared to nearby $PM_{2.5}$ monitoring sites.

7.1.2 Summary Statistics of the Measured Air Toxics and Criteria Pollutants

Air Toxics
Tables 7.2 (Category B) and 7.3 (Category C) provide the mean, median, 25th and 75th percentile concentrations and coefficient of variation for the Study area monitoring sites.

For Category B, six air toxics are reported at more than one site and most are very similar in concentration across the monitoring sites. Only one air toxic is reported across all sites

for Category B, 2-butanone, also known as methyl ethyl ketone. The GIBI site concentrations are higher for 1,3-butadiene and hexanal as compared to the concentrations at the other sites. The GIBI site reports the most number of air toxics, generally carbonyls, in this category.

All sites in Category C reported the following air toxics: acetaldehyde, acrolein, benzene, carbon disulfide, carbon tetrachloride, chloromethane, dichlorodifluoromethane, dichloromethane, formaldehyde, toluene, trichlorofluoromethane, and trichlorotrifluoroethane. The following air toxics were reported at both the GIBI and SPWT sites: m,p-xylene and o-xylene. Propionaldehyde was reported for only one site, SPWT. The following air toxics were reported for the GIBI and no other sites: benzaldehyde, ethylbenzene, and valeraldehyde.

For Category C, the variability is much greater for those air toxics (benzene, carbon disulfide, formaldehyde) with known point source releases in the area.

More comparisons will be presented in Subsection 7.4.

Criteria Pollutants
Summary information for the criteria pollutants will be presented in Subsection 7.4.7 and Appendix R.

7.1.3 Air Toxics Concentrations in Perspective

In this Subsection an attempt is made to provide a better perspective on the measured air toxics through a series of questions and answers.

How Does the Upwind (Background) Site Compare to the Perimeter Sites in the Study?
Two types of monitor locations – upwind and perimeter - were implemented for the Study. The upwind monitor (BISP) was sited to capture background measurements of air toxics upwind from the industrial sources in the Study area since the predominant wind direction is from the southwest. Three perimeter sites were sited in locations east and northeast of the Study area to provide air quality measurements downwind of the industrial sources. A comparison was made between the air toxic concentrations obtained at the BISP monitor and the perimeter sites. Fewer air toxics were detected at the BISP monitor. Of the 24 air toxics reported in categories B and C, only 16 were detected at the BISP monitor.

The variability in concentrations found in the industrial area was compared by ratio of the annual averages at each perimeter site to the background site. The ratios are shown in Figure 7.2 for each of the 16 air toxics detected at BISP. Ratios equivalent to one indicate similar concentrations for the perimeter monitors as compared to the background monitor. The ratios for benzene, formaldehyde, hexanal and toluene at the GIBI are much higher than the other perimeter sites, indicating a source influence for these air toxics on the GIBI monitor concentrations. All three ratios for chloromethane and

trichlorotrifluoroethane and two sites for dichloromethane are less than one, indicating a source influence for these air toxics on the BISP monitor concentrations.   The ratio for carbon disulfide at SPWT indicates a source influence on the monitor concentrations.

An Analysis of Variance (Tukey test on log transformed data) was conducted between BISP and the perimeter monitors' air toxics concentrations. Nine air toxics were found to be statistically different at the BISP monitor. Table 7.4 summarizes the results of this comparison. Three halogenated organic compounds (chloromethane, dichloromethane, and trichlorotrifluoroethane) were found to be statistically higher at the BISP monitor; indicating this monitor is affected by a source (or sources) for these air toxics. An evaluation of the wind direction and concentration for these three air toxics indicates a source (or sources) in the south, southwest direction (See Appendix M).

For six air toxics (acetaldehyde, acrolein, benzene, carbon disulfide, formaldehyde and toluene), the BISP monitor reports significantly lower air concentrations compared to the perimeter monitors. Four of these six air toxics also were found to significantly contribute to health risk concerns for the area as discussed in Subsection 7.2.2. For six air toxics (2-butanone, carbon tetrachloride, dichlorodifluoromethane, hexanal, proprionaldehyde, and trichlorotrifluoromethane) the monitor concentrations at BISP were not statistically different than the concentrations obtained at the perimeter sites.

What Are the Local Concentrations of Air Toxics?

The New York State ambient air toxics monitoring program was first established in 1985 with a focused network as part of the Staten Island/New Jersey Urban Air Toxics Assessment Project. The network expanded in 1990 to a statewide network. The goal of this monitoring network is to characterize air quality related to toxics in the State.

The results from the statewide monitoring network were compared to the Tonawanda results for the same time period as this Study. The statewide monitoring network consisted of 12 monitors, characterized as the following types: 7 urban, 2 industrial, 1 rural and 2 source sited. The rural monitor was removed for this comparison and will be discussed later in this Subsection. The results for categories B and C were combined. Only16 air toxics consistently (>50% above detection limit) report measurable air concentrations for both the statewide and Study monitors. The comparison of the annual average concentrations for the Tonawanda monitors with the results from the statewide network is shown in Figure 7.3 with concentrations displayed on the log-scale**.** Although this comparison with the state monitors includes some sites impacted by specific sources (e.g., near roadway, landfill, specific industry), this comparison was found to be meaningful when conducted across the full spectrum of different monitoring sites.

The annual average measured concentration at the GIBI site for two air toxics (benzene, formaldehyde) were much greater, as compared to the statewide network average during the same monitoring period. Additionally, the benzene average concentration was higher at the BTRS monitor as compared to the results from the statewide network. For all other pollutants, the Tonawanda results were similar to the average concentrations reported by the statewide network.

How Do Air Toxics Concentrations Compare with Typical National Levels?
Annual average concentrations from the U.S. air toxics network has been prepared by
Sonoma Technology and reported on USEPA's web site (USEPA 2009a). The year 2005
was selected for this comparison since it represented the most recent year with complete
reporting for many monitoring sites.

Monitors reporting greater than 50% detection were selected for the comparison[17]
(categories B and C). Only 12 air toxics consistently (>50% above detection limit) report
measurable air concentrations for both the U.S. and Study monitors. Figure 7.4 shows
the comparison of the Tonawanda (combining all monitor results) and U.S. annual
average concentrations displayed on a log-scale. An Analysis of Variance was conducted
and, for those comparisons statistically significant ($p < 0.05$), the Wilcoxon two-sided
test was performed. Benzene was the only air toxic, statistically significantly higher at
the Study monitors as compared to the U.S. monitors. The benzene annual average
concentration at the GIBI monitor was higher than the 95th percentile value for the U.S.
network and all other Study sites were greater than the median U.S. concentration.
Carbon tetrachloride was not statistically significantly higher, although the Study
concentrations appear to be higher than most of the U.S. monitor concentrations. For all
other air toxics, the Study results were within the 5th and 95th percentile range reported by
the U.S. network. For the following air toxics (acetaldehyde, acrolein, chloromethane,
dichloromethane, propionaldehyde) all Study site average concentrations were below the
U.S. median concentration.

This comparison provided useful information, although it is recognized that the U.S. data
are compiled across different sampling and analysis methods. Additionally, comparisons
have been made between different monitoring time periods and some monitors in the
U.S. network may have been sited to capture source emission releases. Finally, some of
the monitors in the U.S. network may be located near specific sources (e.g., near
roadway, landfill, or specific industry).

**How Do the Benzene Concentrations Compare with National Levels Near Benzene
Emitting Facilities?**
The monitoring data (year 2005) used in the previous section were used for this
comparison. National Emissions Inventory (NEI) data for large stationary sources for the
year 2005 were obtained from USEPA Technology Transfer Network[18]. This inventory
is compiled by USEPA every three years and provides information on chemical releases
from outdoor stationary and mobile sources. All facilities reporting benzene emissions in
the U.S. were selected and the individual emission units were combined to provide a total
benzene annual emission release for the facility. In the Study area, the facility reporting
the largest release of benzene was the Tonawanda Coke Corporation. The reported

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[17] Selected 50% to be consistent with the reporting of Category B (U.S. 2005 network, 2449 monitors
report greater than 50% detection (47% of all sites reporting)) and Category C (U.S. 2005 network, 2910
monitors report greater than 75% detection (56% of all sites reporting)).
[18] Data available online at: http://www.epa.gov/ttn/chief/net/2005inventory.html#inventorydata [accessed
8/17/09]

releases from this facility were above the 95th distribution among all facilities releasing benzene in the 2005 NEI. Therefore, to create an equivalent comparison between the Study results and the air monitoring concentrations from the U.S. network, only facilities reporting annual releases greater than the 95th percentile were selected. Monitors reporting benzene concentrations above the MDL greater than 50% of the time and within 1.0 mile of these facilities were selected. The benzene concentrations for the U.S. monitors are summarized in Figure 7.5 and the annual averages from the four Study site monitors have been included for comparison.

Benzene concentrations monitored at the GIBI monitor were higher than the highest monitored concentration near a source with facility releases greater than the 95th percentile. The highest monitor concentration based on the selection criteria listed previously is 8.2 μg/m^3. This monitor (located in River Rouge, Michigan) is approximately 0.2 miles from EES Coke Battery LLC, a facility which reported total benzene releases in 2005 of 15.7 tons per year (TPY). In comparison, the Tonawanda Coke Corporation reported 4.5 TPY benzene emissions in 2005 and the GIBI monitor is 0.5 miles. More recently, the facility reported benzene emissions of 4.9 TPY in 2007 and 5.2 TPY in 2008.

An important limitation of this evaluation is that there is no knowledge of whether the monitors in the U.S. network are sited downwind of the nearby facilities. The influence of wind direction on monitor concentration is demonstrated in Figure 7.5 by comparison of the GIBI and SPWT monitor concentrations. Both the GIBI and SPWT monitors are within 1.0 mile of the Tonawanda Coke. The SWPT monitor is not in the predominant downwind direction from the facility and the resulting annual average concentration at this monitor is fairly low (below the 25th percentile concentration across US monitors located near sources). Whereas the annual average concentration at GIBI monitor, which is downwind from Tonawanda Coke, is higher than the maximum concentration among all the monitors selected.

This evaluation also excludes monitors located near a large congregation of small release sources, which could result in high benzene monitor concentrations. Additionally, this approach assumes the benzene monitor concentrations are primarily from local point sources. Benzene emissions from mobile and area sources also contribute to monitored concentration.

What Are Rural Concentrations of Air Toxics?
The average concentration for the rural monitor at Whiteface Mountain (Essex County) for the same time period as the Study was compared with the Study results. NYSDEC has been operating an ambient air monitor at Whiteface since 1989. The monitor is located in an undeveloped area in the Adirondack Park and is sited at an elevation of 2050 ft. As shown in Figure 7.6, the concentration of the air toxics generally associated with mobile source releases (such as benzene and toluene) are an order of magnitude higher in the Study area as compared to Whiteface. An Analysis of Variance (Tukey test on log transformed data) was conducted and the mean concentrations of following air toxics were statistically significantly higher in the Study area as compared to Whiteface

Mountain; acetaldehyde, benzene, carbon tetrachloride, dichloromethane, formaldehyde, toluene, and trichlorotrifluoroethane.

How Do Ambient Concentrations Compare with National-Scale Air Toxics Assessment Results?[19]

The National-Scale Air Toxics Assessment (NATA) is USEPA's ongoing comprehensive evaluation of air toxics in the U.S. (USEPA 2009b). USEPA conducts NATA to provide a screening tool to identify and prioritize air toxics, emissions source types, and locations that are of greatest potential concern in terms of contributing to population risk. The NATA models emission information from the NEI, an emission inventory of outdoor stationary and mobile sources which is compiled every three years, to derive annual average ambient concentrations. Estimated population exposures are then modeled from the concentration information. Finally, the potential cancer and noncancer public health risks due to inhalation of air toxics are characterized.

The most recent assessment available, which modeled the 2002 emission inventory, was used. The NATA annual average air concentration estimates are modeled to a population-weighted census-tract point (centroid). Therefore, the centroid closest to the Study monitor was selected for comparison for all sites except BISP. The closest census-tract centroid to the BISP monitor is located east in the industrial census tract (029008400) along Kenmore Avenue. The BISP monitor is surrounded by residential development and the modeled concentrations in the tract containing this monitor is a better representation. Only the air toxics that met the suitability criteria (categories B and C) were used in this evaluation. NATA models all xylenes as mixed isomers therefore, all isomers were combined for this comparison.

The Figure 7.7 displays, on a log-scale, the annual average concentrations for the four NATA result census tracts and the Study area monitor concentrations. For acrolein, the monitoring results were consistently higher than the modeled results. The GIBI monitor results were higher, in some cases by an order of magnitude, as compared to the NATA results for the following air toxics: 1,3-butadiene, acrolein, benzene, ethylbenzene, formaldehyde, and total mixed xylenes.

Table 7.5 shows the predicted-to-observed ratios for the NATA modeled concentrations versus the Study area monitored concentrations. For the following air toxics, the NATA modeled results were within a factor of two of the monitoring results for all sites: acetaldehyde, carbon tetrachloride, chloromethane, ethylbenzene, propionaldehyde, and total mixed xylenes. In general, it can be concluded that the 2002 NEI used in the NATA model was fairly accurate in the reporting of emissions for a number of air toxics. The inventory clearly has under reported acrolein emissions for the entire Tonawanda area

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[19] The summary statistics and graphical comparisons as listed in the QAPP were not conducted since all predicted-to-observed ratios could be presented in one table. Additionally, it was determined that no further knowledge would be gained by doing similar comparisons for the 1996 NATA and 1999 NATA because of the age of the emission inventories and the NATA modeling procedures and tools have become more refined leading to a better estimation of ambient concentrations in the 2002 NATA version.

and under reported 1,3-butadiene, benzene, ethylbenzene, formaldehyde, and propionaldehyde emissions for sources near the GIBI monitor.

As a risk assessment screening tool, it is preferable that NATA modeled concentrations are similar to measured ambient concentrations for those air toxics where the ambient measured concentrations are higher than the AGC. For acrolein, the NATA modeled concentration estimates are approximately an order of magnitude lower than the ambient monitor concentrations in this Study. Therefore, the risks predicted by NATA would be an order of magnitude lower than the actual risk. At the GIBI monitor, the NATA model concentration estimates for benzene are nearly an order of magnitude lower than the ambient monitor concentrations. The risk predicted by NATA at this location also would be almost an order of magnitude lower than the actual risk. In general, NATA emission inventory, and therefore model results, appear to be under predicting concentrations and risks for those air toxics dominated by point source contributions (such as benzene, formaldehyde) in the Study area.

How Do the Pollutants Compare with Each Other?
Comparisons between pollutants at the different monitoring sites were conducted graphically and statistically. Box plots for each of the air toxics in categories B and C were produced and are shown in Appendix G. The data were found to be log-normally distributed, and therefore, a Tukey test for multiple comparisons was performed on log-transformed data and the means (geometric means) were compared. Table 7.6 summarizes the statistical comparison across all sites.

Box plots for the following air toxics show little variability across the sites and this is confirmed statistically: 2-butanone, carbon tetrachloride, dichlorodifluoromethane, propionaldehyde and trichlorofluoromethane.

Greater variability is seen in the following air toxics and many of the mean comparisons were statistically different: acrolein, benzene, dichloromethane, formaldehyde, toluene, and trichlorotrifluoroethane.

The GIBI site reports much greater variability (shown graphically in Appendix G) and the greatest difference in mean concentration compared to the other sites was found for the following air toxics: 1,3-butadiene, acetaldehyde, acrolein, benzene, formaldehyde, m,p-xylene, o-xylene, and toluene. The following air toxics met the suitability criteria (Categories B and C) for only the GIBI monitor; benzaldehyde, ethylbenzene, and valeraldehyde.

The box plot and statistical comparison indicates there is a source for trichlorotrifluoroethane near the BISP monitor, which has little impact on the other three monitoring locations.

Does Tonawanda have a Unique Set of Compounds?
In the Study area, the concentrations of benzene and formaldehyde were much higher, as compared to, other industrial and urban monitors in the State.

7.2 Public health interpretation of measured air concentrations

7.1.1 Approach for Evaluating Risk

Air Toxics
To evaluate potential non-cancer health risks, the monitored concentrations in the Study were compared with NYSDEC's AGC. Interim AGCs were derived for three aldehydes; benzaldehyde, butyraldehyde and hexaldehyde and details of the approach used to develop the interim AGCs can be found in Appendix H. To evaluate potential excess inhalation cancer risks, the monitored concentrations in the Study were compared to the AGCs derived from inhalation unit risk (IUR[20]) values. For those air toxics that were not or could not be monitored, an air dispersion modeling analysis was conducted and the predicted concentrations were compared to AGCs as presented in Subsection 7.3.

Many organizations and agencies derive annual exposure limits to protect workers or the general public from adverse exposures to toxic air contaminants. Each one of these exposure limits requires extensive research and development time. As such, NYSDEC often uses the health-based guidance concentrations published by other agencies or organizations to derive health-based guideline concentrations.

AGCs are ambient annual based guideline concentrations that were developed to protect the public's health from effects which may be associated with long-term (e.g., lifetime) exposure to an air pollutant. AGCs are based on the most conservative cancer or non-cancer annual exposure limits. For the evaluation of risk in this Study, only inhalation exposure to HAPs was investigated.

AGCs based on reference concentrations assess the risk for non-cancer effects. USEPA has defined a reference concentration as an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups such as children) that is likely to be without an appreciable risk of deleterious effects during a lifetime of exposure (USEPA, 2002a). AGCs derived from cancer studies are defined as a chemical concentration in air that is associated with an estimated excess lifetime human cancer risk of one per one-million people (1×10^{-6}).

An evaluation of potential health risks for the non-cancer compounds was conducted by comparing the 12-month average concentration (considered an annual concentration) obtained in the Study to the AGC for each chemical. To evaluate potential non-cancer effects, a "hazard quotient" was calculated by dividing the annual measured concentration by the reference concentration. A hazard quotient that is equal to or less than one is generally not considered to be a significant public health concern. If the

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[20] The IUR is an upper-bound estimate of the excess cancer risk resulting from a lifetime (assumed 70 years) of continuous exposure to the air pollutant at a concentration of $1\mu g/m^3$ in air.

annual concentration of an air toxic exceeds the reference concentration, there may be concern for potential non-cancer health effects. However, for most chemicals, the reference concentration (defined above) is set at an exposure level that is lower (often by as much as 100- or 1000-times) than exposure levels that cause health effects. Exceedance of a reference concentration usually triggers a case-by-case evaluation of whether actions to reduce exposures should be taken. Generally, the greater the hazard quotient, the greater the level of concern.

To calculate the excess lifetime inhalation cancer risk, the annual measured concentration was multiplied by the chemical specific inhalation unit risk (IUR) estimate as shown in the following equation:

Cancer risk = annual measured air concentration ($\mu g/m^3$) x IUR ($\mu g/m^3$) $^{-1}$

($\mu g/m^3$ = micrograms of air toxic per cubic meter of air)

The AGCs are based on a one-in-one-million excess cancer risk. This annual concentration is derived by using the following formula:

$$\frac{\text{One-in-one-million risk } (1 \times 10^{-6})}{\text{IUR}} = \text{AGC}$$

There is general consensus in the scientific and regulatory communities that an increased lifetime cancer risk of one per one-million (10^{-6}) or less is not a significant public health concern and that an increased cancer risk level of greater than 100 per one-million (10^{-4}) may warrant measures to reduce the risk (e.g., exposure reduction measures). Risk levels that fall between 10^{-4} and 10^{-6} usually warrant further evaluation (e.g., the actual vs. potential exposure, "background" exposure, and the strength of the toxicological data), with the need for risk reduction measures depending on where in that range the risk estimate falls[21].

The risk estimates presented in this Study assume that the exposure to the air pollutant is at the level of the mean concentration measured or predicted at the specific monitoring location for 24 hours per day and 7 days per week, over 70 years. No adjustments are made to account for an individual's time and activity patterns (e.g. time spent at work or school). Risks for cancer are generally expressed as individual risk (i.e. the risk borne by

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[21] In 1980, the Supreme Court struck down the Occupational Safety and Health Administration (OSHA) policy of reducing benzene concentrations to the lowest technologically feasible level. The Judges concluded that OSHA could regulate benzene emissions only if it found that benzene posed a significant risk of harm. This ruling is known as the "Benzene decision". As part of the policy decision making process for section 112 of the Clean Air Act, the Benzene decision and subsequently future District of Columbia Circuit Court rulings required USEPA to make a determination of "safe" exposure level (i.e., representing an acceptable degree of risk and to establish an "acceptable cancer risk range"). USEPA adopted a policy that a lifetime excess cancer risk of approximately 100 in-one- million for the most exposed person would constitute acceptable risk and that the margin of safety should reduce the risk for the greatest possible number of persons to an individual lifetime cancer risk no higher than one in one million (Benzene Decision, 1980).

an individual in a larger population). As presented above, the estimates of cancer risk are usually expressed as statistical probabilities (e.g. the additional risk of developing cancer is one-in-one-million).

There is inherent uncertainty in the use of health-based comparison values (NYSDEC's AGCs) which are generally derived from animal or human data on a chemical. Scientists account for this uncertainty when extrapolating data from animal or human studies to non-cancer or cancer endpoints. For non-cancer endpoints, scientists use uncertainty factors to develop a reference concentration. The reference concentration represents an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups such as children) that is likely to be without an appreciable risk of deleterious effects during a lifetime of exposure. Animal or human studies with cancer endpoints lead to the development of an inhalation unit risk estimate which represents an upper-bound estimate of the excess cancer risk resulting from a lifetime (assumed 70 years) of continuous exposure to the air pollutant at a concentration of $1\mu g/m^3$ in air.

Criteria Pollutants
The results of the monitoring for CO, and SO_2 were compared to the current NAAQS. $PM_{2.5}$ monitoring results were compared to nearby monitors.

7.2.2 Results from Risk Evaluation

Air Toxics
Category A1
The air toxics in this category were detected less than the MDL concentration 50% of the time and the AGCs are below the MDL. A risk evaluation was not conducted because it could not be determined whether the annual average was above or below the AGC.

Category A2
The air toxics in this category were detected less than the MDL concentration 50% of the time. The risk estimate for these air toxics are qualitatively discussed because the AGC is above the MDL, even though there is low confidence deriving an annual average concentration for this category.

A check on the potential annual average concentration was conducted to verify the risk statements. The MDL concentration was conservatively assumed for all those compounds detected below the MDL and the sample concentrations that were detected were retained. An estimated annual average concentration was calculated which is considered to be conservative (an overestimate) because for those samples not detected, the actual concentration would be below the MDL.

For each air toxic, the estimated annual average concentrations were compared to the AGC and it was found that, for all air toxics in this category, the estimated annual average was lower than the AGC value. Therefore, the air toxics in this category are not expected to be a public health concern.

Category B
Table 7.7 shows the results for the risk evaluation for the air toxics in Category B. The
air toxics in this category were detected in at least 50% to less than 75% of the monitored
air samples and therefore there is less confidence with this data when making definitive
risk statements.

For the non-cancer evaluation, all hazard quotients were well below a value of one and
range from 7.4×10^{-5} to 8.7×10^{-3}. These results indicate that individual air toxics in this
category are not expected to be a public health concern for non-cancer effects.

As shown in Table 7.7, 1,3-butadiene was the only air toxic in this category with an AGC
based on a cancer endpoint. The cancer risk estimates are 2.7 and 7.3 in-one-million (2.7
$\times 10^{-6}$ and 7.3×10^{-6}) for the BTRS and GIBI sites, respectively. State-wide data (for the
same time period as this Study) for 1,3-butadiene show an average cancer risk estimate of
3.6 in-one-million (range 1.8×10^{-6} to 5.3×10^{-6}) for urban and industrial locations. The
cancer risk estimate at the BTRS monitor is therefore lower than the average State-wide
risk for this air toxic. The cancer risk at the GIBI monitor is approximately 36% higher
than the highest 1,3-butadiene concentration found at a monitor in New York City.
Compared to data across the country (year 2005), the cancer risk attributable to 1,3-
butadiene at the BTRS and GIBI monitors is below the U.S. monitoring average value of
12 in-one-million (12×10^{-6}).

Category C
Table 7.8 shows the results for the risk evaluation for the air toxics in Category C. The
air toxics in this category were detected in greater than 75% of the air samples and
therefore there is high confidence with this data when making definitive risk statements.

For the non-cancer evaluation, the hazard quotients range from 3.5×10^{-6} to 22. Acrolein
is the only air toxic with a hazard quotient above one. Acrolein is a difficult air toxic to
monitor accurately[22] and is currently only monitored at two sites in the State in addition
to the Study sites. The acrolein results have been reported, although some laboratory
quality assurance thresholds[23] were exceeded. The hazard quotient for acrolein at the two
monitoring locations in the State network was 18 and 23. The hazard quotient for
acrolein at the Study site monitors was similar to the values reported by the other two
monitors in the State. Acrolein also is monitored to a limited degree by other states. The
acrolein hazard quotients at the monitors in the Study are below the U.S. monitoring
(year 2005) average hazard quotient of 39 (range 2.2 to 120)[24] .

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[22] Acrolein is a difficult air toxic to monitor accurately because the concentrations are affected by humidity
and the chemical reacts with the liner of the sampling device (a summa canister). See Section 5 for
additional information.
[23] See Appendix E Quality Assurance for VOCs and Carbonyls
[24] The hazard quotient evaluation for acrolein is based on a limited number of monitors in the U.S. network
which report greater than 50% detects (43 monitors) for the 2005 results.

At all four Study monitoring sites, four air toxics (acetaldehyde, benzene, carbon tetrachloride and formaldehyde) were above a one per one-million cancer risk estimate. A risk comparison from State-wide urban and industrial monitors and for all monitors in the U.S. is shown in Figure 7.8.

For acetaldehyde, the cancer risk estimate at BISP and SPWT was below the state average, whereas the other sites were above the State average. In comparison, these four sites are below the U.S. average for acetaldehyde.

The benzene cancer risk estimate at all Study sites was close to or above a 10 in-one-million cancer risk with an estimated risk at the GIBI monitor of 75 in-one-million. The benzene cancer risk estimate at all four sites was above the State average and above the U.S. average at the BTRS and GIBI monitors. Figure 7.9 shows a comparison of the benzene risk estimate for the Study monitors and all the other State monitors. To minimize the scale, the benzene risk estimate at the GIBI monitor (75 in-one-million) was not included. The estimated benzene risk at the BISP and SPWT monitors is similar to the risk estimates found at the NYC monitors. The estimated benzene risk at the BTRS and the GIBI was much higher, indicating that these monitors were potentially affected by a benzene source in addition to the mobile source contributions commonly found at other urban areas and NYC. Additional analyses are presented in Subsection 7.4 which includes an evaluation of potential benzene point sources.

The cancer risk estimate at all the Study sites for carbon tetrachloride, a ubiquitous air toxic with a long half-life, was similar to the annual average concentrations found at other monitor locations in the State and U.S.

The formaldehyde cancer risk estimate for the Study sites was slightly higher than the State average at the BISP, BTRS and SPWT monitors, whereas the cancer risk estimate found at the GIBI monitor was higher than the maximum value found in the State network. In comparison, the cancer risk estimate for formaldehyde at the BISP, BTRS, and SPWT monitors was below the U.S. average and the cancer risk estimate at the GIBI monitor was above the U.S. average.

Criteria Pollutants

Carbon monoxide has an hourly standard of 35 ppm and an 8-hour standard of 9 ppm. There were no exceedances of these standards at the only monitor where it was measured (BTRS) during the Study period. The CO maximum hourly concentration and average annual concentration (of all the hourly concentrations in the Study period) were 1.4 ppm and 0.29 ppm, respectively.

Sulfur dioxide has three Federal standards: a 3-hour secondary standard[25] of 0.5 ppm, a 24-hour standard of 0.14 ppm, and an annual standard of 0.03 ppm. There were no

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[25] The secondary standards set limits to protect public welfare, including protection against decreased visibility, and damage to animals, crops, vegetation, and buildings. All other NAAQS values displayed in this report are primary standards which are limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly.

exceedances of these standards at the only monitor where it was measured (BTRS) during the Study period. The SO_2 maximum hourly concentration and average annual concentration (of all the hourly concentrations in the Study period) were 0.058 ppm and 0.0029 ppm, respectively.

$PM_{2.5}$ has a 24-hour NAAQS of 35 $\mu g/m^3$ and an annual NAAQS of 15 $\mu g/m^3$. A comparison with the NAAQS for PM2.5 was not conducted with the Study results because the monitoring method is not considered a federally approved method. A comparison with the monitoring results obtained at the Buffalo and Niagara Falls monitors was conducted since those monitors both use a federally approved method. This comparison is further supported by the fact that $PM_{2.5}$ monitoring concentrations are generally the result of regional transport from sources outside the monitoring area. Therefore, it can be expected that exceedances of the NAAQS at the Buffalo and Niagara Falls monitors also would likely occur at the Study site monitors if the primary influence in monitor concentrations was regional in nature. On five dates (8/3/07, 8/29/07 9/6/07, 4/18/08 and 4/19/08) during the Study period, the $PM_{2.5}$ monitoring results exceeded the NAAQS at either the Buffalo or Niagara monitors. On all five dates, the Study $PM_{2.5}$ concentrations were also above 35 $\mu g/m^3$ for at least one monitor in the Study area. Only one date (9/7/07) during the Study was the $PM_{2.5}$ above 35 $\mu g/m^3$ at one Study monitor, but not above this value for Buffalo or Niagara Falls monitors. The remaining Study site monitors on this date were within 15% to 27% of the Study monitor value. Additionally, a graph of the $PM_{2.5}$ daily concentrations was produced (not shown) across the Study period to provide a day-by-day comparison between the Buffalo and Niagara Falls monitors with the Study monitors. In general, it can be concluded that the Study site monitoring $PM_{2.5}$ concentrations were influenced by regional transport since the concentrations were very similar to the comparison monitoring concentrations at Buffalo and Niagara Falls.

The averages for the Study period at the Buffalo and Niagara Fall monitors were 12 $\mu g/m^3$ and 11 $\mu g/m^3$, respectively. These 12-month averages, although not calculated across a calendar year, do not exceed the NAAQS annual average. In comparison, the Study monitoring 12-month averages were very similar with values of 11, 13, 13 and 11 $\mu g/m^3$ for the BISP, BTRS, GIBI and SPWT monitors, respectively.

7.2.3 Limitations of the Risk Evaluation

The risk estimates do not account for other sources of exposure such as indoor or occupational. Additionally, the risk estimates assume that people reside at the monitor location and that these values are not attenuated by time spent at other locations (such as work, school, etc.). This study is not able to determine an individual's overall exposure. Other factors (such as smoking, hobbies and occupations using solvents) can lead to increases exposure to HAPs and contributes to the overall uncertainty in the estimates provided in this report.

Conservative cancer risk estimates have been provided in this Study for the air toxics, which assumes continuous exposure for 70 years (365 days per year, 24 hours per day) at

the monitor locations and that the monitor concentrations remain constant for 70 years. In addition, all air toxics with a cancer risk associated with them are based upon the upper-bound excess lifetime cancer risk resulting from continuous exposure to an air contaminant. The USEPA defines the upper bound as "a plausible upper limit to the true value of a quantity. This is usually not a true statistical confidence limit." The use of an "upper limit" means that the true risk of developing cancer from exposure is not likely to be higher and may be lower than the estimates provided in this Study.

7.3 Public Health Interpretation of Modeled Air Concentrations

Part of the Study grant was to utilize and comment on the USEPA's air dispersion modeling software called the Regional Air Impact Modeling Initiative (RAIMI). In addition to air dispersion modeling capabilities, RAIMI is a software program designed to review and modify data output. The RAIMI program allows the user to input multiple sources and emission scenarios in order to predict ambient air concentrations at various locations in the representative study area. The emission inventory complied in Appendix F provided invaluable data for running the RAIMI model. For a more detailed description of the RAIMI model, see Appendix I and for the evaluation of the RAIMI modeling tool, see Appendix J. To establish a degree of confidence with the modeled predictions, a model-to-monitor ratio comparison is conducted with those pollutants capable of being monitored. The model-to-monitor comparison can be found in Appendix L.

This Subsection will address the cancer risk drivers that were not capable of being monitored with methods applied during the Study period.   With the exception of Benzene Soluble Organics (BSO) and naphthalene, all of the identified carcinogenic compounds were monitored and classified as either Category B or C compounds during the one year study period. It was necessary to model the BSO and naphthalene emissions to obtain a complete picture of the potential carcinogenic risk in the Study area. Naphthalene was not included as BSO because BSO compounds have greater than 16 carbons and naphthalene only has 10 carbons in its molecular structure. BSO and its constituents will be defined and discussed in later Subsections.

When conducting community studies, the use of air dispersion models to predict ambient concentrations of HAPs, in addition to, the actual monitoring of HAPs is essential and is recommended by the USEPA's, a Tier 2 analysis (USEPA, 2004b). Modeling offers the ability to estimate trace quantities and mixtures of HAP concentrations that cannot accurately be measured. Also, the modeling results can be substituted for a costly monitoring network in order to make regulatory decisions for specific sources of HAPs.

Subsections 7.3.1 and 7.3.2 present the potential health risks associated with simultaneous exposures to multiple HAPs. Section 7.3.1.1 discusses the characterization and evaluation of Coke Oven Emissions. The predicted ambient air concentration of Coke Oven Emissions will be referred to as benzene soluble organics (BSO) throughout this report. In section 7.3.1.2 the risks attributable to BSO, naphthalene and PAH will be evaluated to provide a total cancer risk for the Study area. Subsection 7.3.2 presents the Hazard Index for the monitored and/or modeled non-cancer compounds in four Study area neighborhoods chosen based upon locations where either citizen complaints have been documented, schools are located, and/or have been designated environmental justice areas.

7.3.1 Evaluation of Inhalation Cancer Risk

7.3.1.1 Benzene Soluble Organics (BSO), a Surrogate for Coke Oven Emissions

Many sources in the Study area, both stationary and mobile, emit polycyclic organic matter (POM). POM is identified in the Clean Air Act Amendments of 1990 as a HAP. POM is a broad class of compounds, which includes all organic compounds with more than one benzene ring and a boiling point greater than or equal to 212 ºF. The principal formation mechanism for POM occurs during the fuel combustion process for many source categories. Polycyclic aromatic hydrocarbons (PAHs) are a subset of POM and seven specific PAHs have been identified as probable human carcinogens. They are referred to as the 7-PAH group. The emissions of POM are a by-product from all combustion sources. The largest combustion source in the Study area is NRG's Huntley coal-fired power plant. NRG recently authorized the installation of a fabric filter to replace the older electrostatic precipitators in order to reduce emissions of particulate in general. This, in turn will also reduce emissions of POM. Another large source of POM and ultimately Benzene Soluble Organics (BSO) is the Tonawanda Coke Corporation.

Coke Oven Emissions are identified in the 1990 Clean Air Act Amendments as a HAP. Coke Oven emissions have also been classified by the USEPA as a known human carcinogen. The Tonawanda Coke Corporation is the sole source of Coke Oven Emissions in the Study area. Coke Oven Emissions are characterized as consisting of a mixture of organic chemicals, metals, and POM. The semi-volatile organic constituents of Coke Oven Emissions are termed BSO, which is considered an appropriate surrogate for quantifying the cancer risk associated with Coke Oven Emissions.

The term BSO is based on a test method used to quantify coke oven emissions directly from the coking operations. The POM is collected on a sampling filter that is dissolved in benzene, then the benzene is evaporated off and the organic matter that is left behind is classified as BSO (USEPA, 1998). The probable human carcinogenic compounds within BSO include the carcinogenic 7-PAH group, which can account for 3 to 10 percent of the BSO (USEPA, 1998). The BSO risk level incorporates the Inhalation Unit Risk Estimate (IUR) for Coke Oven Emissions to calculate the potential inhalation excess cancer risk associated with these emissions.

7.3.1.2 Inhalation Cancer Risk Analysis

The modeled and measured concentrations for the various carcinogenic contaminants will be added together for each monitoring location. The carcinogenic HAPs emitted from sources in the Study area are: acetaldehyde, benzene, BSO, 1, 3- butadiene, carbon tetrachloride, dichloromethane, formaldehyde, and naphthalene. Naphthalene has been identified as a carcinogen by California EPA (CALEPA, 2009)[26]. The USEPA's Center of Environmental Assessment investigated the potential carcinogenic potency of naphthalene and posted the following statement on the Integrated Risk Information System (IRIS): "An inhalation unit risk estimate for naphthalene was not derived because

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[26] NYSDEC has not identified naphthalene as a carcinogen.

of the weakness of the evidence (observations of predominant benign respiratory tumors in mice at high dose only) that naphthalene may be carcinogenic in humans." Naphthalene is not included as BSO because BSO compounds have greater than 16 carbons and naphthalene only has 10 carbons in its molecular structure.

The emissions of BSO and naphthalene were modeled with AerMod (USEPA, 2007b) and RAIMI to determine the potential concentrations occurring outside of the Tonawanda Coke facility property boundary. Tonawanda Coke Corporation has the largest reported amount of BSO and naphthalene emissions in the Study area (USEPA, 2002b). To assess the total individual inhalation cancer risk associated with exposure to multiple HAPs, the modeled and measured cancer risk estimates for the various HAPs will be added. Combining the inhalation cancer risk for each HAP is a conservative public health approach providing a total estimated individual inhalation cancer risk for the Study area.

Within the March 2005 Risk Assessment Document for the Coke Oven MACT Residual Risk, the USEPA presented the maximum individual risk and the population risk for carcinogens and non-carcinogens. This is discussed further in Appendix K.

In the public meetings held by NYSDEC, individual cancer risk was presented as a statistical probability (expressed as the number of individuals at risk per million people). These risks were derived at the particular monitor locations for each HAP; for example, the individual cancer risk for exposure to benzene was determined to be 15.4 in-a-million at the BTRS monitor. The modeling results of BSO and naphthalene also will be expressed as the number of excess estimated cancer cases per million individuals. Finally, the individual inhalation cancer risk will be presented based upon the monitored and predicted concentration at the four monitoring sites.

Benzene Soluble Organics
For the GIBI site, the modeled ambient air concentration of BSO emissions from Tonawanda Coke Corporation was predicted to be 0.875 µg/m^3. The concentration modeled at the GIBI site is based upon the Maximum Achievable Control Technology (MACT) emission limit for BSO from coke batteries. The cancer risk is calculated using the IUR for Coke Oven Emissions from the USEPA Integrated Risk Information System (IRIS). The ambient air concentration of coke oven emissions that corresponds to a one-in-a-million cancer risk is 0.0016 µg/m^3 (USEPA, 2009d).

Table 7.10 presents the HAP specific and total inhalation cancer risk for the measured and modeled HAPs. The inhalation cancer risk based upon modeled BSO emissions ranges from 26 in-one-million at the upwind BISP monitor to 547 in-one-million at the GIBI monitor.

PAH Monitored Data
After the implementation of the MACT requirements for coke oven batteries, the calculated cancer risk from BSO was found to be very high. BSO is used as a surrogate for coke oven emissions. In the final USEPA residual risk assessment for coke oven emissions, two HAPs (BSO and benzene) were responsible for the elevated cancer risk

estimate for the Tonawanda Coke Corporation. However, even though there was a high estimated maximum individual cancer risk (100 per million) for HAP emissions from the Tonawanda Coke Corporation, the decision was made by the USEPA that the risk was acceptable due to concerns that adjustments for uncertainties had led to an overestimation of risk in the surrounding community (USEPA, 2004c).

To gain a greater understanding of the predicted BSO concentration, the NYSDEC installed a PAH monitor at the GIBI site after the one year monitoring study was completed in an effort to verify the modeling results for BSO and naphthalene. The annual concentration (11 months) for the total PAHs monitored was 0.122 $\mu g/m^3$, as compared to the predicted concentration for BSO of 0.875 $\mu g/m^3$. The PAH analysis method reports the results for 21 PAH compounds, plus naphthalene.

According to the USEPA Locating and Estimating Air Emissions from Sources of POM (USEPA, 1998), the PAH compounds monitored at the GIBI site accounted for approximately one-half of the total BSO emissions. The PAH annual averaged concentration measured for the 21 compounds was 0.122 $\mu g/m^3$. Using the one-half approximation, the total BSO could more or less be doubled and estimated to be 0.244 $\mu g/m^3$. This is a conservative assumption since there are other sources of PAHs in the Study area. Using these assumptions, the BSO cancer risk calculated from the monitored data was found to be substantially below the predicted 547 in-one-million cancer rate and closer to 150 in-one-million. The unadjusted modeled risks for the BTRS and SPWT monitoring sites were 98 and 65 in-one-million, respectively.

The cancer risk associated with the measured PAH concentrations at the GIBI site was only 1.9 in-one-million. This large range of cancer risk estimates between the modeled BSO and measured PAHs concentrations results in considerable uncertainty associated with the cancer risk estimates associated with the BSO model predictions.

Naphthalene
The predicted GIBI concentration for naphthalene based upon the modeling of actual emissions reported by Tonawanda Coke was 0.128 $\mu g/m^3$, while the PAH monitor captured higher than expected concentrations. The annual measured concentration (11 months) for naphthalene at the GIBI monitor was 0.679 $\mu g/m^3$. This value is five times greater than the modeled estimate and would indicate that either another large source of naphthalene was in the area or the reported emissions were underestimated.

7.3.1.3 Air Toxic Cancer Risks in Perspective

Table 7.9 provides the ambient air concentration results of the four monitoring sites and the projected inhalation cancer risk. The risks identified above are overly conservative because they add the inhalation cancer risk for all identified carcinogens even though these different contaminants may not have additive effects. This approach is used as a starting point to identify which air toxics need to be evaluated for further reductions. This approach assumes that an individual lives at the monitor location 24-hours per day, 7 days per week, for 70 years and does not alter their activities.   It is very possible that

someone would live in a particular location for their lifetime, but not likely that they would remain at that location 24-hours per day, 7 days per week. In the USEPA's NATA study, the USEPA applies another step or tier, called an exposure assessment, with the modeled concentrations. As stated on the NATA webpage:

> Estimating exposure is a key step in determining potential health risk. People move around from one location to another, e.g., outside to inside, commute to work, etc. Exposure isn't the same as concentration at a static site. People also breathe at different rates depending on their activity levels. For these reasons, the average concentration of a pollutant that people breathe, i.e., exposure concentration, may be significantly higher or lower than the concentration at a fixed location (USEPA, 2002c).

The USEPA uses census data, human activity pattern data, and indoor/outdoor concentration relationships to estimate a range of more realistic inhalation exposure concentrations for a particular location. These human activity patterns try to account for the many different activities a person undergoes within the day. Exposures can be altered for individuals exercising or engaged in heavy physical labor due to increased breathing rates. Spending a portion of the day in an office environment is different than time commuting or time spent indoor at home. All of these activities need to be considered in order to estimate an individual's overall exposure. This report did not evaluate these adjusted inhalation exposures because the purpose of the Study was to determine if further regulatory actions are needed to reduce the burden of ambient air pollution in the Tonawanda community. Table 7.9 shows the total inhalation cancer risk for each site. The monitored air toxics results reflect the actual emissions from sources in the Study area, while those predicted from modeling represent the allowable emission limits. The PAH monitoring results at the GIBI site provides a perspective between the measured concentrations from the actual emissions of BSO and the predicted concentrations from the allowable emission limits of BSO. Overall, the calculated difference between actual and modeled PAHs is approximately 25 percent. This ratio between the modeled and monitored results for BSO at the GIBI site could be applied to the other sites to determine an overall actual monitored inhalation cancer risk.

Table 7.9 shows that the total monitored inhalation cancer risk at the background site BISP was 90 in-one-million. This calculated risk is driven by the monitored concentration for formaldehyde of 42 in-one-million is consistent with the two residential sites.   The downwind residential monitoring site, BTRS, has a total monitored inhalation cancer risk of 170 in-one-million. When using an adjusted modeled BSO concentration to account for actual emissions, the cancer risks are greater than 150 in-one-million for the BTRS. The difference between these upwind and downwind inhalation cancer risk values provide a strong basis for further compliance monitoring and regulatory actions to reduce the inhalation cancer risk in the Tonawanda community.

7.3.2 Hazard Index Analysis of Four Selected Neighborhoods in the Tonawanda/Kenmore Area

7.3.2.1 Chronic Non-Cancer Health Effects

Using the modeling results from the RAIMI software program, the hazard index was calculated for the non-cancer compounds known to be emitted from facilities in the Study area. For this analysis, four specific geographical areas were chosen based upon locations where either citizen complaints have been documented, schools are located, or which have been designated environmental justice areas. The four locations are:
        1.) Kaufman Ave.
        2.) Ken-Ton Occupational School and Neighborhood Location
        3.) Tonawanda School District Location
        4.) Esminger Playground Neighborhood

To establish the potential non-cancer health consequences from inhaling an air pollutant over a lifetime, the measured or predicted air concentration of a pollutant can be divided by its health-based benchmark concentration to produce a ratio of the two concentrations. The ratio of the measured or predicted concentration and the health-based concentration is called the hazard quotient (HQ) for non-carcinogens. The potential risk is elevated when the resultant ratio calculation is greater than 1.0. The hazard index is the sum of hazard quotients for all of the air contaminants evaluated. USEPA cautions the use of the Hazard Index (HI) approach as follows (USEPA2002b):

> The hazard index is the sum of hazard quotients for substances that affect the same target organ or organ system. Because different pollutants may cause similar adverse health effects, it is often appropriate to combine hazard quotients associated with different substances. EPA has drafted revisions to the national guidelines on mixtures that support combining the effects of different substances in specific and limited ways. Ideally, hazard quotients should be combined for pollutants that cause adverse effects by the same toxic mechanism. The HI for respiratory irritation is only an approximation of the aggregate effect on the respiratory system (i.e., lungs and air passages) because it is possible that some of the substances cause irritation by different (i.e., non-additive) mechanisms. As with the hazard quotient, aggregate exposures below a HI of 1.0 will likely not result in adverse noncancer health effects over a lifetime of exposure. However, an HI greater than 1.0 does not necessarily suggest a likelihood of adverse effects. Furthermore, the HI cannot be translated to a probability that adverse effects will occur, and is not likely to be proportional to risk. A respiratory HI greater than 1.0 can be best described as indicating that a potential may exist for adverse irritation to the respiratory system.

The HI results for the four areas identified above are listed in Table 7.10. The HI results represent the potential contribution from point and area sources, but not the mobile sector. The top five HQs are shown for each location.

Acrolein
In each neighborhood, acrolein was modeled and monitored as one of the compounds with the highest HQs, but the modeling results were underestimated as compared to the monitoring results. The average model-to-monitor ratio across all four monitoring sites was 0.09. The HI presented for the neighborhoods located near the monitors, the Tonawanda School District and the Ken-Ton Occupational School, are estimated low

because the monitors indicate the actual measured concentration of acrolein is approximately ten times higher than the modeled concentration. The highest monitored acrolein concentration was recorded at the GIBI site.

Monitoring Site	Acrolein Concentration ($\mu g/m^3$)
Beaver Island Site	0.32
Brookside Terrace	0.33
Grand Island Blvd.	0.43
Sheridan Park Water Tower	0.34

Although the upwind and residential sites appear to be slightly different they are statistically similar in concentration. The three point sources of acrolein in the Tonawanda area inventory are 3M Tonawanda, Tonawanda Goodyear, and Tonawanda Coke with reported emissions of 31, 57, and 37 pounds per year, respectively. For the mobile source sector, the NATA 2002 estimated concentrations for acrolein are 3 to 4 times higher than the Study's calculation, but as shown in Table 7.5, NATA 2002 also under predicts the total acrolein concentration by a factor of 10. Combining the monitored data for acrolein with the other modeled compounds would result in a HI above one for all the Study sites.

Naphthalene
As discussed in the Inhalation Cancer Risk Analysis section, naphthalene was monitored at the GIBI after the Study period. A comparison of monitored concentration to the modeled value indicates an underestimate of the model by a factor of 5.3. The modeled naphthalene concentration in the four neighborhoods may be under estimated.

Chronic inhalation studies on animals determine that naphthalene aggravated cells in the olfactory and respiratory system. The IRIS database (USEPA, 2009d) established a reference dose concentration for naphthalene of 3.0 $\mu g/m^3$ in 1998, and this value has been adopted by the NYSDEC as the AGC. The annual concentration modeled at the Kaufman Ave. neighborhood was 0.131 $\mu g/m^3$ and resulted in a hazard quotient of 0.04. However, the potential underestimation of naphthalene, as determined from the GIBI monitor results, could change this concentration by a factor of five. The maximum 24-hour concentration measured at the GIBI site was 2.93 $\mu g/m^3$. Twenty-eight percent of the 24-hour naphthalene concentration measurements at the GIBI site were greater than 1.0 $\mu g/m^3$. In consideration of exposures to other air toxics, it is conceivable that the days with the higher naphthalene monitored concentrations could be playing a significant role in the complaints of eye and respiratory irritation in the Kaufman area neighborhood when combined with other known irritants in the area.

The USEPA's Residual Risk report did not document any non-cancer compounds exceeding a HQ of 1.0 for the Tonawanda Coke facility. The highest HQ recorded was for benzene at 0.2. The HQ cited for naphthalene was 0.004, whereas the GIBI monitor recorded a HQ of 0.23. The USEPA's approach was to examine each compound emitted

from an emission source, (e.g. battery doors leaks) and establish a HQ. HQs were summed to establish an HI for an emission source. The combined HI for naphthalene was 0.262 for the Tonawanda Coke facility. The other point sources of naphthalene identified in the area are NOCO Energy, NRG Huntley Steam Station, and Tonawanda Goodyear, with emissions reported at 39, 20, and 90 pounds per year, respectively. Tonawanda Coke reported releases of 3,000 pounds a year of naphthalene.

7.3.2.2 Air Toxic Non-Cancer Risks in Perspective

Using the RAIMI software program, an HI of 1.03, was calculated for the Kaufman Ave. location with the top five contributing compounds being acrolein, sulfuric acid, hydrochloric acid, naphthalene, and ammonia. As explained above, the HQ represents a measured or modeled concentration divided by the health-benchmark concentration. The endpoints for the development of the health benchmarks for these specific compounds are based on irritation effects. Although a detailed exposure assessment analysis could be conducted to evaluate daily variability for an individual's exposure, the variability based on meteorological conditions is likely be much greater than the variability based on daily activity. Meteorological conditions that are conducive to increasing the concentrations of air toxics, including irritants, are stagnant warm air. Similar to alerts issued by the NYSDEC and the NYSDOH for high ozone and high particulate days, these events tend to occur on days with minimal wind movement. Work displayed in Section 7.4 of this report showed how daily concentrations of monitored air toxics increased on calm wind days. The NYSDEC Region 9 office has received many complaints from citizens living in the Kaufman Ave area of upper respiratory and eye irritation. These events would be considered an acute health episode and future air pollutant reduction strategies need to be implemented to reduce emissions from multiple sources which create high concentrations of air pollutants associated with acute irritation events.

The air monitoring strategy was not conducive for evaluating short-term exposures and acute health effects but rather was designed to investigate chronic health outcomes. Short-term exposures are better evaluated with sampling time frames on the order of one to a few hours. For the air toxics evaluated in this study, a daily average was collected, limiting the ability to evaluate acute health effects. The modeling analysis conducted above evaluated air contaminants for which this Study was not able to monitor through the methods selected (TO-11 and TO-15) such as sulfuric acid, hydrochloric acid, and ammonia. The chronic toxicity endpoint for these air contaminants is irritancy, an endpoint that is commonly associated with acute exposures.

7.3.3 Limitations

The use of modeling to predict ambient air concentrations has inherent uncertainty and limitations. The type of air dispersion model (RAIMI and AerMOD) used in this assessment is a Gaussian plume model. The Gaussian models assume an ideal steady-state of variable meteorological conditions over long distances, idealized plume geometry, complete conservation of mass, and exact Gaussian distribution. These ideal conditions rarely occur at one location. The modeling of these types of conditions leads

to an overestimate of actual concentrations and is conducted to provide a conservative estimate, protective of public health.

Additionally, a number of assumptions are made during the development of the modeling inputs. For example, USEPA used the Buoyant Line Plume model and ISCST3 model to calculate ambient concentrations resulting from the dispersion of contaminants from the Tonawanda Coke facility for the Coke Oven Residual Risk Assessment. Unique to the coking process are the high temperatures attained in the coke oven battery. These high temperatures add to the dispersion of emissions from the coking process and subsequently the pushing process. Appendix E, of the Residual Risk Assessment, details the enhanced plume calculation completed by USEPA. USEPA included the following statement in their document "coke ovens facilities produce significant heat from large, parallel oven batteries, which behave as low-level buoyant line sources. Because of the parallel-line source configuration, plume rise is enhanced as ambient air is not fully entrained into the plume." The buoyant line plume model (BLP), which was used in the Residual Risk Assessment, was specifically developed to stimulate the plume rise from multiple line sources subject to downwash. The models used by NYSDEC did not employ enhanced buoyancy calculations.

The modeled and measured inhalation cancer risk estimates were added to assess the total cancer risk associated with exposure to multiple HAPs. The addition of the inhalation cancer risk is a conservative public health approach and was conducted to provide a total estimated inhalation cancer risk for the Study area. An inherent assumption is made that exposure to multiple HAPs results in an additive effect on cancer outcomes and that each HAP has the same cancer endpoint. In addition, all air contaminants with a cancer risk associated with them are based upon the upper-bound excess lifetime cancer risk resulting from continuous exposure to an air contaminant. The USEPA defines the upper bound as "a plausible upper limit to the true value of a quantity. This is usually not a true statistical confidence limit." The use of an "upper limit" means that the true risk of developing cancer from exposure is not likely to be higher and may be lower than the estimates provided in this study.

The hazard quotient was obtained by combing the hazard index for each of the HAPs. This calculation assumes that each HAP affects the same target organ or organ system. This approach was utilized in this Study to provide a screening-level conservative estimate based for non-cancer effects.

Finally, the model estimates do not account for other sources of exposure such as indoor or occupational and these estimates were not attenuated by time spent at other locations (such as work, school, etc.).

7.4 Assess the Relative Contributions of Various Air Pollution Sources and the Influences of Various Meteorological Parameters

The evaluations conducted in this Subsection were done primarily to support the risk assessment analyses and to identify potential sources, especially for those air contaminants with measured concentrations exceeding NYSDEC's AGCs. As stated previously, increased cancer risk levels greater than one-in-a-million (10^{-6}) or noncancer hazard quotients greater than one usually warrant further evaluation (e.g., the actual vs. potential exposure, "background" exposure contribution, and the strength of the toxicological data) including the need for risk reduction measures depending on where the risk estimate falls. This Subsection includes the full analyses for the following contaminants, which had measured concentrations above these levels during the Study period at one or more of the four air monitors in the Tonawanda area: 1,3-butadiene, acetaldehyde, acrolein, benzene, carbon tetrachloride and formaldehyde. Expanded analyses of additional contaminants that were evaluated for other purposes, such as, in support of discerning point versus mobile sources are provided in appendices. The expanded wind directionality analyses for these additional contaminants are provided in Appendix N.

7.4.1 Methods used to Evaluate the Influence of Wind Direction on the Measured Air Contaminant Concentrations

During the Study period, hourly meteorological measurements (wind speed, wind direction, ambient temperature, relative humidity and barometric pressure) were collected at the BISP site. Although many parameters were collected, wind direction data was initially used to evaluate the air toxic monitoring concentrations and three different approaches were used: polar plots, time-weight pollution concentration roses [Harrison and Williams 1982, Cosemans et. al., 2008], and comparisons of the wind roses for the concentrations equal to or greater than the 90th percentile and equal to or less than the 10th percentile.

For the first approach, polar plots were created by determining the most frequently occurring hourly wind direction for each monitoring day and assigning it to the 24-hr air toxic concentration for that day. Because the direction of wind is highly variable and wind coming from a range of directions may have similar influences on monitoring concentrations, the hourly wind data were assigned to one of sixteen, 22.5 degree arcs. With this approach, each daily air toxic concentration was matched with the most frequently observed wind direction. This information was then plotted for the entire Study period creating a polar plot diagram[27]. The results of this exercise are discussed in further detail in following Subsection.

The predominant wind direction across the 12-month Study period corresponds to the Study design hypothesis – winds are primarily from the southwest direction. Figure 7.10

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[27] Polar plots - the coordinate system for a polar plot is radius length (r) and theta (q). The distance from the origin of the graph is the concentration (r) and wind direction is the angle theta (q) between the positive horizontal axis. The concentration is plotted at the mid-point of each 22.5-degree arc.

shows the wind rose diagram for the BISP monitor over the time period of the Study. The most prevalent wind direction was from the 190 – 260 degree sector (south, south-west to west, south-west). Roughly 45% (about 637 hours out of 1416 total monitoring hours based on a 1-in-6 day schedule) of the time during the Study, the winds came from this direction, resulting in a higher number of data points in these southwest quadrant directions of the polar plots. However, it is not the overall number of data points in any given direction that indicates a local source(s), but rather, elevated measured concentrations that result when the wind is coming from a certain direction. For example, the carbon tetrachloride pollution roses have more data points in the southwest/south, southwest directions but the resulting concentrations when the wind is coming from these directions are very similar to those concentrations that resulted when the wind was blowing from the other directions (Appendix M). Additionally, an absence of data points for any direction simply indicates that this direction was never the most frequently observed wind direction for any of the sampling days over the yearlong Study. Therefore, no determinations about the presence or absence of a local source in that direction can be made. Directionality of the pollution roses resulting from generally higher monitored concentrations when the wind was blowing from a particular direction(s) indicates a local source(s) of this air contaminant influencing the concentrations at the monitor sites from that wind direction(s).

Polar plots were created for all the Category C and B air contaminants and are located in Appendix M. The summaries of the results for those air contaminants which had measured annual concentrations below DEC's health-based guideline concentrations are included in Appendix N. Two sets of diagrams were created for certain air contaminants because the differences between their concentrations at the various monitoring sites were so substantial. The first set uses the same standardized scale for all four monitor diagrams and the second set maximizes the scale of each monitor diagram to more clearly determine source influences.

For the second approach, time-weighted average (TWA) pollution concentration roses were developed by deriving an average concentration for each 22.5 degree wind direction sector[28]. The concentration average for each wind direction sector was derived by this equation:

$$TWMC_i^d = \frac{\sum c_i h_i^d}{\sum h_i^d}$$

Where $TWMC_i^d$ = time-weighted mean concentration during period i in sector d

c_i = 24-hr concentration during period

h_i^d = number of hours during period i that wind is in sector d

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[28] The QAPP states that fixed 30-degree arcs would be used in this analysis. Upon review of the data and graphical output, it was decided that a more refined approach using 22.5 degree arcs would be applied.

The TWA pollution concentration roses allocate the 24-hr monitored concentrations to the percent of time the wind was blowing from each direction during the day. For example, if a 24-hr air toxic concentration was 10 μg/m³ and the wind was blowing from the southwest 50% of that day, then 5 μg/m³ would be allocated to the southwest and the remaining 5 μg/m³ would be apportioned to the remaining wind directions according to percent allocation.

By reviewing many years of historical meteorological data prior to siting the Study monitors, it was noted that the prevailing wind comes from the southwest. Therefore, the Study design involved the placement of one upwind site (BISP) and three downwind sites to evaluate the air mass moving over the industrial area of Tonawanda on the measured monitor concentrations. The GIBI monitor provided measurements of air toxic concentrations in close proximity to the industrial area. When the wind was blowing in the prevailing direction (from the southwest), the measured concentrations were primarily influenced by the industrial area, which would be upwind of the GIBI monitor in this wind scenario, but with little or no influences from the nearby highway(s), which would be downwind of the GIBI monitor. This can then be compared with the measured concentrations that resulted when the wind was coming from the opposite direction (northeast) without the influences from the industrial area but with the influences of the highway(s). Because the BTRS and GIBI monitors are lined up with respect to the industrial area and the prevailing wind direction, the BTRS monitor allowed for the evaluation of the dispersion of the air contaminants in cases where higher concentrations were observed at the GIBI monitor due to local source impacts from the industrial area. Finally, the SPWT site allowed for the evaluation of monitor results when the wind was blowing over the industrial area from the west as opposed to the prevailing wind direction (from the southwest).

The placement of these four monitors surrounding the Tonawanda industrial area only allowed for the evaluation of sources contributing to the measured air toxic concentrations which are located within that industrial area. The pollution roses depicting these TWA concentrations were superimposed over the four monitoring locations on a map of the Study area. The result is a diagram that shows peaks that point towards the direction of a local source(s) which impact the monitoring site. In those instances when the TWA pollution roses for all four monitors point towards the industrial area, vector lines were added that extend out from the monitor locations along the degree sector lines surrounding the portion of the TWA pollution rose that is pointing towards the industrial area. These vector lines backtrack from the monitor to the local source(s) that are influencing the elevated concentrations observed when the wind was blowing from that particular direction. A triangulation process then indicates the location of a primary local source for that particular contaminant by highlighting the area where the four sets of vector lines intersect. There are instances where the TWA pollution roses point in directions other than towards the industrial area but, while these cases will be highlighted, no local source can be indicated because no triangulation with the other monitoring site's results can be accomplished. The vector lines extending out from the different monitors were given more weight for higher monitor concentrations initially and then subsequently by distance if the concentrations at the different monitors were equal.

Only a subset of the air contaminants for which the polar plots were generated have been depicted in this TWA pollution rose fashion. Those air contaminants which had mean concentrations exceeding their representative health-based AGCs are presented in the body of this report. Several others that were of interest for tracing sources are presented in appendices (Appendix N).

The third approach compares wind roses created from the concentration days at and above the 90th percentile (highest 10%) to the wind roses created from the concentration days at and below the 10th percentile (lowest 10%) to observe the different wind directionality patterns (Appendix O). This method provides the truest representation of the wind direction out of the three tools for comparing measured concentrations and wind directionality because the hourly wind data was not manipulated to be compared with the 24-hour air toxic concentrations. A resultant wind direction vector[29] is shown in the wind rose diagrams.

Finally, benzene/toluene ratios were calculated to investigate the relative contributions from the mobile versus non-mobile sources (Bravo, 2002). In many other studies, often investigating urban areas with larger amounts of vehicular traffic relative to the point sources, the emissions from mobile sources tend to dominate the measured and modeled HAP concentrations. In these cases, the influences from the toluene emissions are much greater than those for benzene, and subsequently, the toluene concentrations dominate the ratio resulting in the use of the toluene/benzene ratio (instead of benzene/toluene) in order to present the ratios as whole numbers. The results in Tonawanda were different in that the benzene emissions, and subsequently, the benzene concentrations are very high and thus dominate the ratio. For this reason, the benzene/toluene ratio was used. The normal range for the toluene/benzene ratio is 3-5 (equivalent to benzene/toluene ratios of 0.2-0.33) in areas dominated by influences from mobile sources, such as urban areas, and 1-2 (equivalent to benzene/toluene ratios of 0.5-1) is considered low to very low.

7.4.2 Analyses of Wind Directionality Influences on Measured Concentrations for Air Contaminants Exceeding DEC's AGCs

1,3-Butadiene
1,3-butadiene was classified as either Category C or B at the GIBI and BTRS monitors so polar plots were generated for these sites only (Appendix M). The GIBI and BTRS 1,3-butadiene polar plots indicate directionality to the south-west with only isolated high concentrations in the other directions.

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[29] The definition of the resultant vector as provided by software program used to create the diagrams (Lakes Environmental) is as follows: "The resultant vector is the dominant direction or mean direction of the vectors. This is calculated by computing the vector resultant or vector sum of the unit vectors that represent the various directions in the data. The magnitude of the resultant vector represents the mean resultant vector length. The direction of the resultant vector is a common way to represent the mean wind direction. The magnitude of the resultant vector for the wind rose represents the frequency count for the mean direction."

The 1,3-butadiene TWA pollution roses have a similar profile to those of benzene where vector lines from all four monitoring sites extending through the industrial area intersect in the same vicinity indicating the same source as a major contributor to the airborne concentrations of this contaminant in the area (Figure 7.11). However, because only the GIBI and BTRS monitors were in category C or B, using the data from the BISP and SPWT monitors where it was based on less than 50% above the MDL has more uncertainty associated with it. The differences between the maximum concentrations at the different locations are not nearly as dramatic with 1,3-butadiene as it is with benzene.

The 1,3-butadiene wind roses at the GIBI, BTRS, and BISP monitor locations are similar to benzene in indicating the same predominant source (Appendix N). Both the GIBI and the BTRS sites indicate that the highest concentration days occurred when the winds came predominantly out of the southwest and that winds from this direction were absent on the lowest concentration days. The BISP site indicates that the highest concentrations include winds from the northeast, whereas the lowest concentrations do not include any winds from this direction. The SPWT site differs in that the winds from the direction of the above referenced source are not the dominant directions for the highest concentration days. The top 10% wind rose shows more of an influence from the east to southeast direction, indicating that perhaps the mobile sources from the adjacent road are acting as an influence at this location. There is a substantially higher percentage of calm winds for the highest concentration days as compared to the lowest concentration days (not only at SPWT but also at the other three sites as well) which also could be influencing this observed effect.

Acetaldehyde
The acetaldehyde polar plots only weakly indicate directionality (Appendix M). The GIBI and, to a lesser extent, the BTRS polar plots both indicated a directionality to the south, southwest/southwest (at 202.5-225°) and to the southeast (at 135°). The GIBI polar plot also indicates directionality to the northeast. The BTRS polar plot has one isolated higher concentration point to the west. The SPWT and BISP polar plots do not show any strong directionality but have isolated high points to the southeast and also have slightly elevated concentration points in the southwesterly direction.

Acetaldehyde is another general product of combustion and the TWA pollution roses for acetaldehyde show some similarities to those for formaldehyde (Figure 7.12). All four TWA pollution roses point in the direction of the city of Buffalo to the southeast. The GIBI TWA pollution rose for acetaldehyde points towards the industrial area and also towards the adjacent highways, although not as strongly with formaldehyde. The TWA pollution roses for the other three sites do not show any real directionality other than pointing to the southeast. Overall, the smaller differences between the maximum concentrations at the various monitoring locations indicate that this air contaminant has fewer major point sources and rather has a more widespread emissions profile.

The wind roses analyses for acetaldehyde are discussed with formaldehyde in a subsequent Subsection below because of the similarities between these contaminants (Figures presented in Appendix O).

Acrolein

The acrolein polar plots weakly indicate directionality (Appendix M). The GIBI and BTRS polar plot indicate directionality to the south, southwest/southwest (at 202.5-225°). The GIBI polar plot has one isolated high point to the southeast. The SPWT and BISP polar plots do not show any real directionality.

While acrolein is also another general product of combustion, it appears to be more generally distributed in nature (Figure 7.13). The GIBI TWA pollution rose points to the industrial area, in addition to, the direction of one of the large petroleum storage facilities in the area and the I-190 highway (northwest). There are only slight indications of potential mobile source influences at the three downwind locations. Similar to acetaldehyde, the relatively equal maximum concentrations indicates acrolein emissions from many smaller spread out sources rather than from isolated major point sources.

Again, because the wind roses analyses for acrolein are similar to formaldehyde, these acrolein results are discussed with those for formaldehyde in a subsequent Subsection below (Figures presented in Appendix O).

Benzene

Benzene is one of the contaminants with a wide range of different concentration levels between the various monitoring sites so the polar plots are provided both with a standardized scale across all four sites and with the scale maximized at each monitoring site Appendix M. The benzene polar plots showed strong directionality. The GIBI and BTRS polar plots clearly indicate directionality to the south, southwest/southwest (at 202.5-225°). The SPWT and BISP polar plots both have one isolated higher concentration point directly to the east. The SPWT polar plot shows directionality to the west, while the BISP polar plot shows directionality both to the northeast and to the southwest. Therefore, all four monitors indicated directionality towards the industrial area.

The TWA pollution roses for benzene at all four monitoring sites also primarily point in towards the industrial area (Figure 7.14). Additionally, the maximum benzene concentrations for the TWA pollution roses at all monitoring sites are very different; indicating that combination of the wind direction and vicinity to the source greatly influenced the concentrations measured. The lower benzene concentrations at BTRS are likely due to the contaminant's dispersion over distance and the lower concentrations at SPWT are likely due to the fact that this is not in line with the prevailing wind direction as it blows over the industrial area. The vector lines extended out from the 22.5° arcs pointing towards the industrial area all intersect in the industrial area. More weight was given to those TWA pollution roses with higher concentrations and which were closer to the industrial area. The circled area in Figure 7.14 where the vector lines intersect indicates the vicinity of a local source(s) influencing the monitored concentrations and is the location of the largest known source of benzene in the area. The GIBI and SPWT, TWA pollution roses also point in other directions in addition to the industrial area. Each of the additional directions appears to follow an adjacent highway or road which

indicates influences from mobile sources when the wind is blowing from those directions. One high concentration day when the wind was blowing directly from the east greatly influenced the directionality of the SPWT TWA pollution rose in that direction.

The wind roses for the highest 10% concentration days versus the lowest 10% for benzene clearly indicate that the highest concentrations resulted when the wind blew from the direction of the largest local benzene source to the monitor location and the lowest concentrations occurred when the winds from this direction were absent (Appendix O). The highest 10% concentration days at both the GIBI and BTRS monitors were when wind was primarily out of the southwest, whereas the lowest 10% concentration days at these same two monitors had no winds coming directly out of the southwest. The resultant wind vector for the highest and lowest 10% concentration days was included on the wind roses. The resultant wind vector indicates both the wind direction in degrees and a percentage indicating how representative this wind direction is for the overall wind patterns during that particular time period. The higher resultant wind direction percentages for GIBI and BTRS (54% and 47%, respectively) over the highest 10% concentration days indicate that the resultant wind direction (210° for GIBI and 215° for BTRS) better represents the combined winds for those days as compared to the lowest 10% concentration days. The resultant wind directions and percentages for the lowest 10% concentration days at GIBI and BTRS were 173° at 29% and 268° at 21%, respectively. The wind roses for the SPWT monitor indicate that the winds resulting in the highest 10% concentrations were out of the west, again from the direction where the largest local benzene source is located (resultant vector at 271° for 28%), whereas the winds resulting in the lowest 10% concentrations clearly indicate a lack of winds from the west (resultant vector at 177° for 22%). The wind roses for the BISP monitor indicated that the winds resulting in the highest 10% concentrations were out of the northeast in the direction of the largest local benzene source (the resultant wind vector was at 101° but only with 32%), whereas the winds resulting in the lowest 10% concentrations again clearly indicate a lack of winds from the northeast (resultant vector at 240° for 77%).

Carbon Tetrachloride
Carbon tetrachloride is a chemical that was phased out in January 1996 by the Montreal Protocol. According to the TRI, the last reported emissions in NYS were in 2001. However, it is a chemical that has been reported to have a half-life of 50 years or more, so it will remain a ubiquitously distributed airborne contaminant for many years to come.

The carbon tetrachloride polar plots did not show any evidence of directionality at any of the four air monitoring sites and a relatively narrow range of concentrations is seen in the diagrams (Appendix M). This indicates that there are no local sources of this air contaminant and the air contaminant concentration is at background level.

The TWA pollution roses for carbon tetrachloride at all four monitoring sites clearly indicate that there is no directionality to the influences resulting in the monitored concentrations (Figure 7.15). Further support of this arises from the equal maximum concentrations at all four locations.

The carbon tetrachloride wind roses do not show any indications of a local source or any influences from the industrial area (Appendix O). Additionally, both the top 10% and the bottom 10% wind roses look similar across all four monitoring sites, with the exception of the missing southwest degree sector in the highest 10% wind rose at the GIBI monitor. All the wind roses except the GIBI highest 10% indicate that wind patterns resulting in either the highest or lowest concentration days simply resemble the general prevailing wind patterns for this area.

Formaldehyde
Formaldehyde also had substantially different concentrations between monitoring locations, and therefore, the polar plots are provided with both standardized and maximized scales (Appendix M). The formaldehyde polar plots do indicate some directionality, but less strongly than with benzene. All four sites indicate directionality to the south, southwest/southwest (at 202.5-225°), but also from several other directions as well. Three of the four sites (GIBI, SPWT, and BISP) also indicate directionality to the northeast. The GIBI polar plot has one isolated high point to the west, northwest. The BTRS polar plot has one isolated higher concentration point directly to the west and also shows slight directionality to the southeast. The SPWT polar plot has isolated high points to the south and southeast. The BISP polar plot has one isolated higher concentration point directly to the south and also indicates directionality to the southeast.

The TWA pollution roses for formaldehyde, which is a general product of combustion, do not clearly indicate a prevailing source in the Tonawanda industrial area (Figure 7.16). However, the differences in the concentrations between the various monitoring sites indicate that local sources are influencing the GIBI monitor more than any of the other three locations. The closest monitoring site, GIBI, does point towards the industrial area, in addition to, pointing along the two major highways adjacent to it. This indicates that this product of combustion is coming both from point and mobile sources in the area. It appears that the formaldehyde concentrations at the other three monitors have greater influences from the direction of the city of Buffalo (from the southeast), and so, are influenced by the local source contribution to a lesser degree. The BISP TWA pollution rose also points in towards the industrial area and the SPWT and BTRS TWA pollution roses indicate some additional minor sources, in some cases also towards roads indicating mobile source influences.

The wind roses for formaldehyde and acetaldehyde are similar, and neither these nor those for acrolein provide strong indications of a large point source in the area as those for benzene did (Appendix O). There are many point sources, as well as, widespread mobile sources of combustion products like formaldehyde, acetaldehyde, and acrolein. The wind roses for formaldehyde, acetaldehyde, and acrolein were unlike those for benzene in that they did not consistently indicate that winds blowing from the industrial area to the monitor resulted in the highest 10% concentration days and an absence of those same direction winds resulted in the lowest 10% concentration days. Both the highest and lowest 10% concentration day wind roses for all three of these contaminants at all four monitoring locations indicate one or more of the three primary wind degree

sectors from the southwest. The remaining wind directions observed do not consistently point toward the industrial area or to a common source. The GIBI highest concentration days do indicate more winds from the south, southwest and southwest (the direction of the industrial area) than the GIBI lowest concentration days for all three contaminants. Only the acrolein wind roses at the BTRS show this. In addition to the lack of an indication of a predominant source in the industrial area, formaldehyde and acetaldehyde at the BTRS also indicate wind patterns that are spread out over more wind directions. The wind roses for SPWT for all three contaminants indicate the reverse of what would be expected if the predominant source was within the industrial area because there are more winds from the westerly direction for the lowest 10% as compared to the highest 10% concentration days. The BISP wind roses also did not indicate any influences from within the industrial area. There are a substantially higher percentage of calm winds for the highest concentration days as compared to the lowest concentration days at all four sites for formaldehyde, acetaldehyde, and acrolein which also could be influencing the differences in concentrations observed.

7.4.3 Upwind versus Downwind Analyses of Measured Air Contaminant Concentrations

By study design, three monitors have been placed in line with the predominant southwest wind direction, which allowed for further evaluation of wind directionality influences. Previous analyses clearly indicated a wind directionality influence on the benzene concentration measured, with the highest concentrations resulting when the wind lined up the largest local benzene source with each of the monitors. The analyses presented in this Subsection further expand on that and evaluate the concentration differences with opposing wind directions which place these three in-line monitors in both upwind and downwind situations. Because there were also indications that this facility and/or a culmination of combustion sources (stationary and mobile) in the Tonawanda industrial area were influencing the concentrations of additional combustion air contaminants at the monitors, several other contaminants were included in the analyses. Due to the differences in average concentrations, three different scale graphs were generated so the trends could be more easily observed. The days were isolated when the most frequent wind direction was from directly out of the southwest (from 225°) lining up the traditionally upwind monitor (BISP) with the largest local benzene source and the industrial area, then the GIBI monitor, and finally the BTRS monitor. This analysis indicated that the average concentrations of all the air contaminants except carbon tetrachloride increased from BISP to GIBI and then decreased from GIBI to BTRS (Figure 7.17). The carbon tetrachloride average concentrations remained relatively constant from one monitoring location to the next. Benzene had by far the largest percent increase from the upwind site to both of these downwind sites with a greater than 2,000% increase at GIBI (compared to the next highest percent increase of just under a 450% increase for m,p-xylene) and an almost 450% increase at BTRS (compared to the next highest percent increase of almost a 250% increase for toluene). Benzene also had the largest percent decrease from the highest average concentrations seen at the GIBI monitor to the reduced average concentrations seen at the BTRS monitor. The average benzene concentration at BTRS was roughly 21% of the GIBI average concentration, compared to

the next largest percent decrease (for formaldehyde) which had a BTRS average concentration that was roughly 37% of the GIBI average concentration.

A similar analysis was then conducted using those days when the wind direction was in the opposite direction, out of the northeast (from 45°), to validate the previous findings. This scenario places the BTRS monitor upwind, followed by the GIBI monitor (which would be after the I-190 interstate but just before the largest local benzene source and industrial area), and finally the BISP monitor would become the downwind site in reference to the industrial area (Figure 7.18). The findings were interesting because the benzene concentrations increased both from those measured at the BTRS monitor to those at the GIBI site and also from those at the GIBI site to those at the BISP site. The average concentrations for all of the other nine air contaminants analyzed, except for carbon tetrachloride, increased in the vicinity of the industrial area at the GIBI monitor but did not increase further after the winds passed over the industrial area and reached the BISP monitor, as those for benzene did. Additionally, the initial increase of benzene from the BTRS monitor to the GIBI monitor was among the smallest of all the contaminants (only carbon tetrachloride and two other contaminants, out of the nine investigated, had smaller percent increases) before the winds reached the industrial area. However, the overall increase in benzene concentrations from the BTRS monitor to the BISP monitor was the largest out of all the air contaminants analyzed (almost a 300% increase for benzene and a roughly 200% increase for the next largest percent increase which was with formaldehyde). Carbon tetrachloride showed very little difference in average concentrations measured across the three monitoring sites.

A line graph showing all the individual days when the winds were blowing over the Study area from the southwest (225°) shows that the concentrations are low at the upwind site (BISP), peak at the GIBI monitor (after the winds have traveled over the largest local benzene source and industrial area), and have decreased away from this source at the BTRS monitor likely due to dispersion (Figure 7.19). The average wind speed for each of the days is included alongside the date. The two days with the highest increased concentration at the GIBI monitor had the second and third highest wind speeds. However, the highest wind speed day (which was roughly 44% and 56% higher than the second and third highest, respectively) only resulted in an increased concentration at the GIBI monitor that was in the middle of the range, potentially indicating increased dispersion. The subsequent change in concentration from the GIBI monitor to the BTRS monitor indicated that the two highest wind speed days resulted in the largest two percentage decreases, again potentially indicating that the higher wind speeds result in greater dispersion.

Scatter plots were generated to compare the benzene, toluene, and 1,3-butadiene concentrations at the GIBI monitor when the winds were coming from the southwest (202.5°-247.5°) versus when they were coming from the northeast (22.5°-67.5°) (Figures 7.4.20-22). The scatter plot with benzene and toluene indicates that when the winds were coming out of the northeast the benzene concentrations were primarily very low but the toluene concentrations were across the full range of concentrations (with the slight majority near the high end of the concentration range). Whereas when the winds were

out of the southwest, the highest benzene concentrations were observed but the toluene concentrations remained consistent to what was observed in the opposite wind direction (Figure 7.20). The scatter plot with 1,3-butadiene and toluene indicates that 1,3-butadiene acts similarly to benzene in that the lowest concentrations were measured when the winds were out of the northeast and the highest primarily were when the winds were out of the southwest (Figure 7.21). The scatter plot with benzene and 1,3-butadiene figure clearly shows the similar influence(s) for these two contaminant concentrations when the winds were out of the southwest versus the northeast (Figure 7.22). The wind rose for the one outlier is provided to show that, although the most frequently observed wind direction for that day was from the northeast, there were several wind directions coming from the southwest direction that combined would total a greater percentage than the one northeast degree sector. This illustrates the limitation of assigning one wind direction sector to represent the overall movement of air mass throughout the day (Figure 7.23).

7.4.4 Background versus Local Source Analyses of Air Contaminants

The following background analysis investigating the spatial variation from downwind to upwind used ratio cut points that were applied previously in a study of air toxics in Alleghany County, PA (Carnegie Mellon University, 2009). This investigative technique was used to determine whether contaminant concentrations can be attributed primarily to regional influences or to local source contributions. The following thresholds were developed in the Alleghany County Study based on changes in the downwind to upwind concentration:

1) $\leq 25\%$ increase indicates regional background contaminant.
2) $> 25\%$ to $< 200\%$ increase indicates moderate effects of local sources.
3) $>200\%$ increase indicates strong effects of local sources.

Initially, the annual mean of the contaminants were used to derive the ratios. Then, a refined analysis of the estimated background concentration, without the predicted impacts from the industrial area influencing the upwind monitor, was performed for a subset of the air contaminants. The difference between the mean concentration for the three downwind sites (GIBI, BTRS, and SPWT) and the upwind site (BISP) (Figure 7.24) are:

CONTAMINANT	GIBI	BTRS	SPWT
1,3-BUTADIENE	+ 370%	+ 36%	+ 21%
ACROLEIN	+ 34%	+ 4%	+ 7%
ACETALDEHYDE	+ 44%	+ 22%	+ 11%
BENZENE	+ 790%	+ 61%	+ 8%
BENZENE/TOLUENE RATIO	+ 330%	+ 23%	- 14%
CARBON DISULFIDE	+ 44%	+ 24%	+ 250%
CARBON TETRACHLORIDE	- 2%	- 1%	- 1%
FORMALDEHYDE	+ 240%	- 7%	- 23%

When the annual mean BISP average was used as the background, the contaminants that are indicated to have experienced strong local source effects are: benzene, formaldehyde, 1,3-butadiene, as well as, the benzene/toluene ratio at the GIBI monitor and carbon disulfide at the SPWT monitor. Those that are indicated to have experienced moderate local source effects are acetaldehyde, acrolein, and carbon disulfide at the GIBI monitor and benzene and 1,3-butadiene at the BTRS monitor. Except for carbon disulfide, there were no contaminants at the SPWT monitor that are indicated to have experienced any local source effects when the annual mean for BISP was used as the background. Because the reported monitoring results for 1,3-butadiene were below the MDL more than 50% of the time at the BISP and SPWT monitors, the 1,3-butadiene downwind to upwind ratios have more uncertainty associated with them.

An additional background analysis was performed because the previous analyses have indicated that the BISP upwind site is influenced from the sources in the industrial area and therefore cannot be considered truly representative of regional background levels. The concentrations were organized in descending order to initially observe which ones appeared to be part of a continuous range, as opposed to, which ones appeared to be outliers. Then the background cut points chosen were placed on the temporal trend graph for the various contaminants to determine if these cut points were appropriate for separating the apparent background from the local source impacted concentration spikes. Finally, the estimated background from this trends analysis was compared to the mean concentrations for the contaminant during those days when the predominant wind was directly out of the southwest (from 225°) and a second downwind to upwind ratio was calculated. In all cases where the trends background analysis was done, this background was lower that the mean BISP concentration when the predominant wind was from 225°. These results indicate that there may still be some source(s) influencing the BISP monitor from the southwest direction as well. Or that the BISP monitor is close enough to the industrial area sources to be influenced on low average wind speed days/days with a high percentage of calm winds by the general spread of the contaminant over the area (even if the wind is from the predominant 225° direction). Additionally, as was seen previously, even if the predominant wind direction is from one degree sector, there can be a higher percentage of winds over a few adjacent wind degree sectors coming from a different general direction. For example, the percentage of winds from 225° might only be 28% but the winds from the north, northeast, the northeast, and the east, northeast might be 24% each, respectively, for a total of 72%. The concentration for this day would be placed into the 225° sector although the overall majority of the winds are generally coming from the opposite direction (northeast) with more variation across these wind sectors.

For the following analysis, it is important to note that the trends background concentration provided is the average for only the concentrations below the cut point indicated in the associated graphs.

For benzene, the trends analysis indicated a BISP background concentration of 0.64 $\mu g/m^3$ (Figure 7.25 and 7.26), as compared to the 225° BISP concentration of 1.0 $\mu g/m^3$, the BISP annual mean of 1.2 $\mu g/m^3$, and a NATA 2002 background of 0.703 $\mu g/m^3$.

Using the roughly 49% lower trends background approximately doubled the ratios to 1,540%, 310%, and 210% increases at the GIBI, BTRS, and SPWT monitors, respectively. Therefore, all three downwind monitors would be considered to have experienced strong local source effects for benzene when this trends analysis background level is used.

For formaldehyde, the trends analysis indicated a BISP background concentration of 1.4 $\mu g/m^3$ (Figure 7.27 and 7.28), as compared to the 225° BISP concentration of 2.3 $\mu g/m^3$, the BISP annual mean of 2.5 $\mu g/m^3$, and a NATA 2002 background of 1.25 $\mu g/m^3$. Using the roughly 44% lower trends background increased the ratios to 420%, 64%, and 37% increases at the GIBI, BTRS, and SPWT monitors, respectively. Therefore, the BTRS and SPWT monitors would be considered to have experienced moderate local source effects for formaldehyde when this trends analysis background level is used.

For acetaldehyde, the trends analysis indicated a BISP background concentration of 0.75 $\mu g/m^3$ (Figure 7.29 and 7.30), as compared to the 225° BISP concentration of 0.80 $\mu g/m^3$, the BISP annual mean of 0.90 $\mu g/m^3$, and a NATA 2002 background of 0.9 $\mu g/m^3$. Using the roughly 17% lower trends background increased the ratios to 80%, 42%, and 37% increases at the GIBI, BTRS, and SPWT monitors, respectively. Therefore, all three downwind monitors would be considered to have experienced moderate local source effects for acetaldehyde when this trends analysis background level is used.

For carbon disulfide, the trends analysis indicated a BISP background concentration of 0.14 $\mu g/m^3$ (Figure 7.31 and 7.32), as compared to the 225° BISP concentration of 0.21 $\mu g/m^3$, and the BISP annual mean of 0.77 $\mu g/m^3$ (there was no NATA 2002 background). Using the roughly 82% lower trends background increased the ratios to 820%, 700%, and 1,420% increases at the GIBI, BTRS, and SPWT monitors, respectively. Therefore, all three downwind monitors would be considered to have experienced strong local source effects for carbon disulfide when this trends analysis background level is used. Even when the 225° BISP concentration (which is roughly 73% lower than the full BISP annual mean) was used, the ratios increased to 530%, 450%, and 910% increases at the GIBI, BTRS, and SPWT monitors, respectively. As stated previously, this would result in all three downwind monitors being considered to have experienced strong local source effects for carbon disulfide.

The acrolein trends BISP background was 94% of the BISP annual mean so it did not change the ratios enough to change their categories for local source impacted. The carbon tetrachloride trends background showed even less change.

For the benzene/toluene ratio, no trends analysis was performed but the 225° BISP concentration was just low enough to change the ratio at the BTRS monitor to a 27% increase over the upwind BISP monitor resulting in it being classified as moderately impacted by local sources as opposed to regional background when the BISP annual means were used.

7.4.5 Analyses Summaries for Wind Speeds and Temperature/Seasonality Influences on Measured Air Contaminant Concentrations

Other meteorological parameter variables (e.g. wind speed, temperature) were investigated to evaluate influences on the monitored concentrations. Similar to wind directionality, the data for these other variables was dichotomized into the highest and lowest 10, 20, or 30% to compare the two extremes and observe the differences between each. Only summaries of these analyses are provided here but the full analyses are included in Appendix P.

The analyses of wind speeds indicated that the concentrations for the following contaminants showed the strongest overall correlations with average wind speed: 1,3-butadiene, acetaldehyde, acrolein, carbon disulfide, formaldehyde, and toluene. The measured concentrations for these contaminants increased with lower average wind speeds. Wind speed did not appear to influence the measured concentrations of benzene or carbon tetrachloride. Finally, the benzene/toluene ratio showed the reverse relationship indicating a direct correlation between the wind speeds and the measured concentrations because of the large differences in toluene but very little difference with benzene.

The temperature/seasonality analyses indicated that the concentrations for the following contaminants showed the strongest overall correlations with average temperature: 1,3-butadiene, carbon disulfide, and formaldehyde. These contaminants also had the largest concentration increases in the summer months as compared to the winter months. However, the monthly trends do not indicate that same correlation with temperature for either 1,3-butadiene or carbon disulfide. The monthly 1,3-butadiene concentrations appear to correlate with the benzene concentrations and similarly do not appear to have any meaningful monthly trends over the year. Indications are that benzene, and 1,3-butadiene to a lesser extent, are dominated more by influences from local point source(s) resulting from the wind directionality (carrying the wind mass from the point source(s) to the various monitors), as compared to, influences from the wind speeds or temperature fluctuations. The indications of a correlation between the 1,3-butadiene concentration and temperature fluctuations could be due to the lower overall emissions and subsequent concentration levels of 1,3-butadiene, as compared to benzene, which does not mask the effect of these underlying influences to the same extent. The same situation might exist with carbon disulfide because there is a predominant source in the industrial area but it is well controlled resulting in lower emissions and subsequent concentrations potentially allowing the underlying effects from temperature fluctuation influences to be observed. Acrolein, toluene, and acetaldehyde concentrations also appeared to be influenced by temperature fluctuations, as observed both through the direct temperature correlations and the summer to winter concentration differences, but to a lesser extent. The monthly trends provide indications of concentration correlations with temperature fluctuations most strongly for acrolein, followed by formaldehyde and then acetaldehyde with the two aldehydes following similar monthly trends. The monthly trends for toluene also provide indications of concentration correlations with temperature fluctuations with a few exceptions, but carbon tetrachloride shows very little monthly average concentration

variability. The average monthly benzene/toluene ratio trend appears to be dominated by the benzene fluctuations resulting in a lack of a meaningful trend. Both benzene and carbon tetrachloride show very little difference between the summer and winter average concentrations and carbon tetrachloride also does not show any direct correlation with temperature. The benzene concentrations were elevated with the higher temperatures versus the lower temperatures, but the percent difference between the two extremes is the lowest out of all nine contaminants analyzed except carbon tetrachloride. Because of the relative differences for benzene and toluene described above, the benzene/toluene ratio showed an opposite relationship with temperature/seasonality as the majority of the other contaminants. The benzene/toluene ratios were increased with the higher temperatures/summer as compared to the lower temperatures/winter.

7.4.6 Analyses Summaries for Day of the Week/Weekday Versus Weekend Trends and Individual Measured Concentrations Trends including Correlating Contaminants

Only summaries of these analyses are provided here but the full analyses are included in Appendix Q. Additionally, these analyses for the benzene/toluene ratio and those measured air contaminants that were below the NYSDEC's AGCs are not summarized in this subsection and are only provided in Appendix Q.

Acrolein and toluene concentrations increase during the weekdays and have the lowest concentrations on Saturday and Sunday and therefore have among the highest percentage increases in weekday concentrations as compared to weekend concentrations. Acetaldehyde had the lowest average concentration on Saturday and the third lowest on Sunday (after Wednesday) so it too had among the highest percentage increases in weekday concentrations as compared to weekend concentrations. The day of the week trends for 1,3-butadiene, benzene, benzene/toluene ratio, carbon disulfide, and formaldehyde do not show any meaningful trends and can be explained by the wind directionality variations. Benzene apparently dominated the influences on the benzene/toluene ratio because it followed the benzene concentration day of the week trend. 1,3-Butadiene also had a trend that was very similar to benzene but did have lower average concentrations on Saturday and Sunday. This resulted in 1,3-butadiene having a lower average concentration for the weekend versus the weekdays, whereas the weekday and weekend concentrations of benzene showed very little difference to one another. Again, this appears to be due to the much higher benzene emissions (and therefore ambient air concentrations) potentially masking any underlying effects observed for the similarly fluctuating 1,3-butadiene, which appears to be generated primarily from the same dominating benzene source. The weekday and weekend concentrations for carbon disulfide and formaldehyde showed very little difference to one another. Because there was a substantially lower average toluene concentration on the weekends as compared to the weekdays with little difference in benzene concentrations, the benzene/toluene ratio was substantially increased on the weekends as compared to the weekdays. The carbon tetrachloride concentrations vary very little for the different days of the week and therefore also differ very little in weekday and weekend average concentrations.

Only the two monitors that were lined up with respect to the largest benzene source had benzene and 1,3-butadiene concentrations which tracked similarly to one another, indicating that the wind directionality and local source emissions are primarily driving the measured concentrations. However, there are indications that wind speed is an underlying influence, but its effects on the benzene concentrations are mostly masked by the wind directionality influences. 1,3-Butadiene shows stronger indications of wind speed influences affecting the measured concentrations. The benzene and 1,3-butadiene concentration trendlines also track very similarly to one another indicating a common source. The individual monitored concentration data points trendline for benzene and 1,3-butadiene did not indicate strong correlations with either average temperature or average wind speeds.

The acrolein concentration trendlines for the different monitors show more variability, potentially indicating that there are more numerous smaller and widespread sources in the area. This, along with the higher reactivity including secondary atmospheric formation and breakdown of acrolein, resulted in the observed variability. The analyses of the individual data point trendlines supports the previous analyses results indicating correlations of the acrolein concentrations with both wind speeds and temperature. Both wind speed and temperature, in conjunction with solar radiation (not measured in this Study) can play a role in these secondary atmospheric reactions.

The formaldehyde and acetaldehyde concentration trendlines track very similarly to one another indicating a common source, but the analyses indicated a lack of a strong influence from wind directionality suggesting direct effects from a local source. However, these carbonyls can form through secondary atmospheric formations so the indications of local source effects could be arising from the emissions of precursors that then lead to increases in ambient air concentrations. The analyses of the individual data point trendlines supports the previous analyses results indicating correlations of the formaldehyde and acetaldehyde concentrations with both wind speeds and temperature.

The carbon tetrachloride concentration trendlines at all four monitors track very closely to one another and the concentration range is tight both indicating that this air contaminant is a background issue being regionally transported into the Tonawanda area. The trendline for the individual monitored concentration data points of carbon tetrachloride did not indicate correlations with either average temperature or average wind speeds.

7.4.7 Analyses of Criteria Pollutants

As discussed previously, CO and SO2 Study monitoring concentrations were below comparable NAAQS, while the PM$_{2.5}$ Study monitoring concentrations were similar to concentrations obtained at nearby monitors. However, an evaluation of temporal and spatial trends, along with correlation with various meteorological parameters, was conducted.

The full analyses for PM$_{2.5}$ are provided in this subsection. The remaining analyses for CO and SO$_2$ are provided in Appendix R.

PM$_{2.5}$ was measured at all four monitoring sites, so this was the only criteria pollutant for which the concentration trendlines at all four monitors could be compared to investigate potential correlations. The trendlines of average daily concentrations at all four monitoring sites track together almost exactly, indicating that it is either a regionally transported background contaminant or that the concentrations measured are driven more by another meteorological variable such as wind speed rather than by wind directionality (Figures 7.33-34). An analysis was conducted with the full set of data and for illustration purposes a subset of the data (first two months) has been provided to better visualize potential weekly trends (Figure 7.34). The day of the week rather than the date is shown on the 2-month graph, so potential weekly/day of the week trends can also be observed. As illustrated, there is no strong overall weekly trend or day of the week effect although there are some indications that the PM$_{2.5}$ concentrations might be slightly lower over the weekends.

The Study monitoring 12-month PM$_{2.5}$ averages were 11, 13, 13 and 11 μg/m^3 for the BISP, BTRS, GIBI and SPWT monitors, respectively. It is interesting to note that the two monitors that were directly downwind of the industrial area and adjacent to (GIBI) or downwind of (BTRS) the highway (with winds from the prevailing southwest direction) had the highest annual average concentrations. Additionally, the third downwind monitor (but which was not sited along that same prevailing wind direction), SPWT, had the next highest annual average concentration, and the upwind monitor, BISP, had the lowest. This was also the most commonly observed ranking of the monitoring sites seen with the average daily concentrations (Figures 7.33-34), which indicate minor contributions to the measured concentrations of PM$_{2.5}$ from sources in the industrial area.

To further investigate the potential presence of any weekly/day of the week trends, all the concentrations for each of the individual days of the week were averaged together and these pooled averages are graphically presented. While all three criteria pollutants had higher concentration averages for the five weekdays combined as compared to the two weekend days combined (Figures 7.35-37), none were substantially different (SO$_2$ +21%, Combined PM$_{2.5}$ +13%, and CO +8%). The PM$_{2.5}$ concentrations at all four monitors increased slightly on Friday before decreasing over the weekend and increasing on Monday (Figure 7.35). Another point of interest is that the three downwind monitors again consistently measured higher PM$_{2.5}$ concentrations than the upwind monitor. Comparing the PM$_{2.5}$ concentration averages for the full year at the three downwind monitors versus the upwind monitor, indicated an 18% increase at the BTRS monitor, a 16% increase at the GIBI monitor, and a 4% increase at the SPWT monitor. This indicates that there are primary (release of PM$_{2.5}$ from nearby sources) or secondary (release of PM$_{2.5}$ precursors) influencing the downwind monitor concentrations. However, when these increases are compared to the increases for those of a point source driven contaminant like benzene (which had downwind concentration increases of 2,000% at the GIBI monitor and 450% at the BTRS monitor), the increases in PM$_{2.5}$ do not appear to be substantial. In fact, the percent difference between the BISP monitor

(which was the upwind site for almost half of the time over the Study year) and the downwind monitors indicates that roughly 80% or more of the $PM_{2.5}$ concentration could be from regional background. This could mask most of the underlying influences. Given the correlation of individual trendlines at all four monitors but with consistently higher concentrations at the downwind monitors versus the upwind monitor, it appears as if these primary and/or secondary emissions from the industrial area along with the right meteorological conditions (such as low wind speed/high calms percentage days) could be influencing the measured concentrations. This meteorological situation would result in stagnant air leading to the temporal variations in $PM_{2.5}$ concentrations observed. No indications of a relationship between wind speeds and $PM_{2.5}$ concentrations were observed using either the daily or the hourly average wind speeds (data not shown). However, before determining that it appeared the similar trendlines between the four monitoring sites was almost entirely due to the regional drift of $PM_{2.5}$ into the area, a potential correlation between temperature and $PM_{2.5}$ concentrations was also investigated. It was surprising to find a strong positive correlation between the short-term changes in short-term (daily) average temperature over consecutive sampling events and the changes in daily $PM_{2.5}$ concentrations (Figures 7.38). However, the mechanism driving this relationship is not understood and a correlation between the long-term temperature trend and the measured $PM_{2.5}$ concentrations does not exist.

No meaningful trends were apparent for $PM_{2.5}$ measured concentration using either monthly and weekly time frames, so only the monthly averages are presented here (Figures 7.39).

Because the criteria pollutants are measured as 1-hour average concentrations, this allowed for an investigation of hourly trends. The individual daily $PM_{2.5}$ trends (2 weeks worth of which is shown in Figure 7.40) do not indicate any apparent meaningful trend(s). Figure 7.40 was generated from the GIBI monitoring concentrations data, but the same lack of any meaningful trends was observed with the concentration data from the other three monitors (data not shown). However, after the short-term influences from the hourly variations in meteorological conditions are diminished by pooling 6 months worth of data into combined concentrations, the underlying trends could be observed Only 6 months of data being pooled into each hour of the combined time of day averages was needed to bring out these hourly trends. The $PM_{2.5}$ trendline showed an increase in concentration starting midday and continuing into the evening before leveling off until the night time hours when the concentrations then began to steadily fall until they leveled off again in the morning hours (Figure 7.41). While all four monitors show this same general trend, the trendline for the monitor that is the farthest distance from the industrial area, BTRS, seems to have a lag time as compared to the trendlines of the other three monitors.

Several individual days with different wind directionality patterns across all four monitoring sites were subsequently investigated and it was observed that the concentration influences at the BTRS monitor had a lag time of one to two hours when compared to the other monitors (GIBI, SPWT, and BISP). This effect was found to be independent of wind direction (Figure 7.42-44). These results suggest that $PM_{2.5}$ sources

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in the area influence local monitor concentrations, albeit only incrementally, as illustrated in concentration fluctuations between the monitor that is located the farthest away from the industrial area (BTRS) and the other monitors. The lag time in the concentration fluctuations (apparently due to influences of sources in the industrial area) between the closer monitors and farthest monitor are understandable when the wind is blowing in the prevailing southwest direction (Figure 7.42), because the BTRS site would be the last to be affected by the windblown $PM_{2.5}$. Although, when the fluctuations at the upwind BISP monitor and at the GIBI and SPWT downwind monitors track together, the $PM_{2.5}$ dispersion appears to be traveling out in all directions, including opposite to the wind direction which appears to be counter intuitive. This lag time can also be explained when there is a high percentage of calm/low winds (Figure 7.43), because then the $PM_{2.5}$ would be expected to be able to spread out over the entire Study area influencing the closest monitors first and then the farthest monitor. What is not understood is how this same lag time is observed when the wind is blowing from the northeast (in the direction opposite to that which would transport $PM_{2.5}$ emissions from sources in the industrial area to the BTRS monitor) (Figure 7.44), again because the $PM_{2.5}$ dispersion appears to be traveling out in all directions including opposite to the wind direction.

7.4.8 Limitations

Three different methods were applied to evaluate the influence of meteorological information on the monitored concentrations, since a limitation of the study is the collection of air toxic concentrations over a 24-hour average and the collection of meteorological information (especially wind direction) on an hourly basis. The two methods, polar plots and time-weight average (TWA) pollutant roses, introduced some uncertainty in the analysis.

In the creation of the polar plots, each daily air toxic concentration was matched with the most frequently observed, hourly wind direction for the day. This exercise assumes that the assignment of one wind direction to the concentration is the best representation of the wind influence for the day. It has certain advantages over selecting the resultant wind direction which may, in some cases, indicate a direction the wind never came from for a particular day. When there are numerous data points in a wind direction, it can create a graphical illusion of an influence from a particular direction although the measured concentration may not be elevated.

The TWA pollutant roses allocate the 24-hr monitored concentrations to the percent of time the wind blows from each direction during the day. The TWA pollutant roses can be influenced by days with high concentrations and wind directions with limited number of hours. Our research did not adjust for these biases whereas others (Harrison and Williams 1982, Cosemans et. al., 2008) apply formulaic approaches to reduce the outlier and limited data influence.

For some of the air toxics, the comparison of these two constructs provides conflicting information. For example, the polar plot for formaldehyde at the GIBI monitor indicates sources in the southwest and northeast directions. Whereas, the TWA pollutant rose

suggests greater influences from sources northwest (along the I-190 thruway) and northeast directions. In contrast, the results for benzene at the GIBI monitor indicate a source in the southwest direction for both the polar plot and TWA pollutant rose diagrams.

These two constructs in conjunction with other pieces of information, such as emissions from facilities, were used in this Study to indicate the location of potential sources.

An implicit assumption with pollution roses is that the wind measured is identical to the transport wind from the source to the monitor site. Pollutant releases from tall stacks leads to different trajectories than near ground sources. Additionally, trajectories can vary during unusual wind patterns (such as veering and backing wind) (Cosemans et. al., 2008).

Finally, the Study design only allows for the triangulation of sources within the perimeter of the four monitors

8. Source Identification

Within the Study area, there are a variety of sources releasing air toxics. This section will focus on the HAPs exceeding NYSDEC's annual guideline concentrations (AGCs). At all four monitoring sites, the ambient concentrations of acetaldehyde, acrolein, benzene, carbon tetrachloride, and formaldehyde were above their respective AGCs. At two monitoring sites (GIBI and BTRS), ambient concentrations of 1, 3-butadiene were detected above the AGC. For the HAPs monitored in this Study, there are direct emissions of these HAPs, as well as, the secondary atmospheric formation for a subset of these HAPs.

All the HAPs exceeding the AGC, with the exception of carbon tetrachloride, are fossil fuel combustion by-products. Emissions of 1,3-butadiene, acetaldehyde, acrolein, benzene, and formaldehyde are all associated with the combustion of fuel by motor vehicles and the combustion of fuels for electricity, industrial processes, and residential space heating. In addition to combustion by-products, these HAPs are used as chemical intermediates in the production of plastics, organic chemicals, solvents, and other consumer products. Three of the HAPs (acetaldehyde, acrolein, and formaldehyde) also are formed during the breakdown of other organic chemicals within the atmosphere by a process known as photochemical oxidation (e.g. breakdown by sunlight and reactions with ozone, hydroxyl, and nitrate radicals). For example, the formation of acrolein and formaldehyde is associated with the photochemical oxidation of 1, 3-butadiene.

The multiple sources and secondary formation of these HAPs make source identification very difficult. However, by combining the following factors: 1) point and mobile source inventory; 2) the statistical analysis of the monitored data; and 3) the investigation of wind direction, wind speed and other potential influences; the NYSDEC attempted to establish a profile of contributing sources to a particular monitor or series of monitors.

1, 3-Butadiene

Emissions
1, 3-Butadiene (butadiene) is released from both stationary and mobile sources. Ambient concentrations of butadiene are primarily associated with mobile source emissions, unless there are large stationary sources using it to produce synthetic rubber or plastics. In the atmosphere, butadiene is expected to undergo rapid destruction via photochemical reactions, with a reported half-life of 1 to 9 hours. It has been shown to be short-lived in the presence of sunlight and free radicals (USEPA, 2002d).

The 2002 NATA emission inventory for Erie County shows that mobile source emissions account for 99.3% of the reported annual 85 tons per year. NATA reports 34 pounds per year from major point sources and 1000 pounds per year from area sources in Erie County. The Tonawanda Study's emissions inventory data documents 40 pounds per year from Tonawanda Coke Corporation and 52 pounds per year from Tonawanda Goodyear. The largest reported source in the inventory, at 140 pounds per year, is Valley Retread Corp. which is located on corner of Sawyer Ave and Kenmore Ave and currently

holds a Registration Certificate. Mobile source emissions in the Study area were calculated to be approximately 1500 pounds per year. Based upon the Study's inventory data, NATA's major point source approximation is underestimated.

Source Identification
The measured concentrations of butadiene are categorized as Category C pollutants at only the GIBI and BTRS monitors. The concentration difference between the two sites is statistically significant using a Tukey test performed for log-transformed data and the geometric means. This indicates that the GIBI monitoring site is detecting a greater concentration for butadiene than the downwind BTRS site. The possible reason for this finding is that the emissions from mobile sources on Interstate 290 and the Tonawanda Coke Corporation will dissipate with distance as the air mass moves toward BTRS. Butadiene is a highly reactive HAP and will decay rapidly under certain conditions, so it is not transported very far from the emission source.

The two tools used for wind analysis in the Study report; polar plots and time-weighted average (TWA) pollution concentration roses (see section 7.4) were invaluable to assess the emission patterns of butadiene. The butadiene polar plots for the GIBI and BTRS monitoring sites indicate directionality to the south-west with only isolated high concentrations in the other directions (Appendix M). The butadiene TWA pollution roses have a similar profile to those of benzene where the vector lines from all four monitoring sites extend through the industrial area and intersect in the same vicinity similar to the airborne concentrations of benzene (Figure 7.14). Under several analyses performed in Section 7.4, benzene and butadiene track similarly to one another (similar timing of the concentration increases and decreases). These trend correlations indicate that the mobile source sector and/or point source sector emissions are coming from the same location. The results for butadiene were detected in less than 50% of the monitoring samples at the BISP and SPWT monitoring sites.

Using the background data analysis presented in Section 7.4.4, Background versus Local Source Analyses of Air Contaminants, the concentration increases of butadiene are calculated at 370% and 36% for the GIBI and BTRS monitoring sites, respectively. These two values are interpreted to indicate strong effects of local sources for the GIBI site and moderate effects of local sources for the BTRS site. A limitation of this conclusion is the utilization of the butadiene concentration at the BISP site to estimate local source contribution. The results for butadiene were detected in less than 50% of the monitoring samples.

The above factors indicate the measured butadiene concentrations at the GIBI and BTRS monitoring sites have point source contributions beyond the expected mobile source sector emissions. The largest reported local point source of direct butadiene emissions, Valley Retread Corp. is located south, southwest from the SPWT monitoring site. The emissions of Valley Retread Corp. are based upon voluntary data submitted by the company and the modeled air concentration of the emissions reported does not indicate an exceedance of the AGC.

Based upon the individual facts that butadiene is a known by-product of combustion processes, its strong signal identified in the TWA pollution roses and its tracking with benzene concentrations indicates that Tonawanda Coke Corp. is substantially contributing to the elevated concentrations measured, which are beyond the contributions expected from mobile sources alone.

Acetaldehyde

Emissions
Acetaldehyde is released from both stationary and mobile sources. It is predominantly a product of combustion and is also extensively used as a chemical intermediate in the production of plastics, resins, and the synthesis of organic chemicals. It also can be formed by the photochemical oxidation of larger hydrocarbons in the atmosphere. It has an atmospheric half-life that ranges from 12 to 24 hours (Verschueren, 1996). The 2002 NATA emission inventory for Erie County shows that mobile source emissions account for 96% of the reported annual 96 tons per year.

According to the Study's emission inventory, the point sources of acetaldehyde in order of the greatest mass emissions reported are: 3M Tonawanda, Tonawanda Goodyear, NRG Huntley power plant, Indeck Yerkes, and the Tonawanda sewage treatment plant. All of the point sources represent combustion or an oxidation manufacturing process generating acetaldehyde. In 2005, 3M Tonawanda reported its largest mass emission rate at 12 tons per year but has instituted technological changes to reduce its emissions. With the reduction of emissions from 3M Tonawanda, the reported emissions within the Study location is 760 pounds per year. 2002 NATA reported major point sources releasing 870 pounds per year of acetaldehyde for Erie County. Within the Study area, the mobile source sector emissions of acetaldehyde were calculated to be approximately 1700 pounds per year.

Source Identification
The average acetaldehyde concentration measured at the GIBI monitor had a significantly higher air concentration as compared to the BISP monitor. The concentrations at the GIBI monitoring site, where a significantly greater concentration of acetaldehyde was detected as compared to the upwind site, indicates there are sources within the Study area. The averaged acetaldehyde concentration at all sites in the Study area was determined to be below the U.S. median result (Figure 7.4).

The acetaldehyde polar plots only weakly indicate directionality from a stationary source (Appendix M). The GIBI and, to a lesser extent, the BTRS polar plots both indicated a directionality to the south, southwest/southwest (at 202.5-225°) and to the southeast (at 135°). The acetaldehyde TWA pollution roses do not indicate directionality for any particular point source, except the GIBI TWA pollution rose pointing towards the industrial area (Figure 7.12).

The hazard index (HI) analysis under Section 7.3, based upon air dispersion modeling, found two processes at 3M Tonawanda contributing to the elevated HI for the Kaufman

area neighborhood. The HI was calculated to be greater than 1.0 for the Kaufman area location. Since 2005, the reported acetaldehyde emissions of 12 tons per year have been reduced by 95% due to technological changes and thermal oxidation. These processes will continue to be monitored as part of the 3M compliance Title V permit to ensure emissions in the Kaufman area location are minimized. The majority of monitored emissions appear to be mobile source driven and no point sources could be identified at this time.

Acrolein

Emissions
Acrolein is released from both stationary and mobile sources and is predominantly a product of combustion. Another source of acrolein is the photochemical oxidation of 1,3-butadiene. The inventory does not account for the secondary formation of acrolein from the breakdown of 1,3-butadiene. The 2002 NATA emission inventory for Erie County shows that mobile source emissions account for 83% of the reported annual 15.3 tons per year.

The Tonawanda Study's emission inventory indicates that the point sources of acrolein in the Study area account for approximately 900 pounds per year. Tonawanda 3M accounted for the majority of emissions at 775 pounds per year reported in the inventory year of 2005, but has instituted technological changes in recent years to reduce its emissions. Mobile source emissions in the Study area were calculated to be approximately 250 pounds per year.

Source Identification
Acrolein is the only air toxic with a hazard quotient (HQ) above one; for all other air toxics the HQ is less than one. Acrolein is a difficult air toxic to monitor accurately, as explained in section 5.0, and is currently only monitored at two sites in the State in addition to the Study sites. NYSDEC elected to report the acrolein results although some laboratory quality assurance thresholds[30] were exceeded. The HQs for acrolein at the two monitoring locations in the State-wide network are 18 and 23. The HQ for acrolein at the Study site monitors is similar to these values reported by the other two monitors in the State. Acrolein also is monitored to a limited degree by other states. The acrolein HQs at the Tonawanda monitors are below the US monitoring (based on 2005 data) average HQ of 39 (range 2.2 to 120)[31].

The average acrolein concentration measured at the GIBI monitor reported a statistically significant higher air concentration compared to the BISP monitor. The acrolein polar plots only weakly indicate directionality (Appendix M). Similar to acetaldehyde, the GIBI and BTRS polar plots indicate directionality to the south, southwest/southwest (at 202.5-225°). The GIBI polar plot has one isolated high point to the southeast. The SPWT and BISP polar plots do not show any distinct directionality and do not show any

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[30] See Appendix E Quality Assurance for VOCs and Carbonyls
[31] The HQ evaluation for acrolein is based on a limited number of monitors in the US network which report greater than 50% detects (43 monitors) for the 2005 results.

strong concentration gradients between the monitoring sites. The acrolein TWA pollution roses do not indicate directionality for any particular point source, except the GIBI TWA pollution rose pointing towards the industrial area (Figure 7.13).

Acrolein is a known by-product of combustion and the Tukey statistical analysis shows a contribution between the upwind and industrial monitoring sites. The similarity between the TWA pollution roses of acetaldehyde and acrolein indicate that the monitor concentrations could be dominated by mobile sources with some contribution coming from Tonawanda Coke's coking operation. Since 2005, the reported acrolein emissions of 770 pounds per year from 3M Tonawanda's two processes have undergone technological changes and thermal oxidation reducing the emissions by 95%. The majority of monitored emissions appear to be mobile source driven and no point sources could be identified at this time.

Benzene

Emissions
Benzene is released from both stationary and mobile sources and is predominantly a product of combustion. Emissions also can occur from the evaporation of oils, fuels, and solvents containing benzene and also can be liberated from the coal coking process. Benzene has an atmospheric half-life of approximately 5.7 days (Verschueren, 1996).

According to the Study's emission inventory, the point sources of benzene in order of the greatest mass emissions reported are: the Tonawanda Coke Corporation, NRG Huntley power plant, NOCO Energy, and Tonawanda Sunoco. The total point source emissions for the study are 26.5 tons per year. The 2002 NATA emission inventory for Erie County shows that mobile source emissions account for 77% of the reported annual 897 tons per year. Mobile source emissions in the Study area were calculated to be approximately 6.5 tons per year.

Toluene/Benzene Ratio
Considerable research has been dedicated to the study of ambient concentrations of air toxics in urban areas. Urban airshed research predominantly focuses on the mobile source sector's emissions of benzene, toluene, ethylbenzene, and xylene. One parameter studied is the ratio between the concentrations of toluene and benzene. The toluene/benzene ratio is used as an indicator to evaluate the mobile versus non-mobile source sector contributions within an urban air shed (Bravo, 2002). A review of urban air quality studies indicates the toluene/benzene ratio ranges from 2 to 10. Statewide data for the same time period during the study shows that monitored concentrations in the New York City area have an average toluene/benzene ratio of 2.7. Other urban areas in the state have an average toluene/benzene ratio of 2.5. The Whiteface background monitoring site has a toluene/benzene ratio of 1.0. As seen with other urban studies, the New York City area is not dominated by heavy industry and the toluene/benzene ratio is driven by mobile sources. The four monitoring sites have toluene/benzene ratios of 1.07, 1.02, 0.29, and 1.38 for BISP, BTRS, GIBI, and SPWT, respectively. These toluene/benzene ratios indicate that the monitors located in the Study area are less

influence by mobile sources than other urban sites. Whereas the rural Whiteface site has a toluene/benzene ratio of 1.0, similar to the Study sites, the annual averaged benzene concentration at Whiteface is only 3% of the annual averaged benzene concentration at the GIBI site and 20% of the concentrations at the other Study area sites. The toluene/benzene ratio and the annual average benzene concentration for the GIBI site clearly demonstrate that the benzene monitoring results are dominated by stationary source emissions and not mobile source emissions. Also, for the BTRS site, the annual average benzene concentration is greater than all other urban monitored sites in the State, clearly demonstrating that the monitored results are dominated by emissions from local stationary sources and not mobile sources.

Source Identification
Comparing the benzene concentration at the GIBI monitor to all other U.S. monitors, the benzene concentration was found to be statistically significantly higher than most other data recorded. The annual average benzene concentration at the GIBI monitor was higher than the 95th percentile value for the U.S. network and average annual concentrations at all of the other Study area monitoring sites were greater than the median U.S. concentration. In section 7.1.3, an analysis of variance was conducted between BISP and the other three monitors to determine if the measured concentrations were significantly different than the upwind site. The GIBI and BTRS annual concentrations were both found to be statistically different than the BISP concentration.

The details in section 7.4.2 - Analyses of Wind Direction Influences on Measured Concentrations for Air Contaminants Exceeding DEC's AGCs showed strong directionality with measured benzene concentrations. The GIBI and BTRS polar plots clearly indicate directionality to the south, southwest/southwest (at 202.5-225°) (Appendix M).

The TWA pollution roses for benzene at all four monitoring sites primarily point in towards the industrial area (Figure 7.14). Also, the maximum benzene concentrations for the TWA pollution roses at the various monitoring sites are substantially different, indicating that the combination of the wind direction (with respect to the orientation of a particular monitor and the coke oven facility) and the vicinity to the source greatly influenced the concentrations measured.

The vector lines extended out from the 22.5° arcs pointing towards the industrial area all intersect in the industrial area right at the largest known source of benzene in the area, the Tonawanda Coke Corporation facility. The wind roses for the highest 10% concentration days versus the lowest 10% concentration days for benzene again clearly indicate that the highest concentrations resulted when the wind blew from the direction of the coke oven facility to the monitor location and the lowest concentrations occurred when the winds from this direction were absent. The highest 10% concentration days at both the GIBI and BTRS monitors were when wind was primarily out of the southwest, whereas the lowest 10% concentration days at these same two monitors had no winds coming directly out of the southwest.

The analysis performed in section 7.4.4 - Background versus Local Source Analyses investigated the spatial variation using downwind to upwind ratios. This investigative technique indicates whether a contaminant was predominantly a regional background pollutant or local source issue. The analysis showed that the measured benzene concentration was a product of local sources within the Study area and not a background pollutant.

Over the course of the Study year, inspections by Regional staff indicated that NOCO Energy and Tonawanda Sunoco were in compliance and their emission control equipment was operating appropriately. The NYSDEC is awaiting sampling results from a USEPA inspection conducted in April of 2009 of the Tonawanda Coke Corporation's waste-water and by-product plant emissions. Air Dispersion modeling of the Tonawanda Coke facility underestimated the monitored concentrations detected at the GIBI even when emissions were increased to the maximum potential (See Appendix L - Model to Monitor Comparison).

The analysis of multiple factors (e.g. wind data analysis, benzene/toluene ratios, and facility specific inspection information that has identified uncontrolled emission points), as described throughout the report, identify Tonawanda Coke Corporation as the single largest benzene source contributing to the high benzene emissions monitored at the GIBI and BTRS monitors.

Carbon Tetrachloride

Emissions
The manufacturing and usage of carbon tetrachloride has been phased out as part of the Montreal Protocol. The only reported emissions of carbon tetrachloride emissions in the Study area are residual emissions from the landfills calculated to be less than 1 pound per year.

Source identification
Section 7.1.3 identified six air toxics where the monitor concentrations at the BISP monitor were not statistically different than the concentrations obtained at the other three sites. Carbon tetrachloride was among this group. Carbon tetrachloride monitored data was similar for the entire State of New York and consistent with the median concentration nationwide.

According to the Toxic Release Inventory and the NYSDEC's Air Facility System, the last reported emissions of carbon tetrachloride in NYS were in 2001. The analyses conducted in section 7.4 did not show evidence of directionality based upon the polar plots or the TWA pollution roses at any of the four air monitoring sites.

Formaldehyde

Emissions
Formaldehyde is released from both stationary and mobile sources. It is predominantly a product of combustion and all sources of fossil fuel combustion for electrical generation, industrial processes, and residential heating will release formaldehyde. According to the Study's emission inventory, the point sources of formaldehyde in order of the greatest mass emission are: Indeck Yerkes, NRG Huntley power plant, and Unifrax Inc. The 2002 NATA emission inventory for Erie County shows that mobile source emissions account for 95% of the reported annual 270 tons per year. Mobile source emissions in the Study area were calculated to be approximately 2.0 tons per year. Currently, regulated sources of combustion are required to report to the NYSDEC only criteria pollutant contaminants and the reporting of formaldehyde for major sources is not mandatory.

Source Identification
In the Study area, the concentrations of benzene and formaldehyde at the GIBI site are much higher, as compared to other industrial and urban monitors in the State. The formaldehyde polar plots indicate some directionality, but less strongly than with benzene (Appendix M). All four sites indicate directionality to the south, southwest/southwest (at 202.5-225°), but also from several other directions as well.

The TWA pollution roses for formaldehyde do not clearly indicate a prevailing source in the Tonawanda industrial area (Figure 7.16). However, the differences in the concentrations between the various monitoring sites indicate that there are more local sources influencing the GIBI monitor than any of the other three locations. The closest monitoring site, GIBI does point towards the industrial area, in addition to, pointing along the two major highways adjacent to it. This indicates that this product of combustion is coming both from point and mobile sources in the area. The BISP TWA pollution rose also points in towards the industrial area and the SPWT and BTRS TWA pollution roses indicate some additional minor sources, in some cases also towards roads indicating mobile source influences.

The wind roses for formaldehyde and acetaldehyde are similar, and neither these nor those for acrolein provide strong indications of a large point source in the area as those for benzene. There are many point sources, as well as widespread mobile sources of combustion products like formaldehyde, acetaldehyde, and acrolein. The wind roses for formaldehyde, acetaldehyde, and acrolein were unlike those for benzene in that they did not consistently indicate that winds blowing from the industrial area to the monitor resulted in the highest 10% concentration days and an absence of those same direction winds resulted in the lowest 10% concentration days. Yearly trends showed increases in formaldehyde emissions in the summer months indicating enhanced secondary formation of formaldehyde during the warmer temperatures.

9. Follow-up Activities

The NYSDEC has identified several follow-up activities, as a result of the air quality Study, which are currently being undertaken or expected to be undertaken in the future. The NYSDEC will provide the monitoring and modeling information to the New York State Department of Health for the assessment of a possible community health study in the Tonawanda community. The NYSDEC will continue to work with the community and the CACWNY to investigate odor and irritation complaints associated with industrial emissions in the area. The NYSDEC will continue to work with local industry in the Study area to implement strategies to improve air quality.

9.1 Air Monitoring

The NYSDEC has continued VOC, carbonyl, and $PM_{2.5}$ monitoring at the GIBI and BTRS locations since the end of the formal USEPA grant program in July 2008. The network was continued to evaluate ambient concentrations of HAPs for an additional year at these sites in relation to the base 2007–2008 sampling period. In addition, these sites will allow the NYSDEC to examine the benefits of current HAP reduction activities and any future regulatory actions that may be undertaken by state or federal agencies to reduce mobile and point source emissions.

The NYSDEC has installed a continuous automated benzene, toluene, ethylbenzene, and xylene (BTEX) monitor at the GIBI site, which collects samples every 15 minutes, to further evaluate the high levels of benzene measured at this monitoring site with a higher degree of temporal resolution. The original study used stainless steel canisters, which collected a 24-hour composite sample. The BTEX monitor will allow the NYSDEC to evaluate time of day trends in BTEX concentrations on a daily basis.

The NYSDEC also has installed a high volume sampler for ambient PAHs measurements at the GIBI site that collects a 24-hour sample on a one-in-six day sampling schedule. This monitor was established to measure ambient PAHs in the study area and the samples gathered are analyzed for 21 specific PAHs, including naphthalene. The sampler was located to measure the PAH impacts from known sources of PAH emissions, such as, the Tonawanda Coke Corporation and Huntley Electric Generating station, as well as emissions associated with vehicle and diesel truck traffic and diesel locomotive engines.

9.2 Compliance Inspections

The NYSDEC has increased compliance inspections of all air pollution sources within the study area and has inspected additional sources outside the study area. Initially, these inspections focused on sources of known benzene emissions in the study area. Inspections of the Tonawanda Sunoco and NOCO Energy Petroleum Distribution facilities have been conducted to assess compliance with state and federal air pollution regulations

During and after the Study period, NYSDEC regional staff visited the Tonawanda Coke Corporation many times to observe facility operations to assess potential sources of HAP emissions and assess compliance with their Title V Air Facility Permit. This continuing effort has already resulted in emission reductions that are outlined in the following Subsection (9.3). In April 2009, the USEPA, with cooperation from the NYSDEC, conducted a comprehensive compliance inspection of the Tonawanda Coke Corporation. The results of this inspection will be available in the near future.   The NYSDEC is also reviewing the state and federal conditions contained in the air permits of the facilities in the Study area to evaluate if these conditions could be rewritten to ensure better work practices and oversight of these practices.

As per the Consent Decree between NYSDEC and NRG, the NRG Huntley Electric Generating Station was required to reduce emissions of particulate, nitrogen oxides and sulfur dioxide. In addition, 6NYCRR Part 246 established a cap for mercury emissions starting in January of 2010 which reduces the emissions of mercury at a minimum of 50%. NRG Huntley replaced the electrostatic precipitators, (which only controlled particulates), with baghouses for particulate control, which also allowed for the injection of powder activated carbon for mercury control, trona injection for SO_2 control and urea injection for additional NO_x control. The baghouses operating since the beginning of 2009 have made a tremendous reduction in the number of opacity violations. The trona, urea, and activated carbon are undergoing performance testing and as of the date of this report are not yet in full operation.

9.3 Hazardous Air Pollutant Reduction Actions

In 2008, the Tonawanda Coke Corporation agreed to control emissions from the light oil storage and loading area of the facility. Current air regulations do not require emission controls on these specific units. Emissions from these operations were controlled by connecting the light oil emission points to the suction side of the coke oven gas collection system, thereby reintroducing the collected emissions into coke oven gas stream for further processing. This resulted in a benzene emission reduction from the facility of approximately 1,700 pounds per year.

In 2009, the Tonawanda Coke Corporation agreed to control emissions from their ammonia still beyond levels required by air pollution regulations. This emission unit includes the processes that steam strip ammonia from the ammonia liquor which is removed as a waste contaminant from the raw coke oven gas collected in the coke battery. The remaining clean water is discharged to the local municipal sewage treatment facility. This emissions point was identified by NYSDEC regional staff during their facility operational observation visits as a large source of uncontrolled ammonia, benzene, toluene, xylene, and naphthalene emissions. The control of the ammonia still will reduce ammonia emissions significantly from their current maximum emission rate of 800,000 pounds per year and will also result in smaller, but significant, reductions of benzene (approximately 3000 pounds per year), toluene, xylene, and naphthalene.

During the April 2009 inspection, a pressure regulator on the coke oven gas system was identified as being a possible source of gas oven emissions. Although the amount of gas released from this source is impossible to determine, Tonawanda Coke agreed to increase the pressure set point of the unit to prevent further releases. Since Tonawanda Coke is currently operating at only 50% capacity, a flare has been installed to combust emissions from the pressure regulator should the need arise when production increases.

As a result of the April 2009 inspection, the USEPA has required a number of emission tests and sampling of the various operations at the Tonawanda Coke facility during 2009 and 2010 to assess compliance with federal laws and regulations. The results of these tests may result in further HAP reductions, as required under the NESHAP program. In addition, the results of these tests could be used to make decisions about updating the current New York State regulation, 6NYCRR Part 214 By-Product Coke Oven Batteries.

10. Conclusions

The results of the Tonawanda Community Air Quality Study indicate there is a need for a focused effort to reduce the amount of some HAPs being released in the community. This goal, which is already underway, will be accomplished through continued compliance inspections of facilities in the area, assessments of technological advances in air pollution control that can be implemented through new regulations and/or voluntary reductions to reduce emissions at existing facilities, and continued efforts to reduce emissions from the mobile source sector (e.g. low emissions vehicle program, increased mileage standards for new vehicles, removal of older vehicles from the roadways, and vehicle inspection and maintenance program). These efforts will be monitored with the continuation of ambient air monitoring at the GIBI and BTRS sites (see Follow-up Activities Section 9 for more details).

The monitoring data indicated that there needs to be a concerted effort by the NYSDEC and the USEPA to evaluate all sources of benzene emissions in the community for reductions. This effort has already commenced with the comprehensive inspections of known stationary sources of benzene emissions in the Study area by the NYSDEC and the USEPA.

The investigation of the annual air concentration predictions from two air dispersion models (RAIMI and AerMod) in relation to our monitoring revealed some unexpected results. The predicted model concentration for benzene using the actual emissions inventory for the Tonawanda Coke Corporation was significantly less than the measurements made at the GIBI site. The scaling up of the benzene emissions to reflect the allowable amount under the NESHAP standards resulted in predicted benzene concentrations that remained well below the measured concentrations at the GIBI site. The reason for this discrepancy appears to be the under reporting of benzene emissions by the Tonawanda Coke Corporation. The additional coke oven facility benzene emissions could be the result of leaks and/or other releases of benzene that are not accounted for by the facility in their annual actual emission statements or they could be the results of inaccuracies in the USEPA approved emission factors used to determine facility emissions. This specific issue is being investigated further by the NYSDEC and the USEPA.

In contrast to our benzene findings, the measured concentrations of carbon disulfide were in close agreement with the model predictions. Carbon disulfide has one large point source of emissions and a small contribution of minor emissions from other sources, with no mobile source contributions. 3M Tonawanda is a major source of carbon disulfide releasing over 150 tons per year. The SPWT monitor is within 1,200 meters of 3M Tonawanda and in the prevailing wind direction. The model-to-monitor ratio at this site was close to one (0.99), indicating that the use of modeling with an accurate emissions inventory will provide an accurate prediction of the near site ambient air concentrations in the community.

The comparisons of our monitoring data to the 2002 NATA results indicate that the 2002 NEI used in the NATA model is fairly accurate for a number of air toxics. The NEI emissions inventory has 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. As a risk assessment screening tool designed to identify areas for further air pollution investigations, it would be preferable for the NATA modeled ambient concentrations to be similar to the measured ambient concentrations for those air toxics that are identified as risk drivers. For acrolein, the NATA modeled concentration estimates are approximately an order of magnitude lower than the ambient monitor concentrations in this Study. Therefore, the risks predicted by NATA would be an order of magnitude lower than the actual risk. At the GIBI monitor, the NATA model concentration estimate for benzene is nearly an order of magnitude lower than the ambient monitor concentration. The risk predicted by NATA at this location also would be almost an order of magnitude lower than the actual risk. In general, NATA emission inventory estimates, and therefore model results, appear to be under predicting concentrations and risks for air toxics dominated by emissions from large point sources (benzene) and for air toxics that are also the products of secondary photochemical formation (acrolein and formaldehyde) within the Study area.

It was difficult to verify the benzene results in the Risk Assessment Document for the Coke Oven MACT Residual Risk (which included an evaluation of Tonawanda Coke) using the benzene monitoring data. The maximum individual cancer risk in the residual risk assessment for benzene emissions from the Tonawanda Coke Corporation was 50 in-one-million. However, isopleths illustrating the risk associated with benzene exposure from the facility were not presented in the residual risk document. The residual risk document presents the population cancer risk as the combined risk of arsenic, benzene, and BSO exposure. An assessment of the population cancer risk in the surrounding community, using cancer risk isopleths in the residual risk document, was limited since the isopleths were not provided on a map of the area. This made it extremely difficult to verify the conclusion of the residual risk assessment that facility wide emissions resulted in only three individuals in the surrounding community with a maximum individual cancer risks that were equal to 100 in-one-million. Based on our assessment of the monitored and modeled data, the maximum individual cancer risk and population cancer risk associated with facility-wide emissions from the Tonawanda Coke Corporation exceeds 10 in-one-million cancer risk for the nine census tract Study area and specific neighborhoods exceed the 100 in-one-million cancer risk level (Figure K-3 in Appendix K). Further work will be conducted on this issue by the NYSDEC and information will be provided to the USEPA. A final residual risk assessment for all individual processes within the Coke Oven source category will be prepared by the USEPA in 2011.

Communicating the science of risk assessments related to exposure to air toxics was an extremely important aspect of this study but the presentation of the Study results, including technical details, through a series of public meetings proved to be challenging. Important goals of our public presentations were transparency and the presentation of the study results in a format that would be understood by the general public. In general, the achievement of these goals varies by audience, but for the most part the NYSDEC was

able to attain these goals. This success was due to our close relationship with the CACWNY. We worked together to develop an understanding of the air quality issues that needed to be addressed and worked together to inform the public and elected officials of our findings.

The management of air quality for hazardous air pollutants relies on the use of cancer and non-cancer risk estimates to determine if any further regulatory actions are needed to reduce air pollution. The results of the Tonawanda Community Air Quality Study clearly indicate that further actions are needed to reduce ambient concentrations of benzene and formaldehyde in the community and that further monitoring must be continued to measure any progress in current and future emission reduction strategies. In addition, a comprehensive evaluation of the allowable hazardous air pollutants emissions associated with the modeled cancer risk predictions from the entire Tonawanda Coke Corporation facility needs to be carefully undertaken.

The results of the Tonawanda Community Air Quality Study have provided a better understanding of the necessary future actions to improve air quality in the Tonawanda area.   The Study also has demonstrated the need for carefully designed community-based air toxics monitoring studies to evaluate the effectiveness of State and Federal regulatory actions to reduce exposures to hazardous air pollutants. NYSDEC remains committed to continue the work initiated by this community Study.

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