Informal Consultation on Local Air Issues in Sault Ste. Marie, Ontario-Michigan under the Canada-United States Air Quality Agreement: Technical Support Document on Air Quality 2001-2003

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Summary Report Prepared for Environment Canada, U.S. Environmental Protection Agency, Ontario Ministry of the Environment, Michigan Department of Environmental Quality and Inter-Tribal Council of Michigan by Potvin Air Management Consulting

Executive Summary

The Executive Summary will summarize the information in the report for the information of the people living in Sault Ste. Marie, Ontario and Michigan and be made available in English and French.

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Introduction

This informal consultation in the Sault Ste. Marie area under the Canada-United States Air Quality Agreement is a cooperative initiative between agencies in Canada, the United States and Sovereign Tribes within Michigan, following a process established under the United States-Canada 1991 Air Quality Agreement. The 1991 Air Quality Agreement is a statement of commitment between the United States and Canada to address transboundary air pollution issues. Its stated objectives include improved information exchange on air quality matters, promotion of air quality goals, coordinated planning and management and the use of innovation to resolve air quality issues. The partner agencies for this work are the U.S. Environmental Protection Agency (USEPA) – Region 5, the Michigan Department of Environmental Quality (MDEQ), the Inter-Tribal Council of Michigan (ITCMI), the Ontario Ministry of the Environment (MOE) and Environment Canada (EC).

A Canada-U.S. Algoma informal consultation group was formed in 1998 to address air quality complaints and concerns from citizens in and around the Sault Ste. Marie area. Complaints received by USEPA Region 5 in 1997 pointed to an overall perception of unhealthful air believed to be caused by emissions from the Algoma Steel Inc. mill located in Sault Ste. Marie, Ontario (Kee, 1998). For example, citizens complained about visible emissions from Algoma Steel Inc. and the formation of an orange-brown haze that hung over the city at night under certain weather conditions. Other common complaints include the periodic appearance, with northwesterly winds, of a silvery fine dust that settles on cars and rooftops, periodic tar-like and sulphurous odours, and discolouration and deposits on boats. Analysis of the silvery fine dust, as ordered by the Chippewa County Health Department, indicated the presence of "silver kish" similar to that produced in the iron and steel manufacturing process. Lastly, it was perceived by some citizens that emissions from Algoma Steel Inc. were a contributing factor to adverse health effects of residents in the Sault Ste. Marie/St. Marys River area of Michigan.

The citizen complaints were judged sufficient to warrant further investigation and quantification. This led to a number of information exchanges and meetings in the spring of 1998 between the U.S. and Canadian Subcommittee I (Program Monitoring and Reporting) members aimed at developing a consultation process, and reporting on it to the Canada-U.S. Air Quality Committee. From this process arose the need to establish a bi-national air quality monitoring program to quantify the levels of air contaminants of interest in Sault Ste. Marie, Michigan and to complement the on-going MOE air quality monitoring program in Sault Ste. Marie, Ontario. The ITCMI assumed the responsibility for the operation of the air quality monitoring network in Sault Ste. Marie, Michigan, with assistance from the USEPA and the MDEQ.

This report provides a summary of the air quality monitoring results for the combined MOE and ITCMI networks for the period 2001 to 2003 for the information of the Air Quality Committee and interested citizens of the Sault Ste. Marie region. This report also provides information on: American, Canadian and Ontario standards for air quality; the air contaminants monitored, along with likely sources, impacts, monitoring methods, available emission inventories and trends; recent and future air pollution abatement efforts for major air emitters in Sault Ste. Marie, Ontario, and recommendations on possible modifications to the monitoring program based on the findings to-date.

1. Sault Ste. Marie Area and Air Emission Sources

1.1 Sault Ste. Marie Area

Sault Ste. Marie Ontario and Michigan are located in the centre of the Great Lakes region, on the banks of the St. Marys River which flows from Lake Superior to Lake Huron as shown in Figures 1a and 1b. The area was first named by native Indians as "Bawating", or "gathering place". In the 1600's, the area became one of the first European settlements and acquired its modern name which means the Rapids of St. Mary (Sault Ste. Marie Convention & Visitors Bureau, n.d.). The bi-national community has a population of 77,815 in Sault Ste. Marie, Ontario (Statistics Canada, 2001) and 16,542 in Sault Ste. Marie, Michigan (U.S. Census Bureau, 2000). According to Statistics Canada, the aboriginal population in Sault Ste. Marie, Ontario was 5,610 in 2001, and the U.S. Census Bureau reported 2,270 Native Americans residing in Sault Ste. Marie, Michigan in 2000.

In the late 1890's, advances in technology and transportation made industrial growth in the Sault Ste. Marie area possible. The arrival of the railway, the completion of the canal and the harnessing of the rapids in the St. Marys River for hydroelectric power set the stage for the development of an industrial complex in Sault Ste. Marie, Ontario (Sault Ste. Marie Public Library Archives, n.d.). Forestry, power generation, shipping and steel are the basis of industry in this city, which makes use of its proximity to the raw materials. With its twin canals, the "Soo Locks" are the only water connection between Lake Superior and the other Great Lakes and are known as one of the busiest locks in the world.

1.2 Air Emission Databases

Information about air emissions from Canadian sources is compiled by EC through the National Pollutant Release Inventory (NPRI) and in Ontario by the MOE through the "Airborne Contaminant Discharge Monitoring and Reporting" regulation (Ontario Regulation 127/01- O. Reg. 127/01). Established in 1992 and legislated under the Canadian Environmental Protection Act, 1999 (CEPA, 1999), the NPRI is a database of information on annual releases to air, water, land and disposal or recycling from all sectors – industrial, government, commercial and others – which are required to be reported to the Government of Canada on an annual basis. Pollutants from mobile sources such as trucks and cars, households, facilities that release pollutants on a smaller scale and certain sector activities, are compiled by provinces and Environment Canada into the Canadian National Emissions Inventory. Both this national emissions inventory and the NPRI can be accessed and searched through an on-line database (Environment Canada - NPRI, http://www.ec.gc.ca/pdb/npri/npri_home_e.cfm.)

In Ontario, O. Reg. 127/01 came into effect in 2001 and applies to the province's industrial, commercial, institutional and municipal sectors. Facilities that meet the reporting requirements must report emissions of the following substances: NPRI substances, criteria air pollutants, greenhouse gases and air toxics. Three classes of facilities are specified under O. Reg. 127/01: electricity generation, sectors that contain large sources and sectors that contain small sources. Air emission reports are issued annually and for the smog season (May 1 to September 30). Reports are available on-line through the MOE's OnAIR web site (Ministry of the Environment – OnAIR, n.d.)

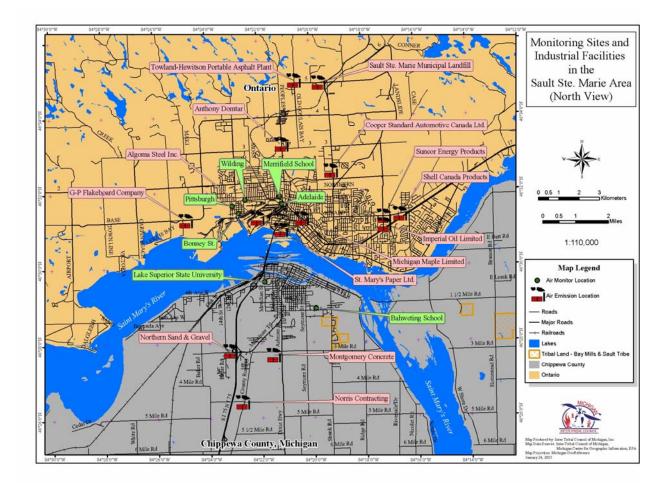
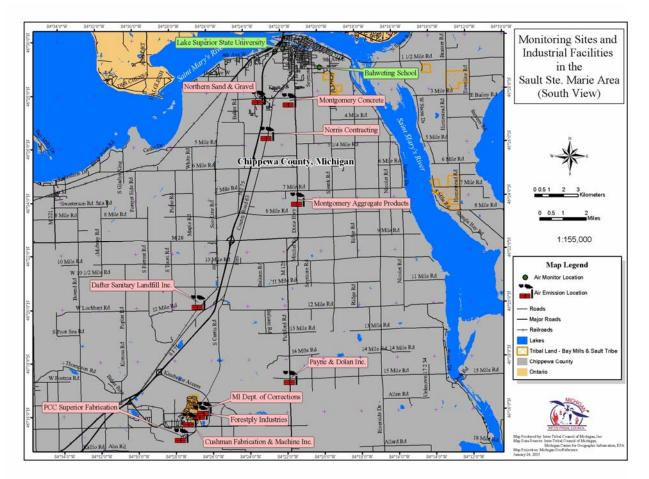


Figure 1a: Monitoring Sites and Industrial Facilities in the Sault Ste. Marie Area (North View)



Note: MI Department of Corrections is referred to in text as Kincross Correctional Facility.

Figure 1b: Monitoring Sites and Industrial Facilities in the Sault Ste. Marie Area (South View).

Data on U.S. emissions is collected by the USEPA in two different databases: the Toxic Release Inventory (TRI) and the National Emissions Inventory (NEI). There are three key differences between the TRI and NEI:

• The NEI is more comprehensive because it includes data for mobile sources and smaller stationary sources, also called "area sources", in addition to industrial source data.

• The TRI contains self-reported industrial data, which may differ from NEI information taken from state and local air agency emissions inventories.

• The NEI is updated every three years and TRI is updated annually.

The TRI contains data on industrial emissions to air and water as well as wastes disposed on-site and off-site. Data are reported by industries for 650 hazardous air pollutants (HAPs) and persistent, bioaccumulative and toxic (PBT) chemicals. The TRI was established as part of the Emergency Planning and Community Right-to-Know Act (EPCRA) of 1986. EPCRA's primary purpose is to inform communities and citizens of chemical hazards in their areas. HAP emissions are reported for individual facilities that emit at least 9.1 tonnes (t.) (10 tons) per year of a single HAP, or at least 22.7 t (25 tons) per year of a combination of HAPs. The TRI can be accessed through the USEPA website (USEPA - TRI, n.d.)

The NEI contains information on criteria air pollutants, precursors of ozone and particulate matter, and 188 HAPs. Emissions inventories have been required for criteria pollutants since 1979 under authority of the Clean Air Act. The NEI data are used by the USEPA for air dispersion modeling, regional strategy development, regulation setting, air toxics risk assessment, and tracking trends in emissions over time. Annual reporting thresholds are as follows for stationary sources emitting criteria pollutants: 91 t (100 tons) for sulphur oxides (SOx, NOx, VOCs, and PM (PM10 or PM2.5); 909 t (1,000 tons) for CO; and 4.5 t (5 tons) for lead.

1.3 Local Air Emission Sources

The largest air emitters in the Sault Ste. Marie area are located on the Ontario side, as shown in Figure 1a, and include:

• Algoma Steel Inc., is a fully integrated steel producer that employs 3000 and has a raw steel production capacity of approximately 2.54 million t per year. Actual production values for the period 1994 to 2004 are presented in Figure 2. Since 2002, production has increased to levels above 1995 to 2000 values. The NPRI and O. Reg. 127/01 databases indicate that of the local industrial facilities, this facility has the largest air emissions of Criteria Air Contaminants (CACs), including particulate matter (PM) and volatile organic compounds (VOCs); trace metals; and polycyclic aromatic hydrocarbons (PAHs) in the Sault Ste. Marie area.

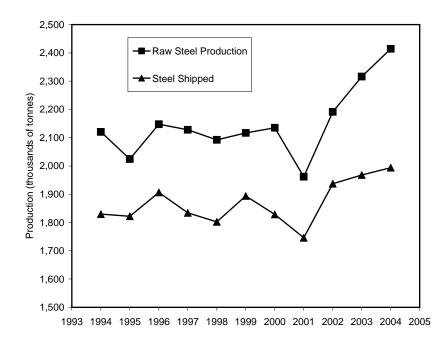


Figure 2: Algoma Steel Inc. Production values 1994 through 2004

- St. Marys Paper Ltd. is a 217,700 t per year ground wood paper mill with 400 employees. It produces paper for magazine publishers and large retail companies for high quality advertising inserts, flyers and catalogues. This facility has reportable air emissions of PM, oxidized nitrogen compounds (NO_x,) trace metals, carbon monoxide (CO), ammonia, phenol, methanol and isopropyl alcohol.
- Brascan Power Corporation (Lake Superior Power) operates a hydro-electric generation station (Francis H. Clergue Generating Station) with an installed generating capacity of 52 megawatts (MW). This facility has no reportable air emissions.
- G-P Flakeboard Company is a medium density fibre board mill, commissioned in 1995 with the latest air pollution control technology, and a rated capacity of 31 t per hour. It has reportable emissions of CO, PM, VOCs, NO_x, methanol and formaldehyde.
- Towland-Hewitson Construction Ltd. operates several portable asphalt plants on a seasonal basis (April to November). It has reportable emissions of PM.
- Suncor Energy Products Inc., Imperial Oil Ltd., and Shell Canada Products each have a gasoline/oil bulk terminal and reportable VOC emissions.
- Michigan Maple Limited is a manufacturer of hardwood (maple, oak, etc.) specialty items such as restaurant cutting blocks, counters, etc. with reportable PM emissions.
- Cooper-Standard Automotive Canada Ltd. is an automotive products manufacturer specializing in automotive fluid handling systems. It has reportable emissions of VOCs.
- Sault Ste. Marie municipal landfill has reportable emissions of VOCs.

Abatement activities for these facilities are described in Section 8.

According to the U.S. NEI, there are no stationary sources in Sault Ste. Marie, Michigan which emit reportable quantities of criteria air pollutants. The TRI air toxics inventory does not indicate any sources of HAPs above the reporting thresholds in Chippewa County. However, the county does include two facilities that emit criteria pollutants or precursors near Sault Ste. Marie as shown in Figure 1b: the Dafter Sanitary Landfill located 16 km south of Sault Ste Marie emits VOCs and the Kinross Correctional Facility (MI Dept. of Corrections) in Kincheloe located 26 km south emits quantities of SO₂ and PM. Also shown in Figure 1b are small point sources of PM in the construction, aggregates and forestry sectors. The NEI also estimates about 20 waste dumps in the county, each of which emits small quantities of VOCs.

Other important sources of local air emissions in the bi-national area include automobile and truck traffic within the urban communities and travelling across the international bridge, freight ship traffic along the St. Marys River, and other non-road mobile sources such as recreational vehicles and agricultural equipment. These mobile sources are significant contributors of PM, VOCs and other precursors of ozone and fine particulate matter. Both communities also contain numerous small emitters such as gas stations, dry cleaners and paint shops. The U.S. NEI has estimates from mobile and small point sources in Chippewa County, however, a comprehensive emission inventory for these mobile and area sources in the bi-national Sault Ste. Marie airshed

has not been completed. As of the time of the preparation of this report the ITCMI has prepared a draft emissions inventory of the bi-national area within a 24 km radius of the two local tribes.

2. The Air Monitoring Network

The transboundary air monitoring network operated by the MOE and ITCMI, for this informal consultation, measures many of the air pollutants emitted by local industries and the mobile sources mentioned above. These include PM, trace metals, VOCs, PAHs and the following trace gases: sulphur dioxide (SO₂), oxides of nitrogen (NO_x) reported as nitrogen dioxide (NO₂), total reduced sulphur (TRS) compounds and ground-level ozone (O₃). As shown in Figures 1a and 1b, the network consists of two sites in Michigan and five sites in Ontario. Sampling site details are presented in Table 1. The monitoring methods used in this study are briefly described in Appendices A to P.

Site	Location	Operating agency	Pollutant	Sampling frequency
Lake Superior		ITCMI	PM _{2.5} (FRM); speciated	1-in-3 days
State Univ. USEPA site code	650 W. Easterday, Sault		VOCs & PAHs	1-in- 6 days
26-033-0901	Ste. Marie, Michigan	-	Wind/ temperature	Continuous
MOE site code:		MOE	PM _{2.5} (TEOM)	Continuous
71080		MOE	Dustfall	Monthly
Bahweting Elem. School USEPA site code:	1301 Marquette Ave., Sault	ITCMI	PM _{2.5} (FRM)	1-in-3 days
26-033-0902 MOE site code: 71081	Ste. Marie, Michigan	MOE	Dustfall	Monthly
			PM _{2.5} (TEOM)	Continuous
Merrifield	Patrick Street, Sault Ste. Marie Ontario	MOE	PM ₁₀ ; speciated	1-in-6 days
School			Soiling index	Hourly
MOE site code:			VOCs & PAHs	1-in-12 days
71068			SO ₂ , NO ₂ , O ₃ , TRS, wind/temp	Continuous
			PM _{2.5} (TEOM)	Continuous
Bonney Street	65 Bonney St.	MOE	PM ₁₀ & TSP; speciated	1-in-6 days
MOE site code: 71042	Sault Ste. Marie, Ontario	MOE	VOCs & PAHs	1-in-12 days
/1042			TRS	Continuous
			Dustfall	Monthly
Pittsburgh MOE site code: 71015	Pittsburgh & Young Streets, Sault Ste. Marie, Ontario	MOE	Dustfall	Monthly
Wilding MOE site code: 71043	Wilding Ave. & Wallace Terrace, Sault Ste. Marie, Ontario	MOE	Dustfall	Monthly
Adelaide MOE site code: 71045	73 Adelaide Street, Sault Ste. Marie, Ontario	MOE	Dustfall	Monthly

Table 1: Bi-national Air Monitoring Network Site

2.1 Sault Ste. Marie Michigan

In Sault Ste. Marie, Michigan, the main site operated by the ITCMI is centrally located at Lake Superior State University (LSSU) and the second site is approximately 3 km southeast on Chippewa tribal lands at the Bahweting Elementary School. The LSSU site is 3.2 km south, and the Bahweting site is about 5.6 km south-southeast of the Algoma Steel Inc. complex. At the LSSU site, the ITCMI operates two collocated $PM_{2.5}$ filter-based samplers using the U.S. Federal Reference Method (FRM). It also operates a $PM_{2.5}$ speciation sampler which collects the ionic and elemental components of particulate matter; a VOC and PAH sampler; and a meteorological station which measures wind speed, wind direction and temperature. The LSSU site also has a continuous $PM_{2.5}$ mass monitor, provided by EC and which operates using tapered element oscillating microbalance (TEOM) technology, and a dustfall sampler provided by the MOE. At the Bahweting Elementary School site, ITCMI operates a filter-based $PM_{2.5}$ sampler and the MOE has a dustfall sampler.

The dustfall sampling sites were established in the fall of 1998. The $PM_{2.5}$ samplers and monitors were commissioned in the fall of 2001, and the VOC and PAH samplers were added in the spring of 2003.

2.2 Sault Ste. Marie Ontario

In Sault Ste. Marie, Ontario, air quality monitoring was initiated by the province in the early 1960s. Since that time, the network has undergone numerous changes which, together with the monitoring results, have been documented in MOE reports (Potvin & McGovern, 1976, 1980; Olivier and Potvin, 1995; Clara and Racette, 1996; Racette, 1997 to 2001). For the period covered in this report, the main sites were located at Merrifield School on Patrick Street, approximately 1.5 km northeast of the Algoma Steel Inc. complex, and on Bonney Street which is in a residential neighbourhood adjoining the northwestern fence line of the Algoma Steel Inc. property.

The three other sites, which monitor only dustfall, are located between 1.1 km to 1.5 km to the northwest (intersection of Wilding and Wallace Terrace, and intersection of Pittsburgh Avenue and Young Street) and to the northeast (Adelaide Street) of the Algoma Steel Inc. complex. All five sites on the Ontario side are operated by the MOE.

The Bonney Street site was established in 1975 with the installation of a hi-vol sampler, to measure total suspended particulate (TSP) and trace metals in TSP, and a dustfall jar. By 1991, the air monitoring program at this site had been expanded to include samplers for inhalable particulate (PM_{10}), VOCs and PAHs, and a continuous TRS monitor. A continuous respirable particulate ($PM_{2.5}$) monitor was installed in 2000 (TEOM) and subsequently moved to the LSSU site in Michigan in 2001.

The Merrifield School site on Patrick Street was established in 1987 and with the 1988 launching of the AQI system in Ontario became the Air Quality Index (AQI) station for the city of Sault Ste. Marie. During the period covered in this report, air monitoring of the following parameters was performed at this site: SO_2 , NO_x , O_3 , TRS, VOCs, PAHs, PM_{10} (speciated), continuous $PM_{2.5}$ (TEOM), suspended particulate as coefficient of haze (COH), and wind speed/direction and temperature at 10 metres above ground.

Dustfall sampling at the Pittsburgh Avenue/Young Street site began in 1970, and at the Adelaide Street and Wilding/Wallace Terrace sites in 1975.

2.3 Comparison of QA/QC Procedures

A subgroup of the Canada-U.S. Algoma Consultation Group was formed in 2002 to review the two countries' respective sampling methodologies and quality assurance/quality control (QA/QC) procedures. The purpose of this evaluation was to ensure that data collected by Canadian and American agencies were comparable and of similar quality. The QA/QC team performed an audit of the ITCMI samplers in July 2003 and also visited the monitoring sites on the Ontario side. The subgroup's findings are documented in the report *Comparison of Quality Assurance Procedures and Regulations – Final* (Canada-U.S. Algoma Consultation Air Quality Group, 2003)

The subgroup found that both governments follow standard protocols related to the collection of ambient air monitoring data. These protocols, which are briefly outlined in the subgroup's final report, are similar in regards to the actual activities which ensure that data collected is of sufficient quality. All air monitoring audit and calibration devices are traceable to the National Institute of Standards and Technology (NIST). Data validation processes are similar and data collected from each government should be of equitable quality when standard protocols are followed.

3. U.S. and Canadian Air Quality Management Programs

There are some similarities and a number of notable differences in the manner with which both countries manage their air quality monitoring, assessment and enforcement programs. The U.S., Canada and Canadian Provinces have established ambient air quality 'limits' based on the best scientific information available to safeguard human health and the natural environment. The 'limits' developed by the respective agencies differ on the list of pollutants they regulate, as well as on the allowable concentrations and averaging times. The criteria and standards for the air contaminants discussed in this report are shown in Tables 2, 3, 4 and 5.

3.1 U.S. Air Quality Management Program

3.1.1 National Ambient Air Quality Standards

The U.S. Clean Air Act requires the USEPA to set mandatory National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment (Table 2) which must be met. The Clean Air Act established two types of national air quality standards. Primary standards set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. Secondary standards set limits to protect public welfare, including protection against decreased visibility, damage to animals, crops, vegetation, and buildings. The USEPA Office of Air Quality Planning and Standards has set NAAQS for six so-called "criteria" pollutants: CO, lead, nitrogen dioxide (NOx), ozone, PM, and SO₂. The Clean Air Act requires the USEPA to review the levels of these standards every five years.

Air quality monitoring data is the basis for determining whether areas are exceeding air concentration limits. Areas that are experiencing or are contributing to air quality violations of the NAAQS are designated by the USEPA as nonattainment for the pollutant in question. Upon designation, areas become subject to an attainment date, or deadline by which they are required to be in compliance with the NAAQS. Generally this date is 5 years after designation, but can vary from 3 - 20 years depending on the pollutant and the severity of the problem.

Once an area is designated as nonattainment for one or more NAAQS, the responsible state agency is required to develop a State Implementation Plan (SIP). The SIP details the steps that will be taken to bring the area into attainment of the standard by the attainment date. These plans may include emissions inventories and modelling assessments as well as specific stationary and mobile source control measures which are set forth in state regulations, orders or legislation. States are generally required to submit these plans to the USEPA for federal approval within 3 years of designation, although this date can vary for certain types of submissions. Once approved by the USEPA, these SIPs and their associated control measures are enforceable at both the state and national levels.

	· · · · · · · · · · · · · · · · · · ·	Onterio		Canada		U.S. NAAQS		
Pollutant	Averaging Time	Ontario	NAA	$\mathbf{Q}\mathbf{Q}^{1}$	CWS ²	Duimanur	Casandami	
	Inne	AAQC	MD	MA	CWS	Primary	Secondary	
PM _{2.5}	24 hours	none	none	none	30*	65 ⁶	none	
$(\mu g/m^3)$	Annual	none	none	none		15 ⁶	same as primary	
PM ₁₀	24 hours	50^{3}	none	none		150 ⁷	none	
$(\mu g/m^3)$	Annual	none	none	none		50 ⁷	same as primary	
	24 hours	120	none	120		260	none	
TSP ($\mu g/m^3$)	Annual	60 ⁴	60 ⁴	70		(historic) 60 (historic)	none	
Dustfall	30 days	$7.0g/m^2/30d$	none	none		none	none	
$(g/m^2/30d)$	Annual	$4.6g/m^2/30d$	none	none		none	none	
Soiling	Annual	0.5 COH	none	none		none	none	
Index	24 hours	1.0 COH	none	none		none	none	
	Annual	20	10	20		30	none	
SO_2 (ppb)	24 hours	100	60	110		140	none	
30 ₂ (ppb)	3 hours	none	none	none		none	500	
	1 hour	250	170	340		none	none	
	Annual	none	30	50		53	same as primary	
NO ₂ (ppb)	24 hours	100	none	110		none	none	
	1 hour	200	none	210		none	none	
	Annual	none	none	15		none	none	
O_3 (ppb)	24 hours	none	15	25		none	none	
C3 (ppu)	8 hours	none	none	none	65**	80 ⁸	same as primary	
	1 hour	80	50	80		120	same as primary	
TRS (ppb)	24 hours	none	none	3.65		none	none	
TK2 (ppu)	1 hour	27	0.7^{5}	10.8 ⁵		none	none	

Table 2: Canadian and American Air Quality Criteria/Objectives/Standards for Criteria Air Contaminants

¹ Canadian objectives are two-tiered: MD = maximum desirable, MA = maximum acceptable

² CWS for PM_{2.5} and ozone to be achieved by 2010

* CWS for $PM_{2.5}$ is 30 µg/m³, 24-hour averaging time, based on the 98th percentile annual concentration averaged over 3 consecutive years.

** CWS for O_3 is 65 ppb, 8-hour running average time, based on the 4th highest annual concentration averaged over 3 consecutive years.

³ Interim criterion ⁴ Geometric mean ⁵ Pro

n ⁵ Proposed objectives

⁶ primary NAAQS for PM_{2.5} is $65 \ \mu g/m^3$, 24-hour averaging time, based on the 98th percentile 24-hour concentration averaged over 3 consecutive years. (This was revised in September 2006 to $35 \ \mu g/m^3$, 24-hour averaging time, based on the 98th percentile 24-hour concentration averaged over 3 consecutive years.) NAAQS for PM_{2.5} is 15 $\ \mu g/m^3$, annual average, based on the annual concentration averaged over 3 consecutive years.

⁷ primary NAAQS for PM₁₀ is 150 μ g/m³, 24-hour averaging time, based on the 99th percentile 24-hour concentration averaged over 3 consecutive years. Primary NAAQS for PM₁₀ is 50 μ g/m³, annual average, based on the annual concentration averaged over 3 consecutive years.

⁸ Primary NAAQS for ozone is 80 ppb, 8-hour running average time, based on the annual 4th highest daily maximum 8-hour concentration

3.1.2 Air Toxics Health Benchmarks

In addition to criteria pollutants, the Clean Air Act also lists 188 HAPs, including several toxic metals, VOCs, and PAHs, which are known or suspected to cause cancer or other serious health effects. The USEPA has established health benchmarks (USEPA, 2002) to estimate potential non-cancer and cancer health risks associated with long-term (chronic) exposure to HAPs. The benchmark for estimating long-term non-cancer health effects is termed its reference concentration (RfC). The RfC is an ambient concentration for a certain HAP thought to be without adverse effects even if a person is exposed over a lifetime. The benchmark used to quantify excess cancer risks is risk specific concentration (RSC), which is the air concentration required to create a particular level of cancer risk. For example, people with a lifetime exposure to a specific HAP equivalent to its 1-in-1 million RSC are believed to have a 1-in-1-million probability of developing the disease. A goal of USEPA air toxics programs is that the greatest possible number of people are exposed to individual lifetime cancer risk from HAPS no higher than approximately 1-in-1 million, and that no person is exposed to HAP concentrations greater than those associated with a 100-in-1 million cancer risk level. To estimate risks associated with long-term exposures, the USEPA cancer risk benchmarks are compared to annual and/or multivear measured concentrations.

The cancer and non-cancer risk benchmarks are not enforceable standards, but are guidelines to be considered with other factors such as the technical feasibility of emissions reductions. They are included in this report to allow a screening-level evaluation of the potential health significance of pollutant concentrations measured in this study and to suggest pollutants that could be further investigated in the bi-national community. The American health benchmarks are listed in Table 3 for trace metals, in Table 4 for PAHs and in Table 5 for VOCs.

		U.S. Health benchmarks (µg/m ³)			
Trace metal	Ontario 24 hr AAQC (µg/m ³) ^a	Non-cancer	Cancer RSC		
		RfC	1-in-1 million	100-in-1 million	
Cadmium ^d	2.0 ^b	0.02	0.00056	0.056	
Chromium ^d	1.5 ^b	0.1	0.00008	0.008	
Copper	50	None	no	ne	
Iron (metallic)	4	None	no	ne	
Ferric oxide	25	None	no	ne	
Lead ^d	2.0	1.5 ^c	none		
Manganese	2.5	0.05	none		
Nickel ^d	2.0 ^b	0.2	none		
Vanadium	2.0	None	no	ne	
Zinc	120	None		ne	

 Table 3: Ontario Criteria and American Health Benchmarks for Trace Metals

^a Limiting effect is health except for iron and ferric oxide (soiling), nickel (vegetation) and zinc (particulate)

^bUpdated standards to be phased-in within 5 years ^c NAAQS based on quarterly average

^d Identified on CEPA toxics list

3.1.3 Regional Haze Rule

In 1999, the USEPA enacted the Regional Haze Rule, a major effort to improve air quality in national parks and wilderness areas. The rule calls for state and federal agencies to work together to improve visibility in 156 national parks and wilderness areas such as the Grand Canyon, Yosemite, and including the Seney Wildlife Refuge in the Michigan upper peninsula.

The rule requires the states, in coordination with USEPA and other agencies, to develop and implement air quality protection plans to reduce the pollution that causes visibility impairment. The first State plans for regional haze are due in the 2003-2008 timeframe. U.S. counties which emit $PM_{2.5}$ and precursors that impact visibility in protected areas will be required to reduce emissions, regardless of their $PM_{2.5}$ attainment status.

		U.S. Health benchmarks (ng/m ³) Cancer Risk		
PAH compound ^d	Ontario 24 hr AAQC (ng/m ³)			
	(1-in-1 million	100-in-1 million	
Benz(a)anthracene	None	9.0	900	
Benzo(a)pyrene	$1.1^{a} \ 0.22^{b} \ 0.3^{c}$	0.91	91	
Benzo(b)fluoranthene	None	9.0	900	
Benzo(k)fluoranthene	None	9.0	900	
Chrysene	None	91	9100	
Dibenz(a,h)anthracene	None	0.8	80	
Indeno(1,2,3-cd)pyrene	None	9.0	900	
Benzo(g,h,i)perylene	None	-	one	

 Table 4: Ontario Criteria and American Health Benchmarks for PAH Compounds

^a For single source ^b Annual average - single source ^c Annual average - all sources ^d All PAHs identified on CEPA toxics list

3.2 Canadian and Ontario Air Quality Management Programs

3.2.1 Canadian National Ambient Air Quality Objectives

Canada has traditionally assessed the impact of anthropogenic activities on air quality and ensured that current emission control policies are protecting human health and the environment by using National Ambient Air Quality Objectives (NAAQOs) as the benchmark. These were first developed in the mid-1970s under the Canadian Clean Air Act (now the Canadian Environmental Protection Act (CEPA)) by a federal-provincial advisory committee on air quality for the following criteria pollutants: SO₂, CO, NO₂, O₃ and TSP. These objectives comprise a two-tiered approach (maximum desirable and acceptable levels), which identify ranges of air quality with specific levels of effect:

• The maximum desirable level is the long term goal for air quality and provides a basis for an anti-degradation policy for unpolluted parts of the country and for the continuing development of pollution control technology.

• The maximum acceptable level is intended to provide adequate protection against effects on soil, water, vegetation, materials, animals, visibility, and personal comfort and wellbeing.

These objectives are not legally enforceable under federal legislation (CEPA) but can be adopted by the provinces as objectives or as enforceable standards using their legislation. Ambient air quality measurements from the National Air Pollution Surveillance (NAPS) network are published annually (since 1972) and the results compared to the NAAQOs. The NAPS air monitoring stations, which include the Patrick and Bonney Street sites in Sault Ste. Marie, are operated by the NAPS network agencies of the federal, provincial, territorial and municipal governments. The NAPS network also measures ambient concentrations of PM_{10} and $PM_{2.5}$ and related metals and ions, and an extensive list of volatile and semi-volatile compounds (Environment Canada - NAPS, n.d.).

Further to a review of the objectives in 1992, a national advisory committee and working group on air quality objectives and guidelines recommended a new NAAQO framework based on two levels: a reference level which is the level above which there are demonstrated effects on human health and/or the environment; and an Air Quality Objective (AQO) which is a concentration that reflects a specified level of protection for the general population and environment, but which also considers aspects of technical feasibility. These levels are based on the development of an extensive science assessment document which reviews the relevant scientific evidence. The original NAAQOs have not been formally revised to the new two-level system which is still subject to peer review and stakeholder consultation.

3.2.2 Canada-Wide Standards

In recent years, through the Canadian Council of Ministers of the Environment (CCME), the federal, and provincial and territorial governments have agreed to establish Canada-wide Standards (CWS) for substances of high priority, consistent with the Canada-wide Accord on Environmental Harmonization. These include particulate matter ($PM_{2.5}$) and ozone, substances that were being developed as AQOs. CWS are science-based in the same manner as AQOs, but they also explicitly recognise and incorporate a number of other factors including technical feasibility and economic issues. They have the explicit buy-in of federal and provincial governments and involve the development of jurisdictional risk management plans to attain the agreed-upon standard.

The CWS for particulate matter and ozone is to be achieved by 2010. Jurisdictions are in the process of implementing and designating their monitoring stations and reporting areas for CWS achievement determination. Each CCME member is responsible for implementing the CWS in its own jurisdiction with measures it deems appropriate: these include pollution prevention planning, voluntary programs, codes of practice, guidelines, economic instruments or regulations (CCME, n.d.)

3.2.3 Ontario

The legislative basis for air quality management in Ontario is the Ontario Environmental Protection Act (EPA) and regulations which are issued under the EPA. General provisions of the

EPA prohibit the release of contaminants to the environment unless authorised under a Certificate of Approval (C of A).

3.2.4 Ontario Point of Impingement Standards

The enabling legislation for the Point of Impingement (POI) standards is Ontario Regulation 346 (O. Reg. 346) of the EPA. There are standards for approximately 90 pollutants based on a half-hour averaging period. These standards were developed on the basis of risk to human health and the environment, coupled with a management assessment of the cost/benefit aspects of achieving the proposed standards. In addition to the POI standards, the MOE also assesses non-regulated pollutants on an as-needed basis and develops interim standards (pending the completion of a risk management framework for air standards), guidelines and approvals screening levels using the same process as for the regulated parameters. The most recent compilation of these values is dated September 2001 (Ontario MOE, 2001) and covers over 300 pollutants.

3.2.5 Ambient Air Quality Criteria

The September 2001 compilation also includes values for the MOE Ambient Air Quality Criteria (AAQC) which are air quality levels deemed desirable in Ontario (Tables 2, 3, 4, and 5). These are defined in Ontario Regulation 337 and form the basis for the development of standards, interim standards and approvals screening levels. The AAQC values are generally set with an averaging time of 24 hours; a small number are annual, 30 day, 1 hour and a few are 10 minute averages (odour-based). The limiting effect may be based on health, odour, soiling, corrosion, particulate, ozone depletion or effects on vegetation. The AAQC are not enforceable unless they are included in a regulatory instrument such as a C of A or a Control Order.

3.2.6 Regulatory and Enforcement Activities

The MOE regulatory and enforcement activities focus on local air quality concerns affecting Ontario's communities. The primary mechanism to assess compliance with the POI standards has been the C of A process, under Section 9 of the EPA. In order to build or expand their operations, industrial and commercial facilities with air emissions are required to obtain a C of A. With certain exceptions, a C of A is required for all new sources of air emissions or proposed alterations to existing sources. Air dispersion modeling (currently O. Reg. 346 models) is used in the C of A process to assess the likelihood of compliance with the POI standards. The process requires the production of a detailed emissions summary and dispersion modeling report, which includes air pollutants for which there are no standards or guidelines if their ground level concentration is deemed unacceptable by the MOE. The C of A process also requires public notification so that concerns from stakeholders about air emissions from a new and/or modified facility are brought forward and addressed in a timely manner.

The EPA also has a provision for the issuance of a Control Order to a company wherein a plan and accompanying schedule for achieving compliance with the POI standards is set out. As long as the company meets the terms and conditions of the order, it will not be prosecuted for the original non-compliance issue. More recently, the MOE has been using a new tool to obtain environmental improvements called an Environmental Management Agreement (EMA). It is a voluntary agreement that complements the requirements of the regulatory process: it incorporates environmental initiatives that go beyond regulatory requirements. An EMA identifies and tracks projects and initiatives that the company and the MOE have agreed to, and that the company is committed to completing under specified timelines. In 2000, EC, the MOE and Algoma Steel Inc. formalised an EMA related to a number of 'beyond compliance' environmental issues, several of which are specific to air emissions.

The MOE can require an industrial emitter to perform off-property ambient air monitoring to ensure compliance with ground-level concentration limits set out in a Control Order, or to compare measured data against AAQC values. The MOE is in the process of transferring its compliance monitoring activities across the province to major industrial facilities, such as Algoma Steel Inc.

The MOE also conducts audits of facilities: under its Selected Targets for Air Compliance (STAC) initiative, a number of facilities in key sectors have been chosen to assess compliance with the requirements of O. Reg. 346. In these audits, the MOE requires industries to identify and assess their air emission sources to determine compliance. In the event that a standard is exceeded, the MOE deals with the individual industrial emitters on a facility-by-facility basis to reduce the non-compliant emission.

The MOE has initiated a consultation process regarding proposed amendments to Ontario's air regulations. The proposal encompasses the introduction of new air dispersion models, the setting of new air standards for 29 compounds or groups of compounds and the adoption of a new risk-based decision making process for implementing new air standards or models. This initiative is part of Ontario's Plan for Clean Air (Ontario MOE, n.d.).

		U.S. Health Benchmarks (µg/m ³)			
VOC Compound	Ontario 24 hr AAQC (µg/m ³) ^c	Non-cancer	Cancer RSC		
	(µg/m)	RfC	1-in-1 million	100-in-1 million	
Acetone ^d	48,000	none	no	ne	
Acetonitrile	None	10	no	ne	
Acrylonitrile ^a	0.6 0.12 ^b	2.0	0.015	220	
Benzene ^a	None	30	0.13	500	
Bromodichloride	n/a	none	none		
1,3-butadiene ^a	None	2	0.033	n/a	
Butyl acetate ^d	248	none	none		
Carbon tetrachloride ^a	2.4	40	0.067	n/a	
Chloroethene	n/a	none	no	ne	
Chlorobenzene	None	1000	no	ne	
Chloroform	1.0 0.2 ^b	98	no	ne	
Cis-1,3-dichloropropane	n/a	none	no	ne	
Cyclohexane	100,000	none	none		
1,2-Dibromoethane	n/a	none	none		
1,2-Dichlorobenzene	n/a	none	none		
1,3-Dichlorobenzene	n/a	none	no	ne	

Table 5: Ontario Criteria and American Health Benchmarks for VOC Compounds

1,4-Dichlorobenzene	95	800	0.091	n/a
1,1-Dichloroethane	200	500	0.63	n/a
1,2-Dichloroethane ^a	2.0 0.4 ^b	2,400	0.038	n/a
Dichloroethene	n/a	none	nor	ne
Dichloromethane ^c	220	none	nor	
1,2-Dichloropropane ^d	2,400	4	0.053	5.3
Diisobutylene	n/a	none	nor	ne
Ethylbenzene	1,000	1,000	nor	ne
Hexane	12,000	200	nor	ne
Isopropyl ether	110,000	none	nor	ne
Methylene chloride	220 44 ^b	1,000	2.1	210
Methyl ethyl ketone	1,000	5,000	nor	ne
Methyl isobutyl ketone ^d	1,200	3,000	nor	ne
Naphthalene	22.5 50 ^e	3.0	none	
a-Pinene	n/a	None	none	
2 – propanol ^d	24,000	none	none	
Styrene	400	1,000	none	
1,1,2,2-tetrachloroethane	n/a	None	none	
Tetrachloroethylene ^a	360	270	0.17	17
Toluene ^d	2,000	400	nor	ne
1,2,4-Trichlorobenzene	400	200	nor	ne
1,1,1-Trichloroethane ^a	115,000	1,000	nor	ne
1,1,2-Trichloroethane	115,000	400	0.063	6.3
Trichloroethylene ^a	115 23 ^b	600	0.5	50
Trichloromethane ^c	500	none	nor	ne
1,2,4-Trimethylbenzene	1,000	none	nor	ne
1,3,5, Trimethylbenzene	n/a	none	nor	ne
Vinyl chloride ^a	1.0 0.2 ^b	100	0.11	11
Xylenes, total ^d	2,300	100	nor	ne

^a Identified on CEPA toxics list ^c Limiting effects based on health except as noted ^e 10-minute average

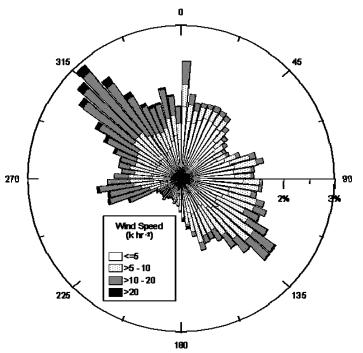
^b Annual average ^d Limiting effect based on odour

4. Meteorology and Air Quality

Weather has a major influence on air quality. The dispersion and behaviour of air contaminants is directly affected by wind, temperature, precipitation, sunshine and the stability condition of the atmosphere. Once released into the atmosphere, air contaminants and precursor substances follow the air currents and undergo chemical transformations, and removal and/or dispersion depending on prevailing meteorological conditions. These conditions also have a significant influence on the speed or the rate at which these processes occur.

Generally, the concentration of air pollutants will decrease with increasing wind speed and viceversa. Air pollution episodes typically occur under light or stagnant winds since the atmosphere is unable to quickly flush out or disperse the pollutants, and these can build up leading to elevated ground-level concentrations. Wind direction determines which areas near or downwind of a source will be affected. Wind directions have seasonal patterns, for example: in many areas of Ontario, winds typically are from the south-southwest, the southwest and the west during the late spring and summer months. During the colder seasons, the winds generally blow from the northwest and the north.

Knowledge of the frequency distribution of wind directions in an area, typically represented in a wind rose diagram, is very important in identifying acceptable sites for new sources of air pollutants near populated areas and in determining the pollution controls or strategies required. A wind rose diagram, produced from data collected at the MOE site on Patrick Street for the period 1998 to 2004 is shown in Figure 3. The prevailing winds at that location were observed to be blowing from the northwest, the southeast and the west-southwest quadrants, with the stronger winds (> 10 km/h) associated with the northwest quadrant. The annual wind data from the Environment Canada weather station located at the Sault Ste. Marie airport, for the period 1990-



2001, are summarised in Table 6. The airport wind data shows very predominant winds from the east and east-southeast sectors and also from the west-northwest and northwest sectors. The strongest winds can be seen to be associated with the northwest and west-northwest sectors. Some of these prevailing wind directions, specifically strong northwesterly winds would direct air emissions from the industrialised western section in Sault Ste. Marie, Ontario across the St. Marys River over Chippewa County, Michigan.

Figure 3: Wind Rose Constructed from Data Collected (1998-2004) at MOE Patrick Street Site

Informal consultation in Sault Ste. Marie, Ontario-Michigan 2001 -2003 Report

Wind Direction Sector	Mean Wind Speed (km/h)	Wind Direction (%)
NNE	10.2	2.0
NE	9.4	2.0
ENE	9.8	3.8
Е	10.7	14.0
ESE	12.0	8.9
SE	10.4	3.8
SSE	9.1	2.4
S	8.8	2.7
SSW	11.2	3.0
SW	13.9	3.6
WSW	15.2	3.5
W	15.9	5.3
WNW	16.9	10.4
NW	19.0	11.3
NNW	17.0	5.8
Ν	12.9	3.5
Calm		13.9

 Table 6: Summary of the Wind Speed and Direction Data from the Sault Ste. Marie,

 Ontario Airport (1990- 2001) – Environment Canada

Ambient temperature plays an important role in the rate of transformation of certain air contaminants. Generally, chemical reactions in the atmosphere are enhanced by warmer temperatures. Hence the formation of secondary pollutants, such as ground-level ozone, is greater in warmer climates. A critical factor affecting the behaviour of air contaminants is the stability condition of the atmosphere. It is driven by the temperature of the air as a function of altitude. This 'temperature profile' dictates whether the air is stable, that is, there is very little vertical movement, or unstable, that is, there is significant vertical movement which is the case with updrafts and downdrafts. Air pollutants released in unstable air can reach ground-level through downdrafts, even if released from elevated stacks. Air temperature normally drops with increasing altitude, however, under certain conditions the opposite occurs over a short range of altitudes and for short time periods, leading to so-called 'temperature inversions'. These often trap air pollutants near ground level resulting in short-term air pollution episodes.

Precipitation, in the form of rainfall and snowfall, effectively washes air pollutants out of the atmosphere. Typically, wet summers result in better air quality due to the dual beneficial effect of precipitation and lower temperatures. This cleansing of the air, however, leads to the wet deposition of contaminants to the ground and to area lakes and streams, some of which can become acidified.

The influence of meteorology on air quality in the Sault Ste. Marie area is best exemplified with ground-level ozone and odourous emissions (such as TRS and VOCs) emitted from local sources. Ground-level ozone is formed when its precursors (VOCs and NO_x) react in the presence of sunlight. Widespread elevated ozone episodes typically occur in late spring and summer under high pressure systems. In many parts of the U.S. and Canada, regional transport

of ozone and its precursors can contribute to elevated ozone levels in downwind communities. The process of ozone travelling to downwind areas is referred to as ozone transport.

In the Sault Ste. Marie area, air pollution episodes can occur when pollutants, emitted from stacks or fugitive sources impinge at ground-level. This 'looping plume' phenomenon typically occurs under sunny conditions from late spring to early fall – from late morning to mid-afternoon – when the air is most unstable and mixes down to the ground entraining parcels of air pollutants released from stacks and also to a much lesser degree from lower level fugitive sources. This phenomenon is aggravated under light winds or stagnant conditions. Short-term episodes can also occur when air pollutants are released below a temperature inversion, which effectively prevents upward dispersion. This can result in an accumulation of air pollutants which is forced to mix down to the ground at elevated concentrations under light wind conditions. From the fall through to the spring, when the atmospheric dispersion conditions are most favorable, the incidence of air pollution episodes is usually lower than at other times of the year. The dispersion of air contaminants can also be adversely affected by local topography, such as hills, valleys and water bodies which can change the stability of the air and local wind patterns. The Sault Ste. Marie area has some of these topographical features.

5. Air Pollutants: Description and Monitoring Results

This chapter presents monitoring results for the pollutants of interest in this study along with pollutant descriptions, sources, and effects. Monitoring methods are briefly described in Appendices A through P.

5.1 Particulate Matter

Particulate matter (PM) is the general term used to describe a mixture of solid particles in air. Due to the different health effects associated with particles of different diameters, they are characterised according to size, ranging from less than 0.1 microns to over 100 microns. The full range of particle sizes, up to about 100 microns, is described as dustfall.

5.1.1 Dustfall

Description, sources and effects

Dustfall comprises the largest and more visible particulate matter, generally in the 25 to100 μ m size range, which settles out from the atmosphere quickly by gravity. Natural sources of dustfall include vegetation fibres, biological material and particles from soil erosion such as silicates and trace metals. Man-made sources can include particles of coal, coke, ash, wood fibres, wood char, paint chips, grain dust and road dust.

In combination with the identification of particles by optical microscopy, this method can serve as a useful indicator of the types and possible sources of particulate matter in areas with dusting issues resulting from heavy soiling. Particles in this size range are not considered as having health-related effects. They are mostly associated with nuisance complaints due to local deposition (soiling) and visibility effects. Anthropogenic sources of dustfall in the Sault Ste. Marie area comprise industrial emissions, construction activities and vehicular traffic.

Monitoring results

The results of the historical dustfall monitoring program in Sault Ste. Marie, Ontario have been reported in several MOE reports since 1976 (Potvin and McGovern,1976; Potvin and McIlveen, 1980; Olivier and Potvin, 1995; Clara and Racette,1996; Racette, 1997 - 2001). The results showed a noticeable impact on dustfall levels in the west end of the city from emissions at the Algoma Steel Inc. facilities and also show progressive improvements since the 1980s. More recent results (November 1998 to August 2000) from the initial phase of the bi-national study indicated that the levels of dustfall in Sault Ste. Marie, Michigan were generally lower than on the Ontario side (Racette, 2000).

During the 2001 to 2003 study period, as shown in Figure 4 along with historical data since 1994, the Ontario annual AAQC of 4.6 g/m^2 (annual) was exceeded each year of the study period at the Ontario sites, with the highest values recorded at the Bonney Street site. The annual AAQC was consistently met at the Michigan sites.

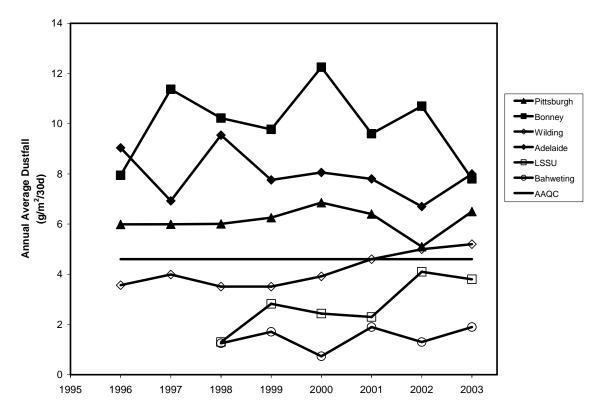


Figure 4: Annual Average Dustfall Values at the Study Sites

Every Ontario dustfall monitoring site recorded exceedances of the monthly AAQC (7 $g/m^2/30$ days) during the study period as shown in Figure 5. The highest exceedance rate (66%) was recorded at the Bonney Street site. The other Ontario sites had exceedance rates ranging from 48% to 21%. Amongst the Ontario sites, Bonney Street recorded the highest monthly value: 24.1 g/m²/30days.

The LSSU site had two exceedances of the monthly AAQC in a data set of 35 samples: an exceedance rate of 6%. A maximum of 25.3 g/m²/30 days was recorded at that site: the highest in the network for the 3-year period. There were no exceedances at the Bahweting site.

The USEPA does not have a standard for dustfall.

The value of dustfall data is enhanced substantially through identification of the collected particulate by optical microscopy. Due to the large historical database at the Ontario sites, only the exceedance samples were analyzed by optical microscopy. On the other hand, all samples collected at the two Michigan sites were optically characterised. The technique estimates the presence of selected particle types as a volume percent of the insoluble dustfall sample observed on a microscope slide. The method is semi-quantitative but is able to indicate the relative abundance and/or presence of classes of particulate matter. The results of these observations for the exceedance samples from the Ontario sites and for all the samples collected at the two Michigan sites are shown in Appendix Q.

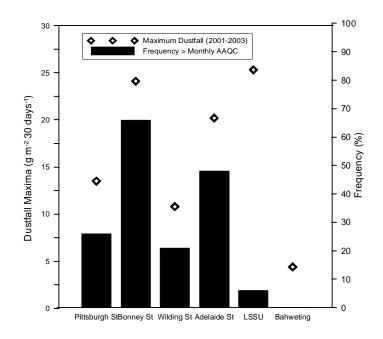


Figure 5: AAQC Dustfall Exceedance Rates and Monthly Maxima for 2001 to 2003

Table 7 interprets the Appendix Q data by ranking annual mean percent values as low (1% to 5%), medium (5% and 20%), and high (greater than 20%), mean values less than 1% were not included in the table. This analysis shows that particles typically associated with the steel and coke manufacturing processes used at the Algoma Steel Inc. facilities, namely coal, coke and kish, were found in dustfall samples at all sites in the network. Particles of coke and kish had the highest relative abundance at most sites. The relative abundance of iron oxide and iron particulate matter was low at all Ontario sites and somewhat higher at the Michigan sites. Silicates, typically from road dust and re-entrainment of sand particles from road sanding operations, were observed in medium amounts at most sites. The highest abundance of silicates was found at the Bahweting site. When present, the levels of wood fibres and wood char were low to medium. The abundance of biological material was medium to high at all the sites.

 Table 7: Summary of Optical Microscopy Analysis of Dustfall Samples (2001-2003)

 showing Relative Abundances of Characterised Particles

	Sampling Site					
Particle Type	Ontario Sites: Analysis of exceedance samples only				Michigan sites: Analysis of all samples	
Туре	Pittsburgh & Young	Bonney Street	Adelaide Street	Wilding & Wallace	LSSU	Bahweting
Coal	L	L	L	L	М	М
Coke	Н	Н	М	Н	М	М
Kish	Н	Н	М	М	Н	Н
Iron oxide & iron	L	L			М	М
Silicates	М	L	М	М	М	Н

Wood fibres	L		М		М	L
Biological material	М	М	Н	Н	М	М
Vegetation fibres/chips			L	L		L
Coal soot	L	L			L	L

Abundance code: L: 1 to 5%M: 5% to 20%H: greater than 20% values less than 1% not included in table

The relative abundance of the observed particle types must also be considered with respect to their contribution to the total mass or loading of dustfall collected along with the presence of algae. One of the five exceedance samples at the Wilding and Wallace Terrace site and 50% of the exceedance samples at the Adelaide Street site were noted to contain algae (see Appendix Q): algae contribute to the total loadings, but are not included in the optical characterization. These samples cannot be verified as actual exceedances. At most of the Ontario sites, exceedance samples that were analyzed were mainly associated with the presence of coke and kish. However, at the Adelaide Street site, high dustfall loadings were primarily due to biological matter.

Dustfall levels at the LSSU site were typically associated with the presence of silicates, wood fibres, biological material, and on a few occasions coke and kish. The LSSU highest dustfall value of 25.3 g/m²/30days had a relative abundance of 53% wood fibres and 28% perlite (a glassy volcanic rock). The other exceedance at the LSSU site of 9.1 g/m²/30days, however, had relative abundance of 57% coke and 28% kish. At the Bahweting site, higher dustfall loadings were generally associated with the presence of silicates, biological material, wood fibres, and iron oxide and iron particulate matter.

The results support earlier findings (November 1998 to August 2000) (Racette, 2000) for dustfall samples collected at the Michigan sites in that optical microscopy analysis of the insoluble component of the dustfall samples from these sites identified components typically associated with steel/coke making processes, such as coal, coke and kish. However, the dustfall loadings were generally low and well within the MOE AAQC.

5.1.2 Total Suspended Particulate Matter

Description, sources and effects

TSP includes PM_{10} and $PM_{2.5}$, as well as larger particles up to about 50 µm in diameter. Historically, TSP has been associated mostly with soiling and visibility effects. Health effects have been associated with finer particulate matter, that is PM_{10} , and especially with $PM_{2.5}$. These are also known as inhalable (PM_{10}) and respirable ($PM_{2.5}$) particles. These smaller particles can penetrate further into the respiratory system than larger particles. Exposure to inhalable and especially respirable particles is reported to be associated with increased hospital admissions and several serious health effects, including premature mortality. People most at risk are those with asthma, cardiovascular or lung disease, as well as children and the elderly. PM includes smoke, fumes, dust, aerosols, fly ash and pollen. Its composition varies with location, season, and atmospheric conditions and typically comprises soil particles, organic matter, sulphur and nitrogen compounds and metals. Particles originate from many different stationary and mobile sources, as well as from natural sources. Industrial sources include iron and steel, pulp and paper, forestry, mining and smelting, aggregates, cement, and construction. In urban airsheds, motor vehicle exhaust, residential wood combustion and road dust are major sources. Natural sources include wind-blown soil, pollen, forest fires, ocean spray and volcanic activity. PM_{2.5} arises both from direct emissions from many types of sources and from atmospheric reactions of gaseous pollutants. For example, SO₂ and NO undergo chemical reactions that result in the formation of sulphate and nitrate particles. Particles generated from re-entrainment of road dust or by crushing and grinding operations tend to consist of larger particles (TSP and PM₁₀). Combustion processes and high temperature metallurgy (e.g., steelmaking, smelting) generate predominantly fine particles such as PM_{2.5}.

The MOE's estimate for TSP emissions by sectors in Ontario for 1995 indicates that emissions from transportation, area fuel consumption and miscellaneous area sources accounted for over 60% of emissions from human activity (Ontario MOE, 1995). These estimates do not include emissions from road dust, construction and agricultural activity which were not sufficiently known at that time.

The EC 2000 particulate emission estimates from human activity within 25 km of Sault Ste. Marie, Ontario are summarised in Table 8 as percentage contributions (Environment Canada – NPRI, n.d.). These estimates, in part, are determined from available emission factors in combination with fuel consumption rates, vehicle kilometres travelled, construction activity, etc. and from available air emissions data reported by industry. Open sources, such as construction, paved and unpaved roads, forest fires, mine tailings, erosion from farmlands and landfill sites, were estimated to account for about 49% of total particulate matter (TPM) emissions, followed closely by emissions from industrial sources (48%). The remainder was attributed mostly to transportation and fuel combustion sources (Ontario MOE, 2002). For the industrial sources, PM emissions reported by the top emitters for 2002 were as follows: Algoma Steel Inc. – 2000 t, G-P Flakeboard Company – 253 t, Domtar Inc. – 103 t, Towland-Hewitson Construction Ltd – 36 t, Michigan Maple Ltd. – 31 t and St. Marys Paper – 27 t. The US national emissions inventory (NEI) does not provide estimates of total particulate emissions.

Source category	TPM	PM ₁₀	PM _{2.5}
Industrial	48	63	80
Fuel combustion	2	4	10
Transportation	1	2	5
Incineration	<1	<1	<1
Miscellaneous	<1	<1	1
Open sources	49	31	4

Table 8: Estimated Percentage Contributions from Human Activity to ParticulateEmissions in the Sault Ste. Marie, Ontario – Environment Canada (2000)

For PM_{10} , EC estimated total emissions of 5147 t in 1999 in Sault Ste. Marie, Ontario: industrial sources contributed 63% followed by open sources at 31%. Transportation and fuel combustion accounted for most of the remaining fraction. For $PM_{2.5}$, EC estimated 1999 emissions at 1978 t: industrial emissions in the Sault Ste. Marie area were estimated to contribute about 80% of $PM_{2.5}$ emissions followed by fuel combustion sources, transportation, fuel combustion and miscellaneous sources. For both PM_{10} and $PM_{2.5}$, the top industrial emitters were as listed above for PM emissions with Algoma Steel Inc. and the G-P Flakeboard Company topping the list.

For Chippewa County in 1999, the NEI reported PM_{10} emissions of 2820 t and $PM_{2.5}$ emissions of 934 t, both almost entirely emitted from area sources (USEPA – NEI, n.d.). For PM_{10} , miscellaneous sources were estimated to account for 80% of the emissions, followed by fuel combustion (9%), waste disposal (5%), off-highway vehicles (4%) and highway vehicle (2%). For $PM_{2.5}$, miscellaneous sources accounted for 43% of the emissions, followed by fuel combustion (26%), waste disposal (14%), off-highway vehicles (12%) and highway vehicles (5%). According to the NEI database, the Kinross Correctional Facility in Kincheloe is the only facility listed with PM_{10} (2.5 t) and $PM_{2.5}$ (1.3 t) emissions in 1999.

TSP Monitoring results

Figure 6 presents TSP results for the Bonney Street site since 1995. The figure shows the yearto-year variability and exceedances of the daily and annual AAQC. The data shows that samples exceeded the annual and 24-hour AAQC in each year of the 2001 to 2003 study period. The annual averages for the study period also exceeded the Canadian maximum acceptable annual AAQO of 70 μ g/m³ (geometric mean) in 2001 and 2003. Annual averages were also consistently higher than the historic U.S. annual standard of 60 μ g/m³ (arithmetic mean). The TSP standard has been replaced in the U.S. by the PM₁₀ standard but is included here for informational purposes.

In 2001, 27% of samples collected exceeded the Ontario 24-hour AAQC of 120 μ g/m³, 26% exceeded in 2002 and 34% exceeded in 2003. Maximum 24-hour values were above the historic U.S. 24-hour primary NAAQS of 260 μ g/m³ in each of the study years. The exceedance frequency of the 24-hour Ontario AAQC is consistent with observations back to 1995 (Figure 6).

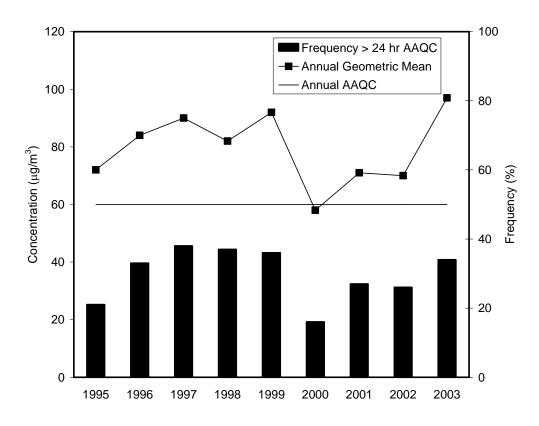


Figure 6: Annual Average TSP Concentrations and 24-hour AAQC Exceedances at the Bonney Street Site

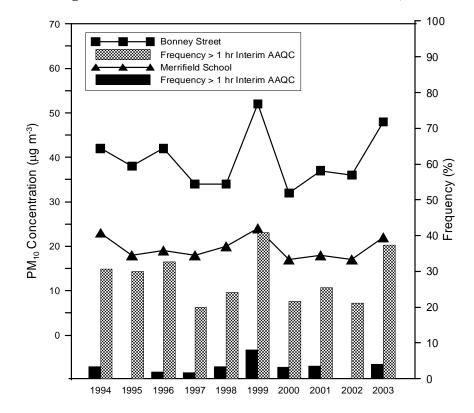
Coefficient of Haze Monitoring Results

In 2001 and 2002, suspended particulate matter, as soiling index, was continuously measured at the Merrifield School site using a paper tape sampler to determine Air Pollution Index (API) values. API values are based on a rolling 24-hour average from hourly concentrations of soiling index and SO₂ concentration. The API network preceded the current AQI system which was launched in 1988. Soiling index measurements are expressed in units of COH as described in Appendix F. In each year of the study period, the annual average soiling index level was 0.2 COH which is lower than the annual AAQC of 0.5 COH. The 24-hour AAQC of 1.0 COH was also met each year with annual maximum 24-hour measurements ranging from 0.7 to 0.9 COH. This sampler was replaced by the TEOM monitor in 2002 which is used to determine the new PM_{2.5} sub-index of the AQI.

The USEPA monitors visual impairment in national parks and wilderness areas as required by the Regional Haze Rule. The U.S sites employ either a nephelometer or transmissometer to measure the degree of light scatter, producing a measure comparable to the COH. However, there are no monitors located in the vicinity of Sault Ste. Marie, Michigan – the nearest visibility monitoring site is in Seney, Michigan approximately 85 miles west of the study area.

PM₁₀ Monitoring Results

 PM_{10} data from 1995 through 2003 are summarised in Figure 7. During the 2001 to 2003 study period, the annual average PM_{10} concentrations at the Bonney Street site varied from 35 to 48 $\mu g/m^3$, which is about twice the levels obtained at the Merrifield School site. There are no annual criterion and objectives for this pollutant in Ontario or Canada. Neither of the two sites had annual averages above the U.S. primary NAAQS of 50 $\mu g/m^3$ (consecutive 3-year average) from 2001 to 2003.





For the study period, the Merrifield School site recorded four exceedances of the Ontario 24hour interim AAQC of 50 μ g/m³ within 149 samples, an exceedance frequency of 3%. At the Bonney Street site 47 of 165 samples were above the AAQC, an exceedance frequency of 28%. There is no Canadian 24-hour objective for PM₁₀. Following the methodology used to determine compliance with the U.S. 24-hour primary NAAQS for PM₁₀, the 3-year average of the 99th percentile values at both Ontario sites was less than 150 μ g/m³ at both sites: 120 μ g/m³ at Bonney Street and 57 μ g/m³ at Merrifield School.

PM_{2.5} Monitoring Results

For the 6140 hours (about 70% of the year) of $PM_{2.5}$ concentration data collected continuously with a TEOM monitor at the Bonney Street site in 2001, the annual average concentration was 13 µg/m³ and the highest 24-hour average was 53 µg/m³. At the Merrifield School site, sufficient data was collected only in 2002 to allow the calculation of the annual average concentration: 9 µg/m³. 2003 data was partially invalidated due to data quality issues with the TEOM monitor.

With the relocation of the TEOM monitor from Bonney Street to the LSSU site in the fall of 2001, there was insufficient data to calculate a 2001 annual average concentration for the LSSU site. For 2002 and 2003, the PM_{2.5} annual average concentrations at that site were determined to be 5 and 6 μ g/m³, respectively: about half the levels calculated at the Bonney Street site in 2001 and somewhat lower than the levels recorded at the Merrifield School site.

Annual averages at all sites were below the new U.S. annual primary NAAQS of 15 μ g/m³. However, compliance with the standard requires determination of the 3-year average over three consecutive years and the use of a sampler approved by the USEPA. The TEOM sampler is not approved for compliance determinations. The USEPA designated counties as in "attainment" or "non-attainment" of the new standard in December 2004. All Michigan counties outside of the Detroit metropolitan area were designated as in attainment of the primary NAAQS. Neither Canada nor Ontario has an annual objective or criterion for PM_{2.5}.

Although there were a number of 24-hour averages over 30 μ g/m³ (mostly at the Bonney Street site), comparisons with the new 24-hour average CWS for PM_{2.5} of 30 μ g/m³ cannot be made with the available data. The achievement of this standard is based on the 98th percentile annual measurement averaged over 3 consecutive years, and is to be attained by 2010. In addition, jurisdictions are required to report on its achievement for population centres over 100,000. The population of Sault Ste. Marie, Ontario is just under 80,000. However, the CCME guidance document on achievement determination states that "jurisdictions may also report on CWS achievement for communities with populations less than 100,000 based on such considerations as regional population density, proximity to sources, local air quality, etc." (Canadian Council of Ministers of the Environment, n.d.).

Although a maximum 24-hour $PM_{2.5}$ value of 87 μ g/m³ was recorded at the LSSU site, comparison of this value with the 24-hour U.S. primary NAAQS of 65 μ g/m³ is not appropriate. The standard is based on a 3-year average of the 98th percentile values for 3 consecutive years; the data set at the LSSU site is less than 3 consecutive years. Additionally, as previously stated, the TEOM sampler is not a FRM and is not approved by the USEPA for regulatory use.

Annual mean $PM_{2.5}$ concentrations obtained from data collected by the filter FRM method at the LSSU and Bahweting sites were essentially identical, ranging from 7.5 to 8.6 µg/m³. Although comparisons with the results obtained from the TEOM monitor are not easily made due to significant differences in sampling methodology and averaging times, these results are similar to those obtained at the Merrifield School site. However, the TEOM at the LSSU site yielded consistently lower annual means (~ 2 µg/m³) than the collocated filter FRM sampler.

5.1.3 Speciated Particulate Matter

Description, sources and effects

Particulate matter comprises a variety of compounds and elements which are either absorbed and/or adsorbed to particles. These substances are naturally occurring in trace amounts but their concentrations in particulate matter may be elevated above background levels near emissions sources. PM composition can assist in determining the origin or source(s) of the particulate matter. This information can be very valuable in the design of air quality management programs to reduce emissions from anthropogenic sources. For example, in eastern North America fine particulate matter is known to comprise sulphate and nitrate compounds emitted into the atmosphere as by-products of SO₂ and NO_x emitting sources. These compounds are implicated in air issues such as smog, acid deposition and reduced visibility.

Exposures to elevated concentrations of some trace metals can have significant effects on the environment and on humans. For example, elevated levels of nickel near nonferrous smelters can cause vegetation injury. Lead is renowned for causing human health effects with well documented neurological effects in children and adults. The banning of lead additives in gasoline and tighter restrictions on industrial emitters such as nonferrous smelters and battery plants has resulted in substantial reductions of lead in the environment. Other metals of concern, due to possible health effects, include arsenic, cadmium, chromium, manganese, nickel and vanadium. These contaminants are emitted to the atmosphere from metallurgical processes used in the metal smelting and iron and steel production industries, from the burning of fossil fuels, from the incineration of municipal waste and from other industrial processes.

The inventory of metals emissions in the bi-national study area is rather sparse and limited to estimated emissions from a few facilities that have emissions above reporting thresholds. Total facility emissions of cadmium, chromium, lead, manganese and zinc were reported as 5.4 kg in Chippewa County for 1999, and as 640 kg in Sault Ste. Marie, Ontario for 2002. Algoma Steel Inc. reported the highest emissions for chromium (1 kg), lead (2 kg), manganese (250 kg) and zinc (50 kg) in 2002. St. Marys Paper reported cadmium emissions of 338 kg in 2002.

Monitoring results

The 2001 to 2003 speciation data for TSP and PM_{10} from the Ontario sites are presented in Table 9. Many metals had numerous measurements below detection limits and conclusions about these should be made with caution. Included are the carbon data in TSP from the Bonney St. site and the sulphate data in PM_{10} from both sites. The carbon data is consistent with historical measurements which show the contribution from the Algoma Steel Inc. coke and steel making processes to the levels of carbonaceous materials in particulate matter at the Bonney St. site. There are no AAQCs for carbon in particulates. The PM_{10} sulphate data are also consistent with historical measurements at these sites, which show slightly higher mean values (from 1 to 1.5 $\mu g/m^3$) at the Bonney Street site. The maximum 24-hour and annual mean concentrations lie within the range found at other sites in the province. Typically, sites in southern Ontario have the highest sulphate levels.

	TSP 2002	-2003	PM ₁₀ 2001-2003				
Species	Bonney S	treet ^a	Bonney S		Merrifield School ^c		
	24hr Max	Avg	24hr Max	Avg	24hr Max	Avg	
Carbon & ions							
Total carbon	100	15.6	NR	NR	NR	NR	
Free carbon	81	11.6	NR	NR	NR	NR	
Sulphates	NR	NR	27.0	4.3	14.3	3.1	
Trace metals							
Cadmium ^d	0.3	0.1 ^d	0.004	0.0003	0.002	0.0002	
Calcium	NR	NR	15.0	2.7	10.0	1.2	
Chromium	0.3	0.03	0.21	0.02 ^e	0.07	0.01 ^f	
Copper	0.81	0.12	0.03	0.01 ^g	0.08	0.02^{h}	
Iron	68.0	6.2	48.0	3.6	24.0	1.5	
Lead	0.90	0.02^{i}	0.33	0.02 ^j	0.08	0.01 ^k	
Manganese	1.8	0.33	1.2	0.2	0.5	0.1	
Nickel	0.31	0.01 ^m	0.2	0.01 ⁿ	0.03	0.003°	
Vanadium	0.3	0.03	0.21	0.02 ^p	0.05	0.01 ^p	
Zinc	NR	NR	0.34	0.04	0.39	0.03 ^r	

Table 9: TSP and PM_{10} Speciation Data ($\mu g/m^3$) for the Sault Ste. Marie, Ontario Sites

^a Based on 164 samples ^b Based on 165 samples ^c Based on 150 samples Light shaded values are near the USEPA high risk (100-in-1 million) benchmark Darker shaded values are above the USEPA non-cancer risk benchmark (RfC)

Darker shaded values are above the USEPA non-cancer risk bench

NR indicates not measured

The following indicate compounds for which more than 20 % of samples had no measurable response:

^d 93% of samples has no measurable response, values replaced with $0.1 \mu g/m^3$

 $^{\circ}22\%$ of samples had no measurable response, values replaced with $0.002\mu g/m^{3}$

^f 55% of samples had no measurable response, values replaced with 0.002 μ g/m³

- ^g 50% of samples had no measurable response, values replaced with 0.005 μ g/m³
- ^h 22% of samples had no measurable response, values replaced with 0.005 μ g/m³

¹74 % of samples had no measurable response, values replaced with $0.01 \mu g/m^3$

^j 64% of samples had no measurable response, values replaced with 0.01 μ g/m³ ^k 74% of samples had no measurable response, values replaced with 0.01 μ g/m³

 $^{m}45\%$ of samples had no measurable response, values replaced with 0.01 µg/m³

 n 62% of samples had no measurable response, values replaced with 0.001µg/m³

 $^{\circ}$ 85% of samples had no measurable response, values replaced with 0.002µg/m³

^p 49% of samples had no measurable response, values replaced with $0.005 \mu g/m^3$

^q 74% of samples had no measurable response, values replaced with 0.005µg/m³

^r25% of samples had no measurable response, values replaced with $0.005 \mu g/m^3$

In ambient air the concentration of metals in TSP is greater than in PM_{10} since PM_{10} is a subset of TSP. Likewise, in ambient air the concentration of metals in PM_{10} is greater than in $PM_{2.5}$. The USEPA recommends the use of the PM_{10} species fraction as the most appropriate for health risk evaluation. The metals in PM_{10} were consistently higher at the Bonney Street site, presumably owing to its proximity to the Algoma Steel Inc. complex which, from available emissions inventories, is a source of some of these metals: this is in agreement with earlier findings (Clara and Racette, 1996; Racette, 1997-2001). With the exception of iron, the 24-hr AAQCs for metals in both TSP and PM_{10} were not exceeded at either site. While the maximum concentrations of iron compounds at both sites were substantially higher than the AAQC for iron (4 μ g/m³) and ferric oxide (25 μ g/m³) (both with soiling as the limiting effect), the AAQC for iron is based on the metallic form, while the analytical method determines the concentration of iron in all forms. Comparison to the AAQC is inappropriate.

There are no Canadian AAQOs for trace metals in PM. Cadmium, chromium, lead and nickel have been placed on the Canadian CEPA toxics list. Also, the MOE has identified cadmium, chromium and nickel on its list of standards to be updated within five years. The U.S. primary NAAQS for lead (1.5 μ g/m³ – quarterly average) was not exceeded at either site.

The annual average concentration of manganese for the study period, at both Ontario sites, exceeds the USEPA non-cancer health benchmark. Additionally, the annual concentrations of total chromium are near the USEPA high risk (100-in-1 million) benchmark. This benchmark for chromium is considered to be conservative since it assumes that all the chromium is in its most toxic form, that is, the hexavalent form (Cr^{+6}). Ambient chromium measurements, undertaken in the early 1990s as part of the Windsor Air Quality Study, revealed that on average 20% of the total chromium concentrations were in the hexavalent form (Bell and Hipfner, 1997). Recent studies in Detroit, MI and Los Angeles, CA have found that the hexavalent form in ambient air is less than 5% of the total chromium concentration (Battelle Memorial Institute, 2003). If one applies the 5% or 20% values to the average chromium concentrations measured at the Ontario sites, the chromium results are at the 1-in-1 million USEPA cancer risk benchmark. In addition, caution must be used when making comparisons with the USEPA cancer risk benchmark. In addition, caution must be used when making comparisons with the USEPA cancer risk benchmarks, which are intended for assessment of long-term (chronic) exposure, due to the small Ontario data set. As stated earlier, these non-cancer and cancer health benchmarks are not enforceable standards, but are broad objectives to be considered with many other factors.

The 2002 to 2003 $PM_{2.5}$ carbon and ion/metal speciation data for the LSSU site is shown in Table 10. The average concentrations of cadmium, chromium, lead, manganese and nickel, were well below the USEPA RfC non-cancer health benchmarks. On the other hand, the average concentration of chromium and cadmium were at the USEPA 1-in-1- million health benchmark. However, these findings are considered preliminary since over 80% of the cadmium results were non-detects and the values were replaced with half the method detection limit (MDL). This was the case for almost half of the trace metals reported for the LSSU site. Also, as previously noted, the chromium data should not be directly compared against the health benchmarks because laboratory analysis did not specify the concentration of hexavalent chromium.

Owing to the significant differences in the sampling methodologies, MDLs and particle sizes sampled, the Ontario and Michigan data sets are not directly comparable. With the exception of cadmium, the Ontario data set yielded higher annual concentrations than those measured at the Michigan site. This may be explained in part by the fact that a larger particle fraction, and thus greater total mass, was captured by the Ontario samplers. The annual average $PM_{2.5}$ sulphate concentrations at the LSSU site (~ 2 µg/m³) were slightly lower than the PM_{10} sulphate values (~ 3-4 µg/m³) measured at the Ontario sites.

	LSSU Site (2002-2003)			U.S. Health benchmarks (µg/m ³)			
Species			Non-cancer	Canc	er Risk		
	Max	Avg	RfC	1-in-1million	100-in-1million		
Carbon							
Elemental carbon	0.9	0.4					
Organic carbon	8.5	3.2					
Ions							
Ammonium	7.0	0.7					
Nitrate	11.7	1.0					
Potassium	0.19	0.03					
Sodium	0.7	0.1					
Sulphate	11.0	1.8					
Trace metals							
Aluminum	0.156	0.013					
Arsenic	0.006	0.001	0.03	0.0023	0.023		
Cadmium	0.023	0.006	0.02	0.00056	0.056		
Chlorine	0.250	0.016					
Chromium	0.012	0.001	0.1	0.00008	0.008		
Copper	0.010	0.003					
Iron	0.373	0.060					
Lead	0.011	0.003	1.5				
Magnesium	0.087	0.015					
Manganese	0.019	0.003	0.05				
Mercury	0.006	0.002					
Nickel	0.003	0.001	0.2				
Phosphorous	0.158	0.005					
Potassium	0.297	0.055					
Selenium	0.004	0.001					
Silver	0.021	0.006					
Sodium	0.459	0.066					
Sulphur	2.990	0.584					
Tin	0.065	0.012					
Titanium	0.015	0.003					
Tungsten	0.017	0.007					
Vanadium	0.005	0.001					
Zinc	0.025	0.006					

Table 10: LSSU Speciation Data for PM_{2.5} and American Health Risk Benchmarks

All measurements below detection limits were replaced with $\frac{1}{2}\,$ the MDL when calculating averages. Shading indicates that over 80% of samples were non-detects.

5.2 Polycyclic Aromatic Hydrocarbons

Description, sources and effects

PAH consist of carbon and hydrogen atoms organised in characteristic molecular structures comprising fused benzene rings. They are a class of semi-volatile organic compounds, meaning that they can be present in the atmosphere in a combination of particulate and gaseous forms. PAHs are formed during the incomplete combustion of almost any kind of organic matter. Anthropogenic sources of PAHs are mainly the result of burning solid or liquid fossil fuels for industrial, heating, cooking or transportation purposes. Sources such as cigarette smoke, vehicle exhaust, asphalt roads, coal, coal tar, coke ovens, agricultural burning, residential wood burning, barbecues and hazardous waste sites have been identified as contributing to ambient air concentrations.

In the late 1970s, the production of metallurgical coke was estimated to represent about 50% of PAH emissions from all sources in Ontario (MOE, 1979; Statistics Canada, 1978). In the absence of a more recent PAH emissions inventory, it is presumed that the most significant industrial source of PAH emissions in Sault Ste. Marie, Ontario is the coke production at Algoma Steel Inc. For 2002, the company reported 5.8 t in atmospheric emissions of PAHs (Environment Canada - NPRI, n.d.; Ontario MOE – OnAIR, n.d.). Other unquantified sources of PAHs in the city also contribute to local PAH emissions, this includes: the transportation sector, residential wood burning, asphalt roads, etc.

PAHs are of significant concern since a number of them are known to be carcinogenic. Epidemiologic studies have reported an increase in lung cancer in people exposed to coke oven emissions, roofing tar emissions and cigarette smoke. The USEPA has classified the 1st seven PAHs listed in Table 11 as Group B2 (probable carcinogens). The compounds listed in Table 10 have all been placed on the CEPA toxics list. Ontario currently only has AAQCs for Benzo(a)pyrene (BaP).

РАН		Ontario (2001-2003)				Michigan (June-Dec 2003)		
Compound		Bonney St. ^b Me		Merri	rifield ^c		LSSU ^d	
Compound	MDL	Max	Avg	Max	Avg	MDL	Max	Avg
Acenaphthalene	NR	NR	NR	NR	NR	.00004	.0070	.0013
Acenaphthylene	NR	NR	NR	NR	NR	.000010	.0117	.0010
Anthracene	NR	NR	NR	NR	NR	.00006	.0407	.0070
Benzo(a)anthracene	0.01	19.8	2.6	6.8	0.7	.00009	.0022	.0002
Benzo(a)pyrene	0.01	13.4	1.8	3.8	0.5	.00012	.0014	.0002
Benzo(b)fluoranthene	0.01	26.5	3.1	6.0	0.8	.00015	.0028	.0004
Benzo(e)pyrene	NR	NR	NR	NR	NR	.00009	.0020	.0003
Benzo(g,h,i)perylene	0.01	16.1	1.9	4.0	0.6	.00008	.0017	.0003
Benzo(k)fluoranthene	0.01	11.3	1.5	2.8	0.4	.00005	.0019	.0003
Chrysene	0.01	23.7	2.9	8.0	0.8	.00004	.0035	.0005
Coronene	NR	NR	NR	NR	NR	.00010	.0004	.0001
Dibenzo(a,h)anthracene	0.01	3.0	0.4	0.7	0.1	.00010	.0003	.0001
Fluoranthene	NR	NR	NR	NR	NR	.00004	.0327	.0041

 Table 11: Summary of PAH Data (ng/m³) Collected at the Bi-national Study Sites

Fluorene	NR	NR	NR	NR	NR	.00005	.0146	.0035
Indeno(1,2,3-d)pyrene	0.01	19.3	2.0	3.9	0.6	.00010	.0019	.00034
Naphthalene ^a	NR	NR	NR	NR	NR	.00004	.0630	.0055
Perylene	NR	NR	NR	NR	NR	.00008	.0003	.0001
Phenthrene	NR	NR	NR	NR	NR	.00006	.2581	.0267
Pyrene	NR	NR	NR	NR	NR	.00009	.0165	.0023

NR "not reported" indicates PAH not analyzed by the MOE lab

^a Reported as a VOC compound by MOE

^d Data for 29 samples

^b Data for 84 samples ^c Data for 85 samples MDL – Method Detection Limit

Monitoring results

A summary of the available PAH data collected at the Ontario and Michigan sites is provided in Table 11. The sampling methods used by the MOE and ITCMI are very different. As a result the MDLs for measurements taken at the LSSU site are about 100 times lower than the MDLs for the method used in Ontario. Regardless, both agencies reported PAH concentrations that were consistently above their detection limits. The data from the Ontario sites is based on over 80 samples collected from 2001-2003, whereas the data from the LSSU site is based on 29 samples collected from June to December 2003.

Concentrations at the LSSU site were much lower, typically by a factor of 1000 to 10,000, than those obtained at the Ontario sites. They were also considerably below the Ontario AAQC for benzo(a)pyrene (BaP) and the USEPA 1-in-1 million health benchmark. Due to the small size of the dataset, the interpretation of results at the LSSU site should be viewed as preliminary. The USEPA will update this evaluation with the ITCMI with a more complete dataset.

On the Ontario side, the annual AAQC for BaP of 0.22 ng/m³ for a single source and 0.3 ng/m³ for all sources was exceeded at both sites in each year. The annual average BaP concentrations at the Bonney Street site were typically 3 to 4 times higher than at the Merrifield site, consistent with earlier findings (Clara and Racette, 1996; Racette, 1997-2001). This is illustrated in Figure 8 which shows the trend in annual average BaP concentrations at the Ontario sites for the period 1994 to 2003. While the annual average concentrations were higher before 1995 (Merrifield School) and 1996 (Bonney Street), since 1996 the BaP annual average concentration at both sites has varied from 1.0 to 2.2 ng/m³. Annual average BaP concentrations at the Bonney Street site were at the 1-in-1 million USEPA cancer risk benchmark, while at the Merrifield School site they were below the benchmark.

During the 2001-2003 study period, the 24-hour AAQC for BaP (1.1 ng/m³) was, on average, exceeded by 44% and 11% of the samples collected at the Bonney Street and Merrifield sites, respectively.

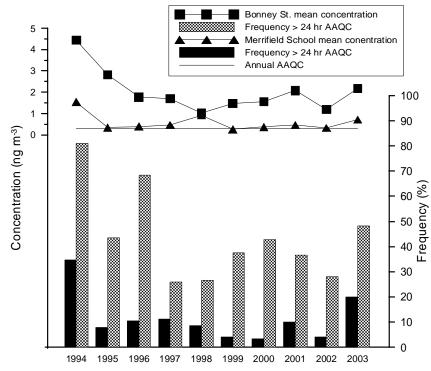


Figure 8: Annual Average Benzo(a)pyrene Concentrations and Exceedance Frequency at the Sault Ste. Marie, Ontario Sites

5.3 Volatile Organic Compounds

Description, sources and effects

VOCs are gaseous pollutants containing carbon and which participate in atmospheric photochemical reactions. Some VOCs can contribute to the formation of ground-level ozone and fine particulate and some are of concern due to their toxic effects on humans. VOCs are emitted to the atmosphere from a variety of anthropogenic sources such as vehicles, fossil fuel combustion, steel-making, petroleum refining, fuel-refilling, industrial and residential solvent use, paint application, manufacturing of synthetic materials (e.g., plastics, carpets), food processing, agricultural activities and wood processing and burning.

Anthropogenic VOC emission estimates by sectors for Ontario in 2001, identified transportation – 29%, general solvent use – 24%, other processes – 17% and residential emissions – 12% as the major contributors (Environment Canada, 2002). Environment Canada estimated VOC emissions from human activity for Sault Ste. Marie, Ontario to be 3782 t in 2000 (Ontario MOE, n.d.). Sector contributions, expressed in percentages, were estimated as follows: miscellaneous sources – 52%, transportation – 24%, industrial sources – 17% and fuel combustion –7%. Incineration and open sources were estimated to account for less than 1%. For miscellaneous sources, the largest contributions were solvent use – 56%, surface coatings – 21%, fuel marketing – 15% and printing – 6%. For industrial sources, VOC emissions reported by the top emitters for 2002 were as follows: G-P Flakeboard Company – 493 t, Algoma Steel Inc. – 113 t, the Shell, Imperial and Suncor petroleum storage terminals – 98 t (combined) and the Sault Ste. Marie municipal landfill site – 20 t (Environment Canada - NPRI, n.d.; Ontario MOE, n.d.).

On the U.S. side, the NEI reported VOC emissions of 5054 t from area sources and 10 t from point sources for Chippewa County in 1999 (USEPA – NEI, n.d.). The area source contributions were as follows: off-highway vehicles – 44%, highway vehicles – 19%, fuel combustion – 16%, solvent utilization – .4%, storage and transport – 7.6% and waste disposal/recycling – 4%. The Dafter Sanitary Landfill site was estimated to have emitted 10 t of VOCs in 1999.

Health effects from short-term exposure to elevated VOC concentrations include eye, nose and throat irritation, headaches, loss of coordination and nausea. Long-term effects from chronic exposure include damage to the liver, kidney and central nervous system. Some VOCs are known or suspected to be carcinogenic to humans. The USEPA has classified a number of VOCs as human carcinogens, such as benzene, which is ubiquitous in both urban and rural environments. Several other VOCs are considered by the USEPA to be probable human carcinogens: 1,3-butadiene, carbon tetrachloride, acrylonitrile, and 1,2 dichloroethane. In addition to these compounds, Canada has added tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene and vinyl chloride to its CEPA toxics list.

Monitoring results

A summary of the collected VOC data is presented in Table 12. AAQCs and health benchmarks are presented in Table 5. The ITCMI and MOE employed different sampling and analytical methods, as a result the detection limits used by ITCMI were typically ten times higher. The MOE collected over 60 samples using a 1-in-12 day sampling schedule during the 3-year study period. The ITCMI collected 32 samples from June to December 2003. The agencies also reported different VOCs: the MOE's routine scan includes 15 compounds in addition to those analyzed by the ITCMI, there are listed in Table 15. It should be noted that the assessment of the VOC data collected at the LSSU is preliminary due to the small dataset.

VOC		Ontario	Data 200	Michigan Data June-Dec 2003				
Compound	MDL	Bonney	' Street ^b	Merrif	ïeld ^b		LSSU ^c	
	MDL	Max	Avg	Max	Avg	MDL	Max	Avg
Acetone ^d	0.02	5.56	1.31	14.0	1.62	NR	NR	NR
Acetonitrile ^f	0.02	0.57	0.24	0.53	0.22	0.58	5.43	0.68
Acrylonitrile ^a	0.01	0.10	0.06	1.30	0.07	0.45	0.46	0.24
Benzene ^a	0.02	51.2	11.5	8.76	2.15	0.16	5.18	1.03
1,3-Butadiene ^a	0.01	0.30	0.06	0.22	0.06	0.22	0.11	0.11
Butyl acetate ^{d f}	0.05	0.42	0.13	0.88	0.18	NR	NR	NR
Carbon tetrachloride ^a	0.02	1.17	0.66	1.05	0.55	0.69	0.77	0.55
Chlorobenzene	0.02	0.11	0.03	0.12	0.02	0.51	0.25	0.24
Chloroform	NR	NR	NR	NR	NR	0.29	0.20	0.14
Cyclohexane	0.01	0.76	0.19	0.89	0.19	NR	NR	NR
1,4-Dichlorobenzene	0.02	0.36	0.09	0.47	0.08	NR	NR	NR
1,1-Dichloroethane	0.01	0.01	0.01	0.02	0.01	0.16	0.08	0.08
1,2-Dichloroethane ^a	0.02	1.20	0.05	0.06	0.02	0.28	0.14	0.14

Table 12: Summary of VOC Data (µg/m³) Collected at the Bi-national Study Sites

	1				1			
1,2-Dichloropropane ^d	0.01	0.04	0.01	0.03	0.01	0.23	0.12	0.12
Ethylbenzene	0.01	4.04	0.70	3.28	0.72	0.30	1.39	0.23
Hexane	0.01	23.80	1.25	29.20	1.39	NR	NR	NR
Isopropyl ether ^f	0.01	0.02	0.01	0.30	0.02	NR	NR	NR
Methyl ethyl ketone	0.05	7.00	0.42	2.64	0.44	0.59	18.76	3.45
Methyl isobutyl ketone ^d	0.02	0.34	0.11	0.86	0.13	0.82	0.82	0.44
Methylene chloride	0.02	31.80	0.90	12.60	0.68	0.17	2.23	0.26
Naphthalene ^e	0.02	22.00	3.51	6.22	0.91	NR	NR	NR
2 – Propanol ^d	0.02	2.80	0.19	3.88	0.22	NR	NR	NR
Styrene	0.02	2.50	0.38	2.06	0.23	0.42	1.32	0.24
Tetrachloroethylene ^a	0.02	0.55	0.14	0.42	0.14	0.61	0.31	0.29
Toluene ^d	0.02	19.60	4.87	17.60	4.20	0.34	25.56	2.92
1,2,4-Trichlorobenzene ^f	0.05	0.20	0.04	0.22	0.04	1.26	0.63	0.63
1,1,1-Trichloroethane ^a	0.01	0.39	0.23	0.30	0.18	0.38	0.22	0.17
1,1,2-Trichloroethane	0.02	0.14	0.03	0.12	0.03	0.33	0.16	0.16
Trichloroethylene ^a	0.02	0.46	0.05	0.40	0.05	0.32	1.35	0.20
1,2,4-Trimethylbenzene	0.01	6.56	1.10	4.97	1.08	0.49	14.61	0.79
Vinyl chloride ^a	NR	NR	NR	NR	NR	0.15	0.08	0.08
m- and p-Xylene d	0.05	14.30	2.56	10.60	2.44	0.69	5.82	1.31
o-Xylene ^d	0.02	5.43	0.91	4.09	0.90	0.30	1.69	0.31

NR "not reported" indicates VOC not analyzed by the respective lab.

All measurements below detection limits were replaced with 1/2 the MDL when calculating averages. Shading indicates that over 80% of samples were non-detects ^b Data for 68 to 69 samples ^c Data for 32 samples

^a Identified on CEPA toxics list

^d Limiting effect based on odour

^e Reported by ITCMI as a PAH compound

f analysis initiated in 2002, data for 38 to 41 samples

^g MDL at MOE lab improved from 0.1 to $0.01 \mu g/m^3$ in 2000

AAOCs and Health benchmarks presented in Table 6.

For some VOCs, such as carbon tetrachloride, the results at the Ontario and Michigan sites were essentially identical, with an average concentration of 0.5 to 0.6 μ g/m³. These levels are above the 1-in-1 million USEPA cancer risk benchmark. Carbon tetrachloride is a well known "background" VOC because it is no longer used in industry but persistent levels remain in the atmosphere and it is subject to long range transport. This compound typically has similar measurements regardless of location: in this study it is a validation that U.S. and Canadian monitoring methods are comparable.

Thirteen of the twenty-five VOCs sampled at the LSSU site had concentrations consistently below the MDLs. Several of these, namely 1,1-dichloroethane, isopropylether and 1,2,4trichlorobenzene, also had concentrations below the MDLs at the Ontario sites.

VOC	Ontario Data 2001-2003								
VOC Compound	MDL	Bonney	v Street ^a	Merrifie	eld School ^a				
Compound	MDL	Max	Avg	Max	Avg				
Chloroethene	0.01	0.02	0.005	0.04	0.006				
Dichloroethene	0.01	1.56	0.13	11.2	0.23				
Dichloromethane ^b	0.02	31.8	0.90	12.6	0.71				
Trichloromethane ^b	0.01	0.14	0.05	0.13	0.05				
Bromodichloroethane	0.02	0.02	0.01	0.01	0.01				
cis-1,3-dichloropropene	0.01	0.01	0.005	0.01	0.005				
1,2-Dibromoethane	0.02	0.02	0.01	0.02	0.01				
Methyl isoamylketone ^c	0.05	0.2	0.03	0.2	0.04				
1,1,2,2-Tetrachloroethane	0.02	0.20	0.01	0.02	0.01				
a-Pinene	0.02	48.8	4.05	6.9	1.63				
1,3,5-Trimethylbenzene	0.01	1.95	0.33	1.48	0.32				
1,3-Dichlorobenzene	0.02	0.05	0.03	0.05	0.03				
1,2-Dichlorobenzene	0.02	0.08	0.03	0.08	0.03				
Diisobutylene	0.02	0.92	0.07	0.38	0.07				

Table 13: Summary of Additional VOC Data (µg/m³) Collected at Sault Ste. Marie, Ontario Sites

All measurements below detection limits were replaced with ½ the MDL when calculating averages. Shading indicates that over 75% of samples were non-detects.

^a Data for 68 to 69 samples ^b Limiting effect based on health

^c analysis initiated in 2002, data for 38 to 41 samples

The maximum 24-hour concentration of acrylonitrile at the Merrifield School site of 1.3 μ g/m³ was above the Ontario interim AAQC of 0.6 μ g/m³ in 2001. (The AAQC prior to 2001 was 100 μ g/m³). In 2001, the interim annual AAQC of 0.12 μ g/m³ was marginally exceeded at the Merrifield School site with an annual mean of 0.14 μ g/m³. The concentrations reported for 2002 and 2003 were considerably lower than the AAQC.

The 2001 to 2003 3-year average acrylonitrile concentration at both Ontario sites was slightly above the 1-in-1 million USEPA health benchmark. Prior to 2000, both Ontario sites had reported non-detectable ambient concentrations. The MDL for acrylonitrile at the MOE lab was improved from 0.1 to 0.01 μ g/m³ in 2000: the data set from the Ontario sites, with the improved detection limit is too small to allow any meaningful conclusions with respect to any possible long-term health impact of this compound in Sault Ste. Marie, Ontario.

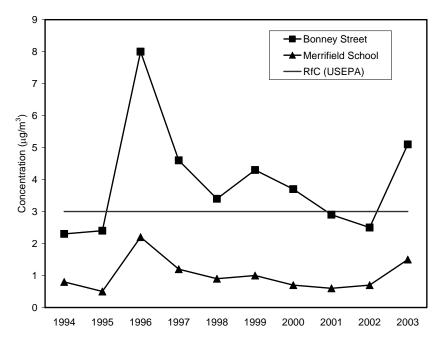
The ITCMI MDL for acrylonitrile at the LSSU site is too high $(0.45 \ \mu g/m^3)$ to allow a comparison with the Ontario AAQC (Table 5). Comparison of the acrylonitrile average of 0.24 $\mu g/m^3$ at the LSSU site with the USEPA cancer risk benchmarks is not appropriate due to the small data set (June to December 2003) and to the fact that over 80% of the samples were below the MDL. In Canada, acrylonitrile is principally used as a feedstock or chemical aid in the manufacture of nitrile-butadiene rubber and in acrylonitrile-butadiene-styrene and styrene-acrylonitrile polymers. It is used to make other chemicals such as plastics, synthetic rubber and acrylic fibres for clothing, blankets, carpeting and other fabrics. At this time, there is no air

emissions inventory for acrylonitrile in the Sault Ste. Marie area and no known users and/or emitters of this substance.

The average naphthalene concentration at the Bonney Street site for 2001-2003 was 3.5 μ g/m³, which is slightly higher than the USEPA non-cancer risk benchmark of 3.0 μ g/m³. At the Merrifield School site, the 3-year average concentration was 0.9 μ g/m³. Algoma Steel Inc. reported naphthalene emissions of 7.9 t in 2002 (EC, n.d.; MOE, n.d.). A review of the historical MOE database shows that since routine sampling began in 1994, average naphthalene levels at the Bonney Street site have typically been four times higher than at the Merrifield School site, as observed in Figure 9.

The 10-year average concentration (1994-2003) at the Bonney Street site was 3.9 μ g/m³, which is higher than the USEPA non-cancer risk benchmark of 3.0 μ g/m³. Since sampling began in 1994, a data set of over 200 samples, the Ontario 24 hour AAQC of 22.5 μ g/m³ for naphthalene was exceeded only once at the Bonney Street site. There were no exceedances during the 2001 to 2003 study period. The 10-year average concentration at the Merrifield School site was 1.0 μ g/m³ and the AAQC was not exceeded.

Naphthalene concentrations were reported as a PAH compound at the LSSU site (Table 11). The average concentration for the period June-December 2003 was 0.0055 ng/m^3 . This concentration is many orders of magnitude lower than those reported for the Ontario sites and is not displayed in Figure 9.





The average benzene concentration at the Bonney Street site for the 2001 to 2003 study period was (11.5 μ g/m³) was considerably higher than measured at the Merrifield School site (2.2 μ g/m³) and the LSSU site (1.0 μ g/m³). This is consistent with data collected at both Ontario sites since 1994 and displayed in Figure 10 which shows that benzene levels at the Bonney Street site are on average five times higher than at the Merrifield School site.

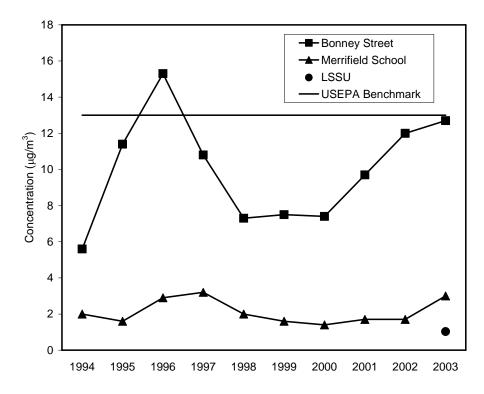


Figure 10: Annual Average Benzene Concentrations at the Ontario and LSSU Sites

Ontario, like most jurisdictions around the world, has not adopted a standard or AAQC for benzene since there is presently no known safe exposure threshold. Benzene, like carbon tetrachloride, is ubiquitous in nature. The USEPA estimates cancer risks associated with benzene inhalation to be in excess of 1-in-1 million in essentially every county of the U.S., in both urban and rural areas (USEPA - NEI, n.d.). The average benzene levels reported for the Bonney Street site are at the high risk benchmark (100-in-1 million) used by the USEPA. The higher concentrations measured at the Bonney Street site are believed to result from benzene emissions associated with the Algoma Steel Inc. facilities. In 2002, the company reported emitting 95 t of benzene to the atmosphere (Environment Canada - NPRI, n.d.; Ontario MOE – OnAir, n.d.). As previously noted, the VOC dataset collected thus far at LSSU is limited to a 6-month period and interpretation is complicated by a high rate on nondetects for many important compounds. The results discussed here should be considered preliminary. Once a larger dataset is assembled, including 2004-05 data, more robust statistical methods should be applied to compensate for measurements below detection limits and to better estimate potential health risks resulting from VOC exposures.

5.4 Sulphur Compounds

5.4.1 Sulphur Dioxide

Description, sources and effects

Sulphur dioxide (SO_2) is a colourless gas with a characteristic acrid smell like that of a struck match. It is created through burning of sulphur-bearing substances such as coal and oil. SO₂ can be transformed to sulphur trioxide (SO_3) , which in the presence of water vapour readily becomes sulphuric acid (H_2SO_4) mist. Sulphur dioxide can also be oxidized to form acid aerosols and it is a precursor to sulphates, which are significant components of fine particulate matter in the atmosphere.

According to emission estimates compiled by the MOE, more than two thirds of the SO_2 annually emitted in Ontario is from smelters, utilities and petroleum refineries. Of these, smelter emissions typically comprise the largest fraction; in 2001, smelters accounted for 44% of provincial emissions (Ontario MOE, 2002). Other industrial sources include steel mills, and pulp and paper mills. Smaller sources include residential, commercial and industrial space heating.

The Environment Canada (EC) emissions inventory of CAC for 2000, estimated total SO_2 emissions of 5640 t for Sault Ste. Marie, Ontario (Environment Canada – NPRI, n.d.). Industrial contributions were estimated at 97% of the total. Transportation and fuel combustion accounted for the rest. Emissions reported by Algoma Steel Inc. accounted for essentially all of the industrial SO₂ emissions above the annual reporting threshold of 20 t. In 2002, Algoma Steel Inc. reported total SO₂ emissions of about 6000 t.

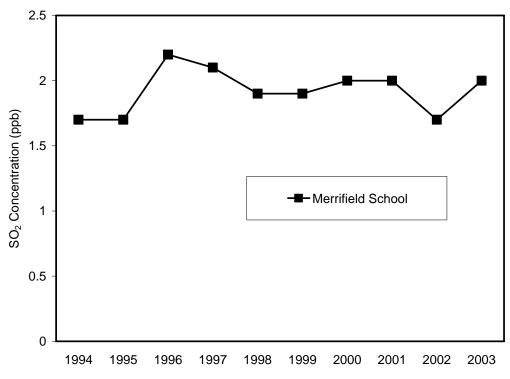
For Chippewa County, in 1999 the NEI reported total SO₂ emissions of 457 t, with the majority (66%) emitted from area sources (USEPA – NEI, n.d.). Transportation was estimated to account for 53% of the emissions (off-highway 39% and highway 14%), while fuel combustion was estimated to contribute 45%. The Kinross Correctional Facility in Kincheloe emitted 155 t, all of the point source SO₂ emissions listed in the NEI.

There is growing scientific evidence that exposure to high levels of SO_2 can result in breathing problems, respiratory illness, changes in the lung's defenses and worsening respiratory and cardiovascular disease. People with asthma, chronic lung disease or heart disease are believed to be the most sensitive to SO_2 . Under certain climatic conditions, elevated levels of SO_2 can damage trees and crops. SO_2 and NO_2 are the main precursors of acidic deposition, mostly acid rain, which results in the acidification of sensitive lakes and streams, accelerates the corrosion of buildings and contributes to reduced visibility. SO_2 also causes the formation of microscopic acid aerosols which have health implications and are thought to contribute to global warming.

Monitoring Results

During the 3-year study period, continuous SO_2 monitoring was performed at the Merrifield School site. Figure 11 presents the annual averages for the period 1994 to 2003. The annual average concentrations varied from 1.7 to 2.2 ppb, well below the Ontario Annual AAQC of 20 ppb, the Canadian maximum desirable AAQO of 10 ppb and the U.S. primary NAAQS of 30

ppb. Likewise the annual maximum 24-hour average concentrations, which ranged from 22 to 26 ppb, were well below the Ontario AAQC of 100 ppb, the Canadian maximum desirable AAQO of 60 ppb and the U.S. primary NAAQS of 140 ppb. The maximum 1-hour SO₂ concentration recorded during the study period was 121 ppb, below the Ontario AAQC of 250 ppb and the Canadian maximum desirable AAQO of 170 ppb. The U.S. currently does not have a 1-hour standard for SO₂, but has a 3-hour secondary NAAQS (500 ppb) that was not exceeded.



No exceedances of hourly AAQC of 250 ppb No exceedances of daily AAQC of 100 ppb No exceedances of annual AAQC of 20 ppb

Figure 11: Annual Average SO₂ Concentration at the Merrifield School Site in Ontario.

5.4.2 Total Reduced Sulphur

Description, sources and effects

Total reduced sulphur (TRS) is a measure of the sulphur-containing compounds. TRS is primarily composed of hydrogen sulphide (H₂S) but also includes methyl mercaptan, dimethyl sulphide and dimethyl disulphide. These compounds have very low odour thresholds, typically at concentrations of about 5 ppb, and have an offensive odour similar to rotten eggs or cabbage.

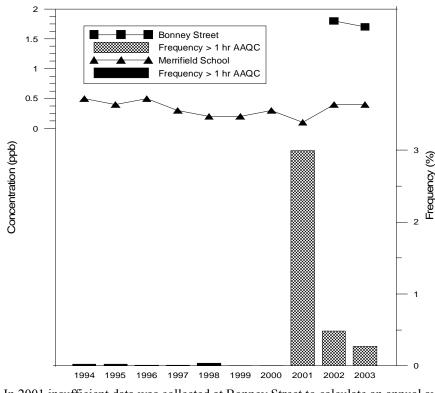
Natural sources of TRS include swamps, bogs and marshes: the TRS is a result of decaying vegetation. Principal industrial sources of TRS emissions include pulp and paper mills which use the Kraft process, steel mills, petroleum refineries and sewage treatment plants under upset conditions.

At concentrations normally found in ambient air, less than about 100 ppb, TRS compounds are not considered a health hazard. However, at higher concentrations resulting from industrial process upsets or accidental releases, sensitive individuals may experience nausea and headaches. These compounds are a primary cause of odours and public odour complaints at some locations in the province.

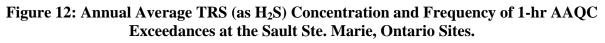
Algoma Steel Inc. is the only industrial facility in Sault Ste. Marie to report TRS emissions (as H_2S) to the MOE (O. Reg.127/01) and the EC NPRI database. The reporting threshold is 3 t per year. For 2002, the company reported 27 t of H_2S emissions. With the possible exception of very localised and isolated emissions from sewage treatment plants during upset conditions, there are no other notable anthropogenic sources of TRS in Sault Ste. Marie, Ontario. St. Marys Paper is a ground wood mill and has no appreciable TRS emissions.

Monitoring Results

Continuous TRS monitoring was initiated in 1987 at the Merrifield School site and in December 2001 at the Bonney Street site. Figure 12 presents annual average data from 1994 through 2003. During the study period of 2001 to 2003, the average TRS concentrations (expressed as H_2S) were 1.8 ppb at Bonney Street and 0.3 ppb at the Merrifield School site. There is no annual or 24-hour AAQC, AAQO or NAAQS for TRS. The annual maximum 24-hour average concentration was 4 ppb at the Merrifield School site and 17 ppb at the Bonney Street site.



Note: In 2001 insufficient data was collected at Bonney Street to calculate an annual average.



At the Merrifield School site, the 1-hour AAQC of 27 ppb was not exceeded during the study period. At the Bonney Street site, 66 hours, or 0.4% of the total number of hours monitored, exceeded the AAQC. Maximum hourly average concentrations of 68 ppb, 59 ppb and 48 ppb were recorded in 2001, 2002 and 2003, respectively at the Bonney Street site. Owing to the low odour threshold associated with TRS compounds, it is possible that from time to time under certain meteorological conditions and northwesterly winds, residents in Sault Ste. Marie, Michigan will notice these emissions.

5.5 Nitrogen Oxides

Description, sources and effects

 NO_x consists of nitric oxide (NO) and Nitrogen dioxide (NO₂). NO is a colourless and odourless gas, while NO₂ is a reddish-brown gas with a pungent and irritating odour. NO has no known adverse or environmental effects; however it can oxidize in the atmosphere to NO₂. NO₂ transforms in the air to form gaseous nitric acid (HNO₃) and organic nitrates. It plays a major role in atmospheric reactions that produce ground-level ozone. NO₂ is also a precursor to nitrates which contribute to levels of fine particulate matter in the atmosphere.

All combustion processes in air produce NO_x . Natural sources of NO_x include lightning and aerobic activity of soil bacteria. These are considered to be small compared to emissions from human activity, which are of greater concern. In Ontario, as in many jurisdictions, the transportation sector accounts for a significant fraction of NO_x emissions from human activity, followed by fossil fuel power generation. Approximately 63% of NO_x emissions in Ontario in 2001 were attributed to the transportation sector (Ontario MOE, 2002). A large fraction of the remaining 37% came from fossil fuel power generation (15%) and incineration processes (11%).

Based on EC estimates, the total annual NO_x emissions in Sault Ste. Marie, Ontario in 2000 were 5537 t (Environment Canada – NPRI, n.d.). Industries account for 71% of these emissions, followed by the transportation sector at 25% and fuel combustion 4%. The largest industrial emitters in the city to report NO_x emissions (expressed as NO) were Algoma Steel Inc. and the G-P Flakeboard company with 2002 emissions of 2155 t and 76 t, respectively.

Other emitters individually emitted less than the reporting threshold of 4 t per year. For Chippewa County in 1999, the American NEI reported NO_x emissions of 4439 t, with mobile sources accounting for 97% of these emissions (43% highway and 54% off-highway) (USEPA – NEI, n.d.). Fuel combustion accounted for most of the rest. The Kinross Correctional Facility in Kincheloe reported NO_x emissions of 31 t in 1999. It is the only facility in the county with NO_x emissions in the NEI database.

 NO_2 is a lung irritant and can increase the chance of respiratory illness by lowering resistance to infection. People afflicted with asthma and bronchitis have increased sensitivity. NO_2 chemically transforms into nitric acid which, when deposited, contributes to lake acidification. HNO₃ can corrode metals, fade fabrics, degrade rubber and damage trees and crops.

Monitoring Results

Ambient concentrations of NO_x were monitored at the Merrifield School site during the study period. Due to instrumentation problems in 2002, there was insufficient valid data (58%) to determine an annual average. The averages in 2001 and 2003 were 16 ppb for NO_x (NO + NO₂) and just over 10 ppb for NO₂: on average, NO₂ accounted for about 60% of the NO_x. The maximum 1-hour (60 ppb) and 24-hour (36 ppb) average concentrations for NO₂ during the study period were well below the 1-hour (200 ppb) and 24-hour AAQCs (100 ppb) and the Canadian maximum desirable AAQOs (210 ppb for 1 hour, 110 ppb for 24 hours). The reported annual means were also well below the U.S. primary NAAQS of 53 ppb and the Canadian maximum desirable AAQO of 30 ppb. The historical MOE data set for the Merrifield School site shows that the annual average NO₂ concentrations typically vary between 10 to 13 ppb, and that the AAQCs, AAQOs and the U.S. primary NAAQS have not been exceeded since monitoring began in 1987.

5.6 Ground-Level Ozone

Description, sources and effects

Ozone is a colourless naturally occurring gas in the upper atmosphere (stratosphere) and it shields the Earth from the sun's harmful ultra-violet radiation. Unlike stratospheric ozone, ground-level ozone is found at the Earth's surface and is a secondary pollutant formed when NO_x , principally NO_2 , and VOCs react in the presence of sunlight (photochemical reaction). Ozone is not directly emitted into the atmosphere (a primary pollutant), as are most other air pollutants. Its formation and transport are strongly dependent on meteorological conditions: changing weather patterns contribute to short-term and year-to-year variability in ground-level ozone are typically recorded on hot sunny days from May through September, between noon and early evening.

Ozone irritates the respiratory tract and eyes. When exposed to ozone, sensitive individuals can experience chest tightness, coughing and wheezing. Children playing outdoors in the summer, when ground-level ozone levels are at their highest, are particularly at risk of experiencing these effects. Individuals with pre-existing respiratory disorders, such as asthma and chronic obstructive lung disease, are also at risk. Ground-level ozone is linked to increased hospital admissions and premature deaths. It also causes visible leaf damage in many crops, garden plants and trees and is responsible for agricultural crop losses each year in Canada and the U.S.,.

Every urban airshed that emits ozone precursors will produce its own 'background' ozone, an amount dependent on the levels of precursor emissions and meteorological conditions. In addition, since local emissions of NO_x are known to remove ozone, it has been demonstrated that ozone levels are higher in rural areas and downwind of urban centres (Ontario MOE, 2003). The amount of locally produced ground-level ozone in the Sault Ste. Marie airshed has not been quantified and but is likely to be small.

Monitoring Results

Figure 13 presents ozone data from 1994 to 2003 collected at the Merrifield School site. During the study period, the annual average ozone concentrations measured at this site ranged from 24.2 ppb in 2002 to 26.8 ppb in 2003. Data collected in the 1990s, shows that annual average ozone concentrations varied between 22 and 26.8 ppb.

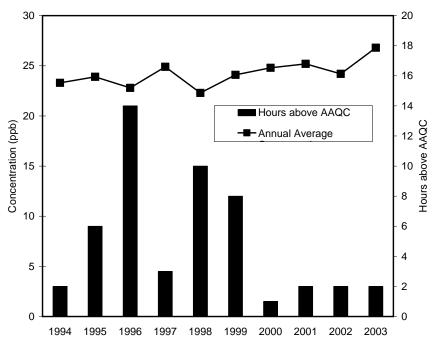


Figure 13: Annual Average Ground-level Ozone Concentrations and Hours Above the 1-hr AAQC at the Merrifield School Site

The year-to-year variability is strongly dependent on meteorological conditions.

A review of the historical provincial data set reveals that the annual average concentrations of ground-level ozone in Sault Ste. Marie, Ontario and other Northern Ontario communities including Sudbury and North Bay, are consistently higher than southern urban areas by about 5ppb (Ontario MOE, 2003). On a province-wide basis, monthly mean ozone concentrations in many southern Ontario cities have been shown to be consistently lower than those in northern Ontario cities, particularly during the colder seasons.

The maximum 1-hour concentration observed during the 2001 to 2003 study period in Sault Ste. Marie, Ontario was 89 ppb, which is higher than the 1-hour AAQC of 80 ppb, but lower than the U.S. primary NAAQS of 120 ppb. The 1-hour AAQC was exceeded twice in each year of the study period. Since 1994, the highest 1-hour average concentration was 98 ppb in 1998. Additionally, the number of hours above the 1-hour AAQC varied from none in 1991 and 1992, to highs of 14 and 10 hours in 1996 and 1998 respectively. This represents less than 0.1% of the hours monitored in a typical year. Since 1990, the Merrifield School site has recorded an average of five 1-hour AAQC exceedances per year, which is one of the lowest rates for urban centres in the province.

6. Air Quality Index (AQI) and Smog Alerts

6.1 Air Quality Index

6.1.1 Description of the AQI System

As scientific evidence mounted during the 1970s and 1980s on health effects associated with air pollutants other than SO_2 and suspended particulate measured as soiling index, the need for an improved air quality reporting system became apparent. In May 1988, the MOE launched its AQI system, partly adopted from the Canadian Air Quality Index and the USEPA Pollutant Standards Index.

The AQI provides the public with real-time air quality information province-wide. In 2002, the AQI network included 36 continuous stations located in 23 urban centres and 7 rural areas (Ontario MOE, 2003). The index is based on hourly averages for some or all the following continuous air pollutants: SO₂, ground-level ozone, NO₂, TRS, CO, and suspended particles (SP) measured as COH. Further details can be found at

In August 2002, Ontario replaced the outdated SP sub-index with the new $PM_{2.5}$ sub-index. This new sub-index provides a more accurate representation of Ontario's air quality and allows the public to make better decisions to protect their health. On a province-wide basis, the introduction of the $PM_{2.5}$ sub-index resulted in a two to three-fold increase in the number of hours the AQI exceeded 49 over that of previous years.

The U.S. has an analogous system, also called the AQI. The USEPA calculates the AQI for five major air pollutants regulated by the Clean Air Act: ground-level ozone, PM, CO, SO₂, and NO₂. The American AQI system has notable differences from Ontario's, starting with the fact that it is based on a different set of air quality standards. More information is available on the USEPA website. The air monitors operated by ITCMI are not linked in to the AQI network. The USEPA uses computer modeling to predict air quality conditions in Michigan's upper peninsula.

6.1.2 Monitoring Results

From 2001 to 2003, the AQI in Sault Ste. Marie, Ontario was very good to good over 93% of the time and the air quality was never in the very poor range. In 2001, the air quality was determined to be in the moderate range for 4.5% of the time, due mostly to ozone and to a much lesser degree TRS. In 2002 with the introduction of the PM_{2.5} sub-index, the air quality was in the moderate to poor range 9.6% of the time due to elevated levels of PM_{2.5} and ozone. In 2003, the AQI was in the moderate to poor range for 7.2% of the time: due to PM_{2.5} and ozone. The AQI values agree with earlier findings which show that air quality at the Merrifield School site is primarily affected by ground-level ozone, PM and occasionally TRS. On the basis of AQI determinations prior to the replacement of the particulate sub-index in 2002, the air quality in Sault Ste. Marie, Ontario ranked as one of the best for the major urban centres in the province.

Index	Category	Carbon Monoxide (CO)	Nitrogen Dioxide (NO ₂)	TRS Compounds	Sulphur Dioxide (SO ₂)	Fine Particulate Matter (PM _{2.5})	Ozone (O ₃)
1-15	Very Good	No known harmful effects	No known harmful effects	No known harmful effects	No known harmful effects	Sensitive population may want to exercise caution	No known harmful effects
16-31	Good	No known harmful effects	Slight Odour	Slight Odour	Some vegetation injury with ozone	Sensitive population may want to exercise caution	No known harmful effects
32-49	Moderate	No noticeable impairment	Odour	Odour	Damages some vegetation	People with respiratory disease at some risk	Respiratory irritation in sensitive people during vigorous exercise; some risk for people with heart & lung disorders; damages very sensitive plants
50-99	Poor	Increased symptoms for smokers with heart disease	Air smells and looks brown; some effect on asthmatics	Strong odour	Odourous; increasing vegetation damage	People with respiratory disease should limit prolonged exertion; general population at some risk	Sensitive people may experience irritation when breathing and possible lung damage when physically active; greater risk for people with heart/lung disorders; damages some plants
100-over	Very poor	Increased symptoms in non-smokers with heart disease; blurred vision	Increased sensitivity for people with bronchitis and asthma	Severe odour; some people may have nausea and headaches	Increased sensitivity for people with bronchitis and asthma; more vegetation damage	Serious respiratory effects even during light physical activity; people with heart disease, the elderly and children at high risk; increased risk for general population	Serious respiratory effects even during light physical activity; people with heart/lung disease at high risk; more vegetation damage

Table 14: Air Quality Index Categories and Pollutants

6.2 Smog Alerts

In the spring of 1993 the MOE initiated a smog advisory program in conjunction with EC. Smog advisories are issued to the public when widespread, elevated and persistent ground-level ozone concentrations (AQI in the poor category) are forecast to occur within the next 24 hours. In May 2000, the MOE modified this program with the following enhancements:

- a two-level air quality forecast that provides a three-day outlook, or smog watch, in addition to the 24-hour smog advisory: a smog watch is called when there is a 50% chance that elevated smog levels are forecast within the next three days;
- the immediate issuance of a smog advisory with the occurrence of unexpected widespread and elevated smog levels forecast to continue for several hours;
- increased frequency of AQI updates on weekdays and weekends; and,
- other public information dissemination improvements (Ontario MOE, 2002)

The City of Sault Ste. Marie is included in the smog advisory program which covers southern, eastern and central Ontario. For the Sault Ste. Marie area (Algoma District), two advisories were issued in 2001 covering 4 advisory days. Only one advisory per year was issued in 2002 and 2003, with three and five advisory days, respectively. The advisories were issued mostly in mid-to late June.

Many urban communities in the U.S. – particularly in the Midwest, East and West Coast – work with the USEPA to issue Air Pollution Action Day advisories to the public. Action days may be triggered by elevated levels of ozone or $PM_{2.5}$. These advisories are listed on the USEPA website (USEPA, n.d.) and announced via local media outlets where an Action Day has been called. However, there are no communities in the Michigan upper peninsula that participate in this system due to the small population size and low pollutant concentrations relative to US air quality standards.

7. Air Pollution Abatement Initiatives in Sault Ste. Marie, Ontario

The following is a brief overview of air abatement initiatives undertaken by major emitters to air, and the provincial and federal governments in addressing air quality issues in Sault Ste. Marie, Ontario.

7.1 Algoma Steel Inc.

A number of improvements were undertaken and programs established to reduce the emissions of airborne contaminants:

- In 1992, the company received a C of A to process waste oil at their facilities for pretreatment and eventual use as fuel in the boiler house. A scrubber was installed on the waste oil processor in 1997 for odour control. Since 2003, no waste derived fuel has been used as a fuel source in the boiler house operations.
- In 1997, as part of the Selected Targets for Air Compliance (STAC) program, the company submitted a total plant air emissions inventory to identify and quantify major sources of air contaminants from its facilities. The report documented all sources of emissions and provided a computer-based modelling system to identify priorities for improvements. The first priority identified were emissions from the steel making shop.
- In 1999, a baghouse was installed to control particulate emissions from the steel making shop.
- In the mid-1990s the Number 5 coke oven battery was shut down as a result of structural and environmental factors. Three coke oven batteries remain in use. In the past several years, improvements to coke making facilities have been undertaken such as coke oven door and jamb replacements at a cost of up to \$10M per year. This repair and maintenance program improves coke quality and process efficiency, and also helps to reduce fugitive emissions from the three operating coke oven batteries.
- In 2000, the MOE, EC and the company formalised an EMA related to nine 'beyond compliance' environmental issues, the following issues are specific to air:
 - by 2005, reduce benzene emission by 85% from the 1993 base, per tonne of coke produced;
 - by 2005, reduce PAH emission by 54% from the 1993 base, per tonne of coke produced;
 - formalise the coke making annual initiatives; and,
 - review alternatives for particulate control at the blast furnace.
- The company has completed its facility air emissions database for operational and fugitive sources. This sophisticated environmental information system is capable of chemical management and compliance reporting using the latest USEPA Industrial Source Complex (ISC) prime modelling capability.

- Algoma Steel Inc. has embarked upon a \$5M (Cdn.) road paving program to reduce particulate levels off-site to be completed in 2005.
- The company controls "de-kishing" emissions through operational changes such as pouring hot metal in the ladles at a reduced rate or stopping to pour when emissions are noted.

7.2 G-P Flakeboard Company

Modern pollution control technology was installed when the plant was commissioned in 1995. Under the STAC program, the company submitted an emissions summary and dispersion modelling report to the MOE. The report concluded that off-property ground-level concentrations of all air contaminants emitted from its facility were in compliance with provincial standards.

7.3 Domtar/Anthony Domtar

Domtar (formerly Agawa Forest Products) installed a natural gas boiler in 1999 to replace the wood waste boiler, essentially eliminating particulate emissions from that facility. The plant is now owned by Anthony Domtar and specialises in the manufacture of wood I joists. The facility has a cyclone baghouse for emissions from space heating, the timber conditioning room and the boiler.

7.4 St. Marys Paper

The company continues to operate Waterloo scrubbers, which it installed in 1990, to reduce particulate emissions from two boilers.

7.5 Sault Ste. Marie Area Hospitals

The biomedical waste incinerator at the Plummer Hospital was shut down in the early 1990s, thereby eliminating associated odour and particulate problems. Under a Control Order requirement by the MOE, the General Hospital decommissioned its biomedical waste incinerator in April 2003.

7.6 Brascan Power Corporation (Lake Superior Power)

Brascan continues to operate its natural gas fired co-generation facility which was installed in 1993.

8. Summary of Findings

The data collected during the study period has helped to further characterise air quality in Sault Ste. Marie, Ontario and to provide new information on air quality in Sault Ste. Marie, Michigan. Although the Canadian and American approaches to air quality management and measurement have significant differences, including the sampling methods employed, the data collected in this study provides valuable information with respect to responding to air quality complaints and concerns from the citizens of Chippewa County. The following is a summary of the key findings:

- The deposition of particulate matter at the Ontario sites, measured as dustfall, was consistently above the Ontario annual AAQC and above the monthly AAQCs 20 to 60 % of the time. Optical microscopy demonstrated that dustfall exceedances at the Ontario sites were typically associated with the presence of kish, coke, silicates and biological debris and that the presence of algae contributed to some of the exceedances.
- The dustfall loadings at the Michigan sites were generally low and well within the MOE AAQC. The annual AAQC was met at both sites; however there were two exceedances of the monthly AAQC in 2002 and 2003 at the LSSU site. Characterisation by optical microscopy of these two samples indicated that the 2002 exceedance was predominantly wood fibre and perlite while the 2003 exceedance was predominantly kish and coke: these two compounds are typically associated with emissions from steel and coke-making. Silicates, wood fibres, and biological debris contributed significantly to dustfall levels at the Michigan sites in addition to contributions by coal, kish, iron oxide and iron, and coke.
- TSP measurements at the Bonney Street site exceeded the annual Ontario AAQC and the Canadian AAQOs during each year of the study period. The 24-hour AAQC and AAQO (maximum acceptable level) were exceeded, on average, for 29% of the samples collected during the monitoring period.
- The levels of suspended particulate matter at the Merrifield School site, measured as coefficient of haze, were below the AAQCs during each year of the monitoring period.
- The levels of PM₁₀ at the Bonney Street site were typically twice the levels measured at the Merrifield School site. Both sites had consecutive 3-year averages below the U.S. NAAQS and consistently met the U.S. 24-hour NAAQS. At the Merrifield School site, 3% of the samples collected from 2001 to 2003 exceeded the 24-hour interim AAQC, whereas 28% of the samples exceeded the interim AAQC at the Bonney Street site.
- From the limited data collected during the study period using a TEOM sampler, the annual average PM_{2.5} concentrations at the Michigan LSSU site were about half the concentrations measured at the Bonney Street site and slightly lower than those at the Merrifield School site. The data set was too small to conclusively determine attainment of the U.S. annual NAAQS. However, the annual concentrations at the Ontario and Michigan sites tentatively appear to be below the value used in the U.S. standard. Comparisons with the new Canadian CWS and the U.S. 24-hour NAAQS could not be made since a minimum of 3 consecutive years of data are required: it is premature to draw conclusions related to compliance/non-compliance of these standards.

- Iron concentrations in TSP and PM_{10} samples collected in Ontario exceeded the iron AAQC: it should be noted that the analysis includes all forms of iron, while the standard is metallic iron.
- With the exception of iron, no metal AAQC was exceeded in the PM_{10} and TSP samples. The U.S. NAAQS for lead was not exceeded at any site. The annual average concentrations of manganese at both Ontario sites were higher than the U.S. benchmark for non-cancer health risks.
- The limited data set collected in this study shows that total chromium concentrations at the LSSU site exceeded the USEPA 1-in-1 million RSC for cancer effects, while at the Ontario sites total chromium concentrations may slightly exceed 100-in-1 million benchmark. The U.S. health benchmark assumes that all the chromium is in its most toxic hexavalent form (Cr⁺⁶). Recent studies have shown that most of the chromium measured in ambient air is in its non-toxic form.
- All PAH concentrations at the Michigan LSSU site were below the Ontario AAQCs for benzo(a)pyrene (BaP) and below the USEPA 1-in-1 million health benchmark. Since the 2001 to 2003 dataset is small, these findings should be viewed as preliminary.
- Exceedances of the 24-hour and annual AAQCs for BaP were reported each year at the Ontario sites. Annual BaP concentrations at Bonney Street were at the 1-in-1 million USEPA cancer risk benchmark, while at the Merrifield School site they were below.
- With the exception of acrylonitrile, the levels of the VOC compounds measured in this study were all within the Ontario AAQCs at the Ontario sites. The interim AAQCs for acrylonitrile at the Merrifield School site were marginally exceeded in 2001. At the Bonney Street site, the 3-year average for naphthalene was slightly higher than the U.S. non-cancer benchmark.
- The average benzene and carbon tetrachloride concentrations were above the U.S. 1-in-1 million benchmark for cancer risk at all sites, which is typical of most urban and rural areas in North America. The average benzene concentrations at the Bonney Street site were considerably higher than at the other study sites and are at the high benchmark (100-in-1 million) used by the USEPA. At the Ontario sites, concentrations of acrylonitrile, 1,3-butadiene and 1,2-dichloroethane (at Bonney Street) were at the 1-in-1 million USEPA health risk benchmark. The assessment of the VOC data collected at the Michigan site should be viewed as preliminary due to the small size of the 2001 to 2003 dataset.
- The SO₂ data collected at the Merrifield School site did not exceed any of the Ontario, Canada or U.S. objectives and standards.
- TRS concentrations were below the Ontario 1-hour AAQC at the Merrifield School site. At the Bonney Street site there were a number of TRS 1-hour AAQC exceedances during the study period.

- The concentrations of NO_x at the Merrifield School site were low during the reporting period. The levels of NO_2 were about 60% of the NO_x and were well within the Ontario, Canada and U.S. objectives and standards.
- The 1-hour ground-level ozone AAQC was exceeded twice each year of the study. This was one of the lowest exceedance rates for urban centres in the province. The annual concentrations of ozone were comparable to concentrations measured in other northern Ontario urban centres. During the study period, four smog advisories were issued for the district of Algoma.
- From 2001 to 2003, the AQI system described the air quality in Sault Ste. Marie, Ontario as being very good to good over 93% of the time. The air quality at the Merrifield School site, based on AQI determinations, was adversely affected mostly by ground-level ozone, PM and occasionally by TRS.

9. Conclusions and Recommendations

This report summarizes ambient air quality data collected in Sault Ste. Marie Ontario and Michigan for the period of 2001 to 2003. Where available, historical data since 1994 onwards is also provided.

The motivation for the study arose from public complaints in Sault Ste. Marie Michigan pointing to an overall perception of unhealthy air believed to be caused by Algoma Steel Inc. in Ontario.

The air quality data collected in this study along with the historical database show that several air pollutants exceed their respective Ontario AAQC in the west end of Sault Ste. Marie, Ontario. Given the limited data set collected in this study, some air pollutants may have concentrations that exceed USEPA cancer risk benchmarks on the Ontario and Michigan sides. These benchmarks are guidelines used in the U.S. as an aid to interpreting the potential health significance of air pollutants and to suggest priorities for emissions reductions.

Canadian agencies are committed to lowering ambient concentrations of air contaminants measured in this study through its regulatory process and with the use of new tools such as Environmental Management Agreements with major air emitters. Significant emissions reduction efforts are underway to achieve that goal. For example, Algoma Steel Inc. has entered into an EMA with the MOE and EC. They have also dedicated significant money to reducing PAH, benzene and particulate emissions.

Algoma Steel Inc. production has increased since 2002. Algoma Steel Inc. production has increased since 2002. Future collaboration will demonstrate if this increase impacts local air quality.

Although the recommendations which include further study will be discussed within the informal consultation to develop plans for joint or independent monitoring and sharing of results, from the air quality data set collected in this study, the following conclusions and recommendations are offered for consideration:

- Air quality monitoring should continue in Sault Ste. Marie, Ontario to track the concentration of air pollutants and to determine the progress and effectiveness of air emissions reduction initiatives.
- If the informal consultation agrees, consideration should be made to terminate dustfall sampling and optical characterization in Sault Ste. Marie, Michigan due to the low levels measured since sampling began in late 1998. Road dust and other particulate not associated with Ontario industry were the most significant contributors to dustfall levels at the Michigan sites.
- Monitoring PM_{2.5} at the LSSU site in Michigan using the TEOM monitor should be maintained until a minimum of three consecutive years of data is collected. This will allow comparisons with the new Canadian CWS and American NAAQS. Upon collection of three consecutive years of data, the study partners need to re-assess the need for continuous real-time PM_{2.5} measurements. At that time, the existing TEOM at the LSSU site may need to be replaced or modified such that the sampling methodology is consistent with the American continuous PM network.

- To further address community concerns, the partner agencies may want to consider a wind direction analysis to gain insight and determine sources on days when standards or health benchmarks were exceeded. This analysis would show the prevalent wind direction on days that LSSU experiences higher VOC and metals concentrations. Similarly it would shed light on contributions to elevated PM and ozone on the Ontario side. The partners may also wish to consider conducting a source apportionment study to quantify the contribution of VOCs, PAHs and other toxics from specific sources in the bi-national area.
- The concentrations of the total chromium at the LSSU site exceeded the 1-in-1-million cancer RSC and the Ontario sites approached the 100-in-1-million RSC. However, the U.S. health benchmarks assume that all chromium is in its most toxin haxavalent form (Cr⁺⁶), whereas recent studies suggest that Cr⁺⁶ comprises between 5 and 20% of total chromium. Thus the Ontario sites were likely between the 1-in-1-million and 100-in-1-million RSCs and LSSU is potentially below the 1-in-1-million benchmark: the study partners may wish to consider measuring Cr⁺⁶ to make that determination. Since Ontario is committed to adopting a standard for Cr⁺⁶ within the next five years, ambient measurements would be useful to determine compliance with this standard. If a binational sampling program is undertaken, the same methodology should be used at all sites.
- On-going measurements of trace metals in the PM_{2.5} size fraction does not appear to be warranted at the LSSU site for health concerns, based on particulate speciation data. However, these data may be useful to the U.S. as part of the PM2.5 speciation trends network. Should additional trace metals data deem to be required for health risk screening, identical sampling methods should be used by participating agencies. The USEPA recommendation of the use of metals data collected in the PM₁₀ fraction should be considered by the study partners.
- Based on the limited PAH and VOC data set collected at the LSSU Michigan site from June to December 2003, it appears that levels of these pollutants in Sault Ste. Marie, Michigan are not likely to pose excess health risks.
- The VOC and PAH data collected in 2004 to 2005 should be reviewed by USEPA and ITCMI to further characterise potential health risks and to help determine if continuation of the PAH and VOC sampling program is warranted. If VOC monitoring is continued, then the ITCMI should investigate an improved laboratory method that could achieve lower detection limits for better comparability to Ontario data.

Glossary

Globbaly	
Acid aerosol	Dispersion of fine particles (smoke) or fine droplets (fog) in air which are acidic. Examples include fine particulate sulphate compounds and sulphuric acid mists.
Acidic deposition	Refers to deposition of a variety of acidic pollutants (acids or acid- forming substances such as sulphates and nitrates) on biota or land or in waters of the Earth's surface.
Air Quality Index	Real-time information system that provides the public with an indication of air quality in cities and towns across Ontario.
AQI station	Continuous monitoring station used to inform the public of air quality levels on a real-time basis; station reports on criteria pollutants.
Air Pollution Index	Basis of Ontario's alert and control system to warn of deteriorating air quality; derived from 24-hour running averages of sulphur dioxide and suspended particles. Since 1988, it is a sub-index of the more comprehensive Air Quality Index.
Air Pollution Advisory	Public is advised when elevated pollution levels are forecast due to sulphur dioxide in combination with suspended particulates.
Airshed	A geographical region of influence, or spatial extent of the air pollution burden.
Ambient air	Outdoor or open air.
Coke	A hard, gray and porous residue (mostly carbon), obtained by destructive distillation of coal in coke ovens driving off coal gas and other volatile components. Has a high heat content and used as a fuel/reducing agent in blast furnaces to turn iron into a molten metal called pig iron for making steel.
Continuous monitoring	
	Measurements of air quality parameters taken every second of the day with an automated air monitor. The results are usually reported as short-term averages (e.g., 1-min., 5-min or 1-hour). Over a 1 year (365 days) period, a perfect data set would yield 8760 hourly averages.
Criteria Contaminants	day with an automated air monitor. The results are usually reported as short-term averages (e.g., 1-min., 5-min or 1-hour). Over a 1 year (365 days) period, a perfect data set would yield

air. Not legally enforceable, like regulatory standards, unless included in a regulatory instrument.

- **Exceedance** Violation of air pollutant levels permitted by environmental protection criteria, objectives or standards.
- **Fine Particulate Matter** Particles smaller than about 2.5 microns in diameter, which arise mainly from condensation of hot vapors and chemically driven gas-to-particle conversion processes; also referred to as PM_{2.5}. These are fine enough to penetrate deep into the lungs and have the greatest effects on health. Also known as respirable particulate matter.
- **Fossil fuels** Natural gas, petroleum, coal and any form of solid, liquid or gaseous fuel derived from such materials for the purpose of generating heat.
- **Geometric mean** Statistic of a data set calculated by taking the nth root of the product of all (n) values in a data set. Provides a better indication than the arithmetic mean of the central tendency for a small data set with extreme values. Typically used when data set is log normally distributed.
- **Global warming** Long-term rise in the average temperature of the Earth; principally due to an increase in the buildup of carbon dioxide and other green house gases, such as methane and nitrous oxide.
- **Ground-level ozone** Colourless gas formed from chemical reactions between nitrogen oxides and hydrocarbons in the presence of sunlight near the Earth's surface.
- **Hazardous Air Pollutants** Air pollutants considered to be toxic, such as certain metals, VOCs and PAHs, which are known or suspected to cause cancer or serious health effects.
- Inhalable particlesRepresent up to 60 per cent of the total suspended particulate
matter; composed of both coarse (diameter 2.6 to 10.0 microns)
and fine (diameter < 2.5 microns) particles; also referred to as
 PM_{10} .
- KishA graphitic form of carbon resulting from the cooling, in ladles, of
hot metal from a blast furnace. Upon cooling, the bath in the
ladles reaches saturation with respect to carbon. The excess
carbon is released to the air in the form of graphite kish
- **Looping plume** Plume released from an elevated stack which is alternately brought down to ground and lifted up due to downdrafts and updrafts in an unstable atmosphere.

Method detection limit	Minimum concentration of a contaminant that can be determined with the method employed.
Micron	A micrometre: one millionth (10^{-6}) of a meter.
Non-continuous station	Station that measures pollutant concentration usually on a 24-hour 1-in-6 or 1-in-12 day frequency (e.g., particulate matter, VOCs and PAHs) using a manual (non-automated) method.
Nitrates	Compounds containing the radical $(NO_3)^-$. Most are soluble in water and when converted to nitric acid (HNO_3) can acidify sensitive aquatic ecosystems.
Ozone episode day	A day on which widespread (hundreds of kilometers) elevated ozone levels (greater than 80 ppb maximum hourly concentration) occur simultaneously.
Particulate matter	Refers to all airborne finely divided solid or liquid material with an aerodynamic diameter smaller than 100 microns.
Percentiles	Obtained from the ranking of data points in percentage categories for the entire data set. The value of the 50^{th} percentile is the median of that data set: half the data points are below and half above that value. For the 98^{th} percentile value, 2% of the data points are likely to be equal to or greater than that value.
Photochemical reaction	Chemical reaction influenced or initiated by light, particularly ultraviolet light.
Precursor pollutant	Usually a primary pollutant which can be transformed (or enable the transformation) into secondary pollutants.
Primary pollutant	Pollutant emitted directly to the atmosphere.
Respirable particles	Particles smaller than about 2.5 μ m in diameter, which arise mainly from condensation of hot vapours and chemically driven gas to particle conversion processes; also referred to as PM _{2.5} . These are fine enough to penetrate deeply into the lungs and have the greatest effects on health.
Secondary pollutant	Pollutant formed from other pollutants in the atmosphere.
Smog	A colloquial term used for photochemical fog, which includes ozone and other contaminants such as fine particulate matter; tends to be a brownish haze.
Smog advisory	Public is advised when elevated pollution levels are forecast due to ground-level ozone and/or fine particulate matter.

Stratosphere	Layer of the atmosphere 10 to 40 kilometers above the Earth's surface.
Stratospheric ozone	Ozone formed in the stratosphere from the conversion of oxygen molecules by solar radiation; ozone found in the stratosphere absorbs much ultraviolet radiation and prevents it from reaching the Earth.
Sulphate	A compound containing the sulphate radical $(SO_4)^{-2}$. It is formed from the gradual oxidation of sulphur. When combined with moisture in the air, it is transformed to sulphuric acid (H ₂ SO ₄) which can acidify sensitive aquatic ecosystems when deposited to ground.
Suspended particles	Suspended particulate matter most likely to reach the lungs (diameter less than 25 microns). Historically measured in Ontario with a coefficient of haze paper tape sampler.
Temperature inversion	A rise in air temperature with increasing altitude, usually over a short range of altitudes. Pollutants released under this inversion layer can effectively become trapped and unable to dissipate upwards, resulting in a build-up of pollutants at ground level.
Wind rose	A pictorial representation of surface wind data (direction and speed) collected from a meteorological tower over a number of years which displays the frequency distribution of wind speed classes, usually over sixteen or thirty six compass directions.

Abbreviations and Acronyms

AAQC:	Ambient Air Quality Criteria (Ontario)
AAQO:	Ambient Air Quality Objectives (Canada)
API:	Air Pollution Index (Ontario)
AQI:	Air Quality Index (Ontario)
AQO:	Air Quality Objective
BaP:	Benzo-a-pyrene
CAC:	Criteria Air Contaminants
CCME:	Canadian Council of Ministers of the Environment
CEPA:	Canadian Environmental Protection Act
C of A:	Certificate of Approval (Ontario)
CO:	Carbon monoxide
COH:	Suspended particulate reported as Coefficient of Haze (Ontario)
CWS:	Canada Wide Standards
EC:	Environment Canada
EMA:	Environmental Management Agreement (Ontario/Canada)
EPA:	Environmental Protection Act (Ontario)
EPCRA:	Emergency Planning and Community Right-to-Know Act
ETS/CEM:	Emission tracking system/continuous emissions monitoring
FRM:	Federal Reference Method (USEPA)
g/m ² /30d:	grams/square meter/30 days (unit of dustfall)
HAPs:	Hazardous Air Pollutants
HFC- 134A:	Hydrofluorocarbon-134A
HNO ₃ :	Nitric acid
H_2SO_4 :	Sulphuric acid
$H_2S:$	Hydrogen sulphide
ISC:	Industrial Source Complex
ITCMI:	Inter-tribal Council of Michigan
LSSU:	Lake Superior State University (Sault Ste. Marie, Michigan)
MACT:	Maximum Achievable Control Technology
MDEQ:	Michigan Department of Environmental Quality
MDL:	Method Detection Limit
MOE:	Ministry of the Environment (Ontario)
MW:	Megawatt
$\mu g/m^3$:	Microgram (10^{-6}) per cubic meter
NAAQS:	National Ambient Air Quality Standards (USEPA)
NAAQO:	National Ambient Air Quality Objective (Canada)
NAPS:	National Air Pollutant Surveillance network (Environment Canada)
NEI : NIST:	National Emissions Inventory (USEPA) National Institute of Standards
_	
ng/m ³ :	Nanogram (10 ⁻⁹) per cubic meter Oxides of nitrogen
NO _x : NO:	Nitric oxide
$NO: NO: NO_2:$	Nitrogen dioxide
1102.	Muogen dioxide

N_2O :	Nitrous oxide
NPRI:	National Pollutant Release Inventory (Canada)
OnAir:	Ontario website for reporting air emissions under Regulation 127/01
O ₃ :	Ozone
PAHs:	Polycyclic Aromatic Hydrocarbons
PBT:	Persistent, bioaccumulative and toxic
POI:	Point of Impingement Standards (Ontario)
PM:	Particulate matter
PM₁₀:	Particulate matter less than 10 microns in diameter
PM _{2.5} :	Particulate matter less than 2.5 microns in diameter
ppb:	Parts per billion (by volume)
ppm:	parts per million (by volume)
QA/QC:	Quality Assurance/Quality Control
RfC:	Reference Concentration (USEPA non-cancer risk benchmark)
SO ₂ :	Sulphur dioxide
SO ₃ :	Sulphur trioxide
SO ₄ :	Sulphate
SIP:	State Implementation Plan (USEPA)
SP:	Suspended particulate
STAC:	Selected Targets for Air Compliance (Ontario)
TEOM:	Tapered Element Oscillating Microbalance
TPM:	Total Particulate Matter (Canada)
TRI:	Toxic Release Inventory
TRS:	Total Reduced Sulphur
TSP:	Total Suspended Particulate matter
USEPA:	United States Environmental Protection Agency
VOCs:	Volatile Organic Compounds

Appendices A to R

APPENDIX A

Method for Measuring Sulphur Dioxide (SO₂) in Ambient Air Using a Pulsed Fluorescent Monitor

The pulsed fluorescent sulphur dioxide (SO_2) monitor operates on the principle that SO_2 molecules excited by ultraviolet light give off radiation.

Pulsating ultraviolet light is focused through a narrow filter into the fluorescent chamber. Here it excites SO_2 molecules which give off their characteristic decay radiation. A second filter allows only this radiation to fall on a photomultiplier tube. Electronic signal processing transfers the light energy impinging on the photomultiplier into a voltage which is in direct proportion to the concentration of SO_2 in the sample stream being analyzed.

More specifically, light in the 230 to 190 nanometre region is used because it exhibits minimal interference by air and most other molecules that are found in ambient air. The pulsed light source emits ultraviolet radiation which acts on the SO_2 in the sample gas producing electronically excited SO_2 . The electronically excited SO_2 can then decay back to the ground state by fluorescence. The following equation outlines the overall reaction where SO_2 is excited SO_2^* , k_f is a rate constant and hv refers to the energy released by the reaction.

$$SO_2^* \xrightarrow{k_f} SO_2 + hv_2$$

The fluorescent radiation impinging upon a detector is directly proportional to the concentration of SO₂, thus forming the basis for this measurement technique.

APPENDIX B

Method for Measuring Nitrogen Dioxide and Nitric Oxide in Ambient Air Using a Chemiluminescence Monitor

The chemiluminescent method is based on the principle that nitric oxide (NO) and ozone (O_3) react to produce electronically excited nitrogen dioxide (NO_2) which emits light between 600 nanometres and 2500 nanometres.

A sample of ambient air is mixed with ozone in a reaction chamber and any NO in the sample reacts with the O_3 instantaneously to produce light. Under conditions of excess ozone, the light produced is proportional to the concentration of nitric oxide and is detected by a photomultiplier tube. The resulting current is amplified, and displayed in terms of the nitric oxide concentration.

For the measurement of NO_2 , the sample stream is diverted through a catalytic converter where NO_2 is reduced to NO. The latter subsequently undergoes the reaction described above together with the nitric oxide originally present in the sample. Concentrations of NO_2 determined from the differences between signals obtained when the sample is passed through the reaction chamber directly and when the sample is diverted through the catalytic converter.

The normal working range for field instruments is 0-1 parts per million (ppm) by volume, or 0-1300 ug/m^3 for NO and 0-2000 ug/m^3 for NO₂, at 25°C and 101.3 kPa.

The detection limit for both NO and NO₂ by this method is 0.002 ppm or about 2.5 ug/m^3 for NO and 4.0 ug/m^3 for NO₂ at 25°C and 101.3 kPa.

Reference Documents:

APPENDIX C

Method for Measuring Carbon Monoxide in Ambient Air Using Gas Filter Correlation Detection

Radiation from an infrared source is chopped and then passed through a gas filter alternating between CO and nitrogen. The radiation then passes through a narrow bandpass interference and enters the optical bench where absorption by the sample gas occurs. The infrared radiation then exits the optical bench and falls on an infrared detector.

A range of 0-50 ppm, parts per million by volume $(0-58 \text{mg/m}^3)$, is suitable for most conditions.

The detection limit is 0.04 ppm.

APPENDIX D

Method for Measuring Total Reduced Sulphur (TRS) Compounds in Ambient Air Using a Pulsed Fluorescent Monitor and High Temperature Oxidizer

Ambient air is drawn through a scrubber where any sulphur dioxide (SO₂) is removed. The sample then enters an oxidizer where reduced sulphur compounds are oxidized to SO₂. The oxidizer temperature needs to be in the range of 800° C to 950° C.

The sample is then passed through a beam of ultra violet (UV) radiation of 190 to 230 nm wavelength. The SO_2 molecules will absorb this radiation and re-emit fluorescent radiation of characteristic frequencies.

The fluorescent light is separated from the UV light by narrow band pass filters and detected by a photomultiplier tube whose output current is proportional to the concentration of sulphur dioxide in the sample. The output signal is processed and displayed on a recorder. The instrument is spanned with hydrogen sulphide H_2S . TRS concentrations are read directly from the recorder's chart as H_2S .

Normal working ranges for field instruments are 0 - 0.5, 0 - 0.1 parts per million (ppm) by volume, or $0 - 700 \text{ ug/m}^3$ as H₂S at 25°C and 101.3 kPa.

APPENDIX E

Method for Measuring Ground-Level Ozone in Ambient Air Using a UV Photometric Monitor

A dual cell UV Photometric design is whereby a simultaneous zero and sample measurement result in increased ozone specificity. Sample enters one cell and reference air (sample with the ozone removed) enters the second cell. Detectors then measure the light intensity transmitted through each cell. During the second half of the cycle, the roles of the two cells are interchanged by appropriate switching of the solenoid valves. Any absorption of UV energy by chemical species other than ozone are cancelled out.

A suitable working range for field instruments is 0 - 0.5 ppm $(0 - 1000 \text{ ug/m}^3)$.

The detection limit (sensitivity) for the measurement of ozone by this method is 1.0 ppb.

APPENDIX F

Method for Measuring Suspended Particulate (SP) as Soiling Index in Ambient Air Using a Paper Tape Sampler

Ambient air is drawn through a circular area of filter paper at a known sampling rate for a onehour sampling period. This operation is repeated automatically on fresh areas of paper at equal time periods. The absorbance of the circular spots or stains is measured in comparison with that of the clean paper with a photometer using white light of wavelength from 500 - 800 nm. For comparison purposes, the absorbance readings are reported in coefficient of haze (COH) units per 1000 linear feet of air sampled.

The soiling index, in terms of coefficient of haze (COH) units, is related to the effect of the sampled atmosphere when it is drawn through a clean white filter paper. One COH unit is defined as that quantity of light scattering by particulate matter, which produces an absorbance equivalent of 0.01:

Absorbance = $log_{10}I_0/I$ I_0 = intensity of light passing through the clean filter paper I = intensity of light passing through the soiled paper

For comparison purposes with similar samples in other areas, COH units are normalised by dividing the absorbance by the volume of sample air expressed in multiples of 1000 linear feet.

Ambient air quality criteria for coefficient of haze outlined in Ontario Regulation 296 are 1.0 COH units per 1000 feet for a 24-hour period and 0.5 COH units per 1000 feet of air for one year.

APPENDIX G

Method for Measuring Total Suspended Particulate (TSP) in Ambient Air Using a High Volume Sampler

The high volume (hi-vol) sampling technique determines the mass concentration of suspended airborne particulate (<100 microns) by drawing a known volume of air through a pre-weighed filter medium. Standard operation of the sampler involves an airflow rate of 1.14 m^3 /minute (40 cfm) using a flow controller and the use of glass fibre filters. The sample is collected over a 24-hour period, midnight to midnight, every one, three or six days. The six-day operating schedule is pre-determined and is consistent throughout Canada and the United-States. This six-day sampling is considered to be representative of the average air quality over a year.

High-volume samples may also be analyzed for trace metals and a variety of compounds.

Reference Documents:

http://www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-2-1.pdf 40 CFR Part 50 Appendix B, Vol 47 & 48 A Guide to Air Filter (TSP and PM₁₀) Sampling and Submission, MOE, May 2003

APPENDIX H

Method for Measuring Inhalable Particulate (PM₁₀) in Ambient Air Using a High Volume Sampler

The high volume (hi-vol) sampling technique determines the mass concentration of airborne particulate by drawing a known volume of air through a pre-weighed filter medium. When equipped with a size-selective inlet head for PM_{10} , the hi-vol sampler can be used to determine the mass concentration of inhalable particulate matter. Standard operation of the sampler requires an airflow rate of 1.14 m³/min. (40cfm) using a flow controller and the use of quartz fibre filters 8 in. by 10 in. in size. The sample is collected over a 24-hour period, midnight to midnight, every one, three or six days. The six-day operating schedule is pre-determined and is consistent throughout Canada and the United-States. This six-day sampling is considered to be representative of the average air quality over a year.

The quartz filters may also be analyzed for trace metals and a variety of compounds.

Reference Documents:

http://www.epa.gov/ttnamti1/files/ambient/inorganic/mthd-2-1.pdf

- 40 CFR Part 50 Appendix B, Vol 62, Appendix M A Guide to Air Filter (TSP and PM₁₀) Sampling and Submission, MOE, May 2003

APPENDIX I

Method for Measuring Total Dustfall in Ambient Air Using a Dustfall Jar Collector

Total dustfall comprises the largest, generally in the 25 to100 μ m size range, and more visible particulate matter which settles out from the atmosphere rather quickly by gravity. It is determined by exposing an open top polyethylene plastic jar to the atmosphere for approximately 30 days. The jar is about 45 cm high and 15 cm in diameter. It is usually secured to a suitable pole or support approximately 3.6 metres above ground. The weight of dustfall material collected during the exposure period is determined and the results expressed in grams/metre²/30 days. In Ontario, the jar is exposed with a 3 mil polyethylene liner, and without the addition of water, ethylene glycol or algaecides.

The settleable particulate collected as dustfall is separated into a water soluble and insoluble fraction. The water soluble fraction can be analyzed for chemical constituents such as trace metals, sulphates, etc. The insoluble fraction can be examined using an optical microscope to determine the identity and possibly the source of the particulate matter. This particle identification typically includes particles of coal, coke, kish, graphite, wood chips/fibres, fly ash, iron oxide and iron, silicates, biological material, vegetation fibres, paint chips, etc.

This sampling technique, by its nature, is subject to considerable interference and variability due to recirculation and loss of material by air currents. Its efficiency is also dependent on the amount of rainfall/snowfall during the exposure period. Nevertheless, this technique, in combination with the analysis of the soluble and insoluble fractions, can be a useful tool to identify dust problem areas and probable sources of dust at a low cost.

The ambient air quality criteria for total dustfall, as outlined in O. Reg. 337, are 7.0 g/m²/30days for an exposure of one month and 4.6 g/m²/30days as an annual average. These criteria are based on soiling as the limiting effect.

Reference Documents: ASTM Method D 1739-98. Standard Method for the Collection and Analysis of Settleable Particulate, ASTM Part 26, p. 340

The Determination of Total Dustfall in Air Emissions by Gravimetry, MOE Laboratory Services Branch, Quality Management Office, Method Catalogue Code DF-E3043A, September 8, 1995

APPENDIX J

Method for Measuring Respirable Particulate (PM_{2.5}) in Ambient Air Using the R&P TEOM[®] Method

The Tapered Element Oscillating Microbalance (TEOM) sampler, developed by Rupprecht and Patashnick (R&P), continuously collects particles on a filter mounted on the tip of a glass element which oscillates in an applied electric field. The glass element is hollow, with the wider end fixed; air is drawn through the filter and through the element. The oscillation of the glass element is maintained based on the feedback signal from an optical sensor. The resonant frequency of the element decreases as mass accumulates on the filter, directly measuring inertial mass. The system is calibrated by placing a gravimetrically determined calibration mass on the filter and recording the frequency change due to this mass.

The method detection limit is about 5 μ g/m³ for a five minute average. Filter lifetimes are usually two to four weeks depending on the ambient levels of respirable particulate at the monitoring site. The TEOM typically operates with an initial filter mass of about 50 mg and a deposited aerosol mass of no greater than 10 mg. It is capable of operating with flow rates through the filter from 0.5 to 5 L/min, with a typical flow rate of 3 L/min. The R&P TEOM[®] ambient particulate monitor provides for averaging periods from 10 minutes to 24 hours and is available with a choice of sample inlets for TSP, PM₁₀, PM_{2.5}, or PM₁₀.

The sampling apparatus and sampled air are kept at a constant temperature. The default value for this temperature is usually 50° C to prevent the measurement of particle-bound water. At this temperature, however, it has been determined that some of the volatile organic compounds and most of the ammonium nitrate in atmospheric particles are volatilised resulting in a loss of particle mass. This loss can be reduced by using a lower sampling temperature of 30° C, but at the risk of interference from water vapor condensation. R&P is testing modifications to the aerosol conditioning process that approximate the nominal filter equilibration conditions (~21° C and ~ 35% relative humidity).

Reference Document: Recommended Operating Procedures for the TEOM Particulate Monitor, Environment Protection Service, Environment Canada, Report No. AAQD98-4, March 1999

APPENDIX K

Method for Measuring Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using a Hi-Vol sampler and Gas Chromatography/Mass Spectroscopy

(Ontario Ministry of the Environment)

Monitoring of PAHs in ambient air is performed with a Hi-Vol sampler (previously described in Appendix G) to pre-concentrate air samples on a Teflon-coated 8" by 10" glass fibre filter. The samples are Soxhlet-extracted from the exposed filter, then cleaned by column chromatography to remove organic interferences. The target PAH compounds are subjected to quantitative GC-MS analysis using the selected ion monitoring (SIM) data acquisition mode.

Typically, the Hi-Vol samplers are operated with a flow controller capable of maintaining a flow of 30 cubic feet per minute (cfm) over a 24 hour sampling period. This provides a total air sample volume of about 1220 m^3 in a 24 hour sampling period.

Before exposure, the filters are pre-cleaned with dichloromethane and proven to be free from contaminants. The exposed filters are wrapped in aluminum foil and kept refrigerated between 4° C to 10° C to avoid sample degradation. They are handled and stored to minimise exposure to automobile exhaust and cigarette smoke. The exposed filters are returned to the lab in coolers within 14 days after sampling and are prepared in the lab for analysis within 21 days from the receiving date. Samples that exceed these timelines are analyzed and reported with a qualifying statement in the final lab report.

The Ontario Ministry of the Environment routine scan for PAH parameters include the following compounds, with a preferred method detection limit of about 0.1 ng/m^3 :

Benzo(a)anthracene Chrysene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene Indino(1,2,3,c,d)pyrene Dibenzo(a,h)anthracene Benzo(g,h,i)perylene

Notes: BaP is the only PAH compound with MOE ambient air quality criteria and is the only corrected as per deuterated internal standards

Reference Documents:	USEPA Method TO-13A
	ASTM Method D6209-98, Vol. 11.03
	MOE LSB Method E3124, Jan. 13, 2003

APPENDIX L

Method for Measuring Volatile Organic Compounds (VOCs) In Ambient Air Using Thermal Desorption and Gas Chromatography-Mass Spectrometry

(Ontario Ministry of the Environment)

This method identifies and quantifies volatile organic compounds (VOCs) in ambient air through the collection of VOCs on a three-phase adsorbent cartridge and analysis by thermal desorption, gas chromatography-mass spectrometry (TD/GC-MS).

Typically, ambient air (sample volume of 7.2 L) is collected over 24 hours on absorbent cartridges (Supelco Carbotrap 300) connected to a sample pump equipped with a flow controller capable of maintaining a flow of 5 cm³/min. The cartridge contains Carbotrap C, Carbotrap B and Carbosieve S-III. The exposed cartridges are stored inside shipping containers at a temperature between 2°C and 10°C and have a shelf life of 8 weeks. The shelf-life of unexposed cartridges is about 5 weeks.

Qualitative identification of target compounds is achieved by comparison of compound retention times, and target and qualifier ions with those of a target calibration standard mixture. Quantification of the VOCs as detected in a field sample is achieved by comparison of the target ion abundances with those from a calibration standard mixture prepared in a static dilution bottle. VOCs are measured in units of nanograms by the TD/GC-MS instrumentation and reported in units of $\mu g/m^3$.

Prior to shipping in the field, cartridges are subjected to a rigorous cleaning procedure using a Tekmar 5100 thermal conditioner. The cartridges are reconditioned if any of the target compounds, with the exception of dichloromethane, are quantified at a level greater than 10 times their accepted detection limit. Typically, a travel blank is included with each set of cartridges sent to a non-network sampling site; for network samples, one travel blank is rotated among all sites according to a preset schedule.

The Ontario Ministry of the Environment routine scan for VOCs includes the following compounds, with detection limits ranging from 0.01 to 0.05 μ g/m³:

vinyl chloride 1,3-butadiene isoprene 1,1-dichloroethene acrylonitrile dichloromethane 1,1-dichloroethane hexane trichloromethane 1,1,1-trichloroethane 1,2-dichloroethane

cyclohexane carbon tetrachloride benzene trichloroethene 1,2-dichloropropane bromodichloromethane cis-1,3-dichloropropene toluene 1,1,2-trichloroethane 1,2-dibromoethane tetrachloroethene chlorobenzene ethylbenzene m,p-xylene styrene o-xylene 1,1,2,2-tetrachloroethane α-pinene 1,3,5-trimethylbenzene 1,2,4-trimethylbenzene 1,3-dichlorobenzene 1,4-dichlorobenzene 1,2-dichlorobenzene naphthalene acetone 2-propanol MEK Diisobutylene MIBK Isopropyl ether butyl acetate Methyl isoamyl ketone acetonitrile 1,2,4-trichlorobenzene

Reference Documents:

USEPA Method TO-15 ASTM Method D6196-97, Vol. 11.03 MOE LSB Method E3314, June 28, 2002

APPENDIX M

Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS)

Compendium Method TO-13A USEPA

Filters and sorbent cartridges (containing PUF or XAD-2®) are cleaned in solvents and vacuum dried. The filters and sorbent cartridges are stored in screw-capped jars wrapped in aluminum foil (or otherwise protected from light). Approximately 300 m³ of air is drawn through the filter and sorbent cartridge using a high-volume flow rate air sampler or equivalent. The amount of air sampled through the filter and sorbent cartridge is recorded, and the filter and cartridge are placed in an appropriately labelled container and shipped along with blank filter and sorbent cartridges to the analytical laboratory for analysis.

The filters and sorbent cartridges are extracted by Soxhlet extraction. The extract is concentrated by Kuderna-Danish (K-D) evaporation, followed by silica gel clean-up using column chromatography to remove potential interferences prior to analysis by GC-MS. The eluent is further concentrated by K-D evaporation, then analyzed by GC-MS. The analytical system is verified to be operating properly and calibrated with five calibration solutions. The samples and the blanks are analyzed and used, along with volume of air sampled, to calculate the concentration of PAHs in the air sample.

This method includes the qualitative and quantitative analysis of the following PAHs specifically by utilizing PUF as the sorbent followed by GC/MS analysis:

Acenaphathene ^a Acenaphthylene ^a Anthracene Benz(a)anthracene Benzo(a)pyrene Benzo(e)pyrene Benzo(g,h,i)perylene Benzo(k)fluoranthene Chrysene ^a Low collection efficiency Coronene Dibenz(a,h)anthracene Fluoranthene Fluorene Benzo(b)fluoranthene Naphthalene ^a Phenanthrene Pyrene Perylene

Reference Documents: http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-13arr.pdf

APPENDIX N

Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/ Mass Spectrometry (GC/MS)

Compendium Method TO-15 USEPA

VOCs are defined here as organic compounds having a vapor pressure greater than 10^{-1} Torr at 25°C and 760 mm Hg. This method applies to ambient concentrations of VOCs above 0.5 ppbv and typically requires VOC enrichment by concentrating up to one liter of a sample volume.

An air sample is collected in a passivated stainless steel canister. Canisters are evacuated and either sub atmospheric or pressurised sampling modes are used. A pump ventilated sampling line is used during sample collection. Pressurised sampling requires an additional pump to provide positive pressure to the canister. Sample air flow and sampling time are regulated.

A known volume of sample is drawn from the canister through a solid multisorbent concentrator to remove as much water vapor as possible and to concentrate the VOCs. The VOCs are then thermally desorbed, entrained in a carrier gas stream, and then focused into a small volume by trapping on a reduced temperature trap or small volume multisorbent trap. The sample is then thermally desorbed and carried onto a gas chromatographic column for separation.

Reference Documents: http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15.pdf

APPENDIX O

Manual Reference Method for Sampling PM_{2.5} in Ambient Air

The Rupprecht & Patashnick Partisol[®] -Plus Model 2025 Sequential Air Sampler was used at the Michigan sites to collect $PM_{2.5}$ samples. This sampler received Federal Reference Method status by the USEPA in April 1998 (Federal Register: Vol 63, page 18911, 04/16/98).

The sampler draws ambient air at a constant volumetric flow rate (~ 16.7 L/min) into a specially shaped inlet and through an inertial particle size separator (impactor) where the suspended particulate matter in the PM_{2.5} size range is separated for collection on a circular 46.2 mm polytetrafluoroethylene (PTFE) filter for the sampling period (typically 24 hours). Each filter is weighed, after moisture and temperature conditioning, before and after sample collection to determine the mass of PM_{2.5} collected. The total volume of air sampled is determined from the measured flow rate at actual ambient temperature and pressure and sampling time. The mass concentration of PM_{2.5} in the ambient air is computed as the total mass of collected particles in the PM_{2.5} size range divided by the actual volume of air sampled, and is expressed in micrograms per cubic meter of air (μ g/m³). The lower concentration limit is a approximately 2μ g/m³ while mass concentrations of at least 200 μ g/m³ should be measurable while maintaining the operating flow rate within the specified limits.

The measurement process is non-destructive, and the $PM_{2.5}$ sample can be use for subsequent physical or chemical analyses.

Additional information on the sampling requirements and sample collection filters is specified in 40 CFR Part 50, Appendix L.

APPENDIX P

Manual Method for Speciation Sampling PM_{2.5} in Ambient Air

A Met One SUPER SASSTM (Spiral Ambient Speciation Sampler) speciation sampler was used at the LSSU site in Sault Ste., Marie Michigan to collect speciated $PM_{2.5}$ samples. This sampler conforms to the USEPA requirements for speciation sampling as proven in USEPA and California Air Resources Board field studies.

The air sampler draws ambient air at a constant volumetric flow rate of 6.7 L/min into a Sharp Cut Cyclone (SCC) designed to remove particles with an aerodynamic diameter larger than 2.5 μ m. The particles are collected in sample canisters loaded with the desired filter media. The sampler incorporates a convective solar radiation shield to maintain the samples within 5° C of ambient temperature. The SUPER SASS speciation sampler has sequential programming to allow multiple day operation; it can sample up to eight days depending on the number of sample channels used per day. Each channel may be operated independently.

Contamination due to field handling of the samples is circumvented by the use of sealed canisters which are loaded in the lab prior to shipment to the speciation field site for deployment. After exposure, the canisters are re-sealed for shipment to the lab.

In this study, 24-hour average concentrations of the following species were determined with the filter media and analytical methods as listed below:

Species	Filter media	Analytical method
Carbon Elemental & organic	Quartz (in tandem)	Thermal optical analysis
Ions Ammonium, nitrate Potassium, sulphate	Teflon or Quartz with denuder for nitrate	Ion chromatography (IC)
Trace metals Listed in Table 10	Teflon	X-ray fluorescence (XRF)

Reference Document:

Particulate Matter (PM_{2.5}) Speciation Guidance Document USEPA, Office of Air Quality Planning & Standards, July/98 http://www.epa.gov/ttnamti1/files/ambient/pm25/spec/specpln2.pdf

APPENDIX Q

Spreadsheets showing the results of the optical microscopy identification analysis for dustfall samples collected during the 2001-2003 study period. This analysis technique estimates the presence of selected particle types as an estimated volume percent of the insoluble dustfall sample observed on a microscope slide. The sites are identified by MOE station identification numbers which are listed in Table 1. For the Ontario sites, due to the available historical data set, these analyses are performed only on samples with particulate loadings above the monthly AAQC of 7.0 g/m²/30 days. For the bi-national study, all samples collected at the Michigan sites are examined by optical microscopy.

The routine scan by the MOE optical microscopist comprises the following particle types: coal, coke, graphite, kish, coal soot, oil soot, fly ash, iron oxide and iron, silicates, slag, moulding sand, wood fibres, wood char, carbonates, biological material, polymers, aluminum metal, vegetation/plant chips, vegetation fibres, and paint chips. Only the particles observed more frequently are listed in the following spreadsheets.

The comment "algae" associated with some samples indicates the presence of algae in the samplers. The mass of the algae is included in dustfall loading values, but is not considered in optical characterization. All compounds labelled as "Trace" have been assigned the value of 0.5 for calculation of averages.

Site 71015 (Pittsburgh and Young Sts, Sault Ste. Marie, Ontario)

Station 71015 (2003)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	4		0										2
Coke	69		64										66.5
Kish	16		15										15.5
Coal soot	0		2										1
Oil soot	0		0										0
Flyash	0		0										0
Iron oxide & iron	2		4										3
Silicates	9		8										8.5
Wood fibres	0.5		0										0.3
Biological debris	0.5		7										3.8
Loading(g/m2/30d)	10.1		9.9										
Station 71015 (2002)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal				•	2			Ū	0				0
Coke									11				11
Kish									86				86
Coal soot									0				0
Oil soot									0				0
Flyash									0				0
Iron oxide & iron									3				3
Silicates									0.5				0.5
Wood fibres									0				0
Biological debris									0				0
Loading(g/m2/30d)									7.6				
Station 71015 (2001)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	bull	100		3	2	2	vui	ing	6	000	1101	Dee	2.3
Coke				57	57	33			23				2.3 49
Kish				27	28	4			45				19.7
Coal soot				0	4	9			3				4.3
Oil soot				0	0	4			0				1.3
Flyash				0	0.5	0			0				0.17
Iron oxide & iron				0	4	0			0				1.3
Silicates				7	2	33			0				14
Wood fibres				6	3	0			0				3
Biological debris				0	0	15			23				5
Loading(g/m2/30d)				13.5	8.4	9.6			8.9				č

St. (1. 71042 (2002)	T	F 1			14		T 1		0	0.4	N	D	• 0/
Station 71042 (2003)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal				2	2	14				4			5.5
Coke				58	37	56				63			53.5
Kish				28	38	24				31			30.3
Coal soot				8	0.5	0				0			2.1
Iron oxide & iron				0.5	0	3				2			1.4
Silicates				4	0.5	3				0.5			2
Wood fibres				0.5	0	0.5				0.5			0.4
Wood char				0	4	0				0			1
Biological debris				0	19	0.5				0			4.9
Loading(g/m2/30d)				8.9	13.5	12.6				9.8			
Station 71042 (2002)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal									0.5	11	0		3.8
Coke									0.5	35	0.5		12
Kish									100	48	98		82
Coal soot									0	0	0		0
Iron oxide & iron									0.5	3	2		1.8
Silicates									0	3	0		1
Wood fibres									0.5	0	0		0.2
Wood char									0	0.5	0		0.2
Biological debris									0	0	0		0
Loading(g/m2/30d)									10.2	8.4	7.7		
Station 71042 (2001)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal			2	6	3	2	3	7	2	3			3.5
Coke			77	47	61	59	23	23	42	45			47.1
Kish			18	47	28	14	28	47	41	44			33.4
Coal soot			3	0	2	0	0	0.5	5	0.5			1.4
Flyash			0.5	0	0	0	0	0.5	0	0			0.1
Iron oxide & iron			0.5	0.5	4	0.5	0	0	0.5	3			1.1
Silicates			0.5	0.5	2	4	0	0	0	0.5			0.9
Wood fibres			0	0.5	0.5	0	0	0	0	0.5			0.2
Biological debris			0	0	0.5	21	46	23	10	0			12.6
Wood char			0	0	0	0	0	0	0	5			0.6
Loading(g/m2/30d)			7.1	12.5	14.7	10.5	17.5	9.5	14.8	9.1			

Site 71042 (Bonney Street, Sault Ste. Marie, Ontario)

Site 71043 (Wilding and Wallace Terrace, Sault Ste. Marie, Ontario)

Station 71043 (2003)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal					2	2	3						2.3
Coke					14	9	48						23.7
Kish					36	0	22						19.3
Coal soot					0	0	0.5						0.17
Iron oxide & iron					0.5	0	3						1.2
Silicates					19	5	0.5						8.2
Wood fibres					0	0.5	0						0.2
Biological debris					19	79	24						40.7
Vegetation fibres/chips					10	5	0						5
Aluminum metal					0	0	0						0
Loading(g/m2/30d)					10.1	10.6	9.2						
					algae								
Station 71043 (2001)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal				0		9							4.5
Coke				76		37							56.5
Kish				11		8							9.5
Coal soot				0		0.5							0.3
Iron oxide & iron				0		0.5							0.3
Silicates				13		5							9
Wood fibres				0.5		0							0.3
Biological debris				0.5		37							18.8
Vegetation fibres/chips				0		0							0
Aluminum metal				0		4							2
Loading(g/m2/30d)				8.1		9.7							4.5

Site 71045 (Adelaide Street, Sault Ste. Marie, Ontario)

Station 71045 (2003)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal				2	0.5	0	0			0	8		1.8
Coke				27	8	6	0.5			28	17		14.4
Kish				13	7	0	0			0.5	0		3.4
Coal soot				0	0	0	0			0	0		0
Iron oxide & iron				3	0	0	0			0	0		0.5
Silicates				14	4	47	0			14	0		13.2
Wood fibres				28	0	0	0			0	0		4.7
Wood char				0.5	0	0	0			0	0		0.1
Biological debris				13	65	47	100			58	67		58.3
Vegetation fibres/chips				0.5	16	0.5	0			0	8		4.2
Loading(g/m2/30d)				11.3	9.4	19.8	12.6			8	8		
					algae	algae	algae						
Station 71045 (2002)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal										0.5	0		0.25
Coke										4	0		2
Kish										4	0		2
Coal soot										0	0		0
Iron oxide & iron										0	0		0
Silicates										2	0.5		1.25
Wood fibres										9	100		54.5
Wood char										0	0		0
Biological debris										81	0		40.5
Vegetation fibres/chips										0	0		0
Loading(g/m2/30d)										10.1	10.7		
										algae			
Station 71045 (2001)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal				4	0	0	0		4	0			1.3
Coke				31	0.5	0	0		37	49			19.6
Kish				30	0.5	0	0		37	23			15.1
Coal soot				0.5	0	0	0		4	0			0.8
iiron oxide & iron				0	0	0	0		0	2			0.3
Silicates				4	0.5	0	10		0	3			2.9
Wood fibres				0	0	0	0		0	0			0
wood char				0	0	0	0		0	0			0
Biological debris				0	100	0	90		18	23			38.5
Vegetation fibres/chips				31	0	0	0		0	0			5.2
Loading(g/m2/30d)				11.3	20.2	16.5	11.1		8.2	7.1			
					algae	Algae	algae						

Site 71080 (LSSU Sault Ste. Marie Michigan)

	Site	/10	<u> 7</u> 00	799L) Sau	lt Ste	e. IVIa	arie n	/lichi	lgan)			
Station 71080(2003)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	18	15	16	4	14	0	7	0	0	0.5	17	0	7.6
Coke	0	14	4	57	0	69	15	9	0	7	0	14	15.8
Kish	69	63	65	28	14	7	26	36	0	0.5	0.5	57	30.5
Coal soot	4	0	0	0	0	0	7	0	0	8	0	7	2.2
Flyash	0	0	0	0	0	0	0	0	0	0	0	0	0
Iron oxide & iron	9	8	7	7	3	6	15	37	85	18	8	15	18.2
Silicates	0	0	8	4	58	18	30	18	10	36	39	7	19
Wood fibres	0	0	0	0.5	0.5	0.5	0.5	0	0.5	31	0	0.5	2.8
Biological debris	0	0	0	0	11	0	0	0	5	0	17	0	2.8
Perlite	0	0	0	0	0	0	0	0	0	0	0	0	0
Vegetation fibres/chips	0	0	0	0	0.5	0	0	0	0.5	0	19	0	1.7
Mineral wool	0	0	0	0	0	0	0	0	0.5	0	0	0	0.04
Paint chips	0	0.5	0	0	0	0	0	0	0	0	0	0	0.04
Pollen	0	0	0	0	0	0.5	0	0	0	0	0	0	0.04
Graphite	0	0	0	0	0	0	0	0	0	0	0	0	3.1
Loading(g/m2/30d)	1.5	1.9	1.3	9.1	1.1	5.7	4.2	5.5	1.6	2.7	2.1	0.6	
						algae							
Station 71080(2002)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	23	3	7	6	3				7	0	0	0.5	5.5
Coke	21	12	21	0	0				14	0	0.5	0.5	7.7
Kish	45	69	50	38	7				30	33	54	49	41.7
Coal soot	0	0	0	0	3				0	0	0	0	0.3
Flyash	5	0	0	0	0				0	0	0	0	0.6
Iron oxide & iron	0	3	3	3	3				7	44	7	26	10.7
Silicates	6	13	7	53	3				0	8	13	13	12.9
Wood fibres	0	0	12	0.5	53				28	15	26	12	16.3
Biological debris	0	0	0	0.5	0				14	0	0	0	1.6
Perlite	0	0	0	0	28				0	0	0	0	3.1
Vegetation fibres/chips	0	0	0	0	0				0	0	0	0	0.0
Mineral wool	0	0	0	0	0.5				0	0	0	0	0.1
Paint chips	0	0	0	0.5	0				0	0	0	0	0.1
Pollen	0	0	0	0	0				0	0	0	0	0.0
Graphite Loading(g/m2/30d)	0 <o.5< td=""><td>0 0.9</td><td>0 1</td><td>0 2.6</td><td>0 25.3</td><td></td><td></td><td></td><td>0 6</td><td>0 0.6</td><td>0 1.3</td><td>0 1.4</td><td>0.0</td></o.5<>	0 0.9	0 1	0 2.6	0 25.3				0 6	0 0.6	0 1.3	0 1.4	0.0
Elouding(g/m2/50d)	-0.5	0.9	1	2.0	20.0				0	0.0	1.5	1.1	
Station 71080(2001)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	0	8	5	0	16		12	16	13	0	0	3	6.6
Coke	16	33	39	0	12		5	13	0	0	30	29	16.1
Kish	62	26	35	0.5	24		23	30	21	70	28	57	34.2
Coal soot	8	0	6	0	0		0	0	13	0.5	0	0	2.5
flyash	0	0	0	0	0		0	0	0	0	0	0	0.0
Iron oxide & iron	0.5	0	5	0.5	0		0.5	8	13	4	5	4	3.7
Silicates	0.5	33	10	100	24		0	0.5	13	9	9	4	18.5
Wood fibres	0	0	0	0	0		0	33	24	17	28	3	9.5
Biological debris	0	0	0	0	24		60	0	10	0	0	0	8.5
	~	v	~	~				v			~	v	5.5

Perlite	0	0	0	0	0	0	0	0	0	0	0	0.0
Vegetation fibres/chips	0	0	0	0	0	0	0	0	0	0	0	0.0
Mineral Wool	0	0	0	0	0	0	0	0	0	0	0	0.0
Paint chips	0	0	0	0	0	0	0	0	0	0	0	0.0
Pollen	0	0	0	0	0	0	0	0	0	0	0	0.0
Graphite	14	0	0	0	0	0	0	0	0	0	0	1.3
Loading(g/m2/30d)	0.8	0.5	2	6.3	4.5	2.8	2.6	1.9	1.7	0.7	1.1	
						algae						

Station 71081(2003)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	24	7	6	13	6	4	5	5	0	0	0	10	6.7
Coke	11	28	23	42	0	0	0	0.5	0	10	0	22	11.4
Kish	65	28	23	26	10	72	18	20	0	0.5	0	22	23.7
Coal soot	0.5	0	0.5	0	6	0	2	11	0	0	0	0	1.7
Iron oxide & iron	0.5	0.5	12	8	0	5	10	21	19	45	23	46	15.8
Silicates	0	13	13	7	13	19	39	43	81	45	52	0.5	27.1
Wood fibres	0	0	0	4	12	0	9	0.5	0.5	0	0	0	2.2
Wood char	0	0	23	0	0	0	0	0	0	0	0	0	1.9
Carbonates	0	0	0	0	0	0	0	0	0	0	0	0	0.0
Biological debris	0.5	0	0	0	53	0	17	0	0	0.5	0.5	0	6.0
Vegetation fibres/chips	0	24	0	0	0	0	0	0	0	0.5	25	0	4.1
Paint chips	0	0	0	0	0	0	0	0.5	0	0	0	0	0.0
Loading(g/m2/30d)	0.5	1	0.9	1.3	4.4	2.4	2.8	2.2	1.8	1.7	3.6	0.5	
Station 71081(2002)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave.%
Coal	17	6	inv	4					34	4	0	0	9.3
Coke	0	10		0					0	9	40	17	10.9
Kish	69	61		66					0	73	17	37	46.1
Coal soot	0	0		0					16	0	0	0	2.3
Iron oxide & iron	2	2		4					34	5	26	9	11.7
Silicates	9	3		9					16	9	9	0	7.9
Wood fibres	3	0		17					0	0	8	37	9.3
wood char	0	0		0					0	0	0	0	0.9
Carbonates	0	0		0					0	0	0	0	0.0
Biological debris	0	0		0.5					0	0	0	0	0.1
Vegetation fibres/chips	0	18		0					0	0	0	0	2.6
Paint chips	0	0		0					0	0	0	0	0
Loading(g/m2/30d)	0.5	<0.5	1 INV	2.1					1.8	0.5	0.5	0.7	
Station 71081(2001)	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ave %
	11	28	9	лрі 19	21	7	12	42	20	23	0	7	16.6
Coal Coke	45	0	38	0	0	0	0	8	20 0	51	0	16	13.2
Kish	23	0	0	19	0	0	37	39	35	0.5	94	64	26.0
Coal soot	25 0.5	13	12	0	0	0	0	0	35 10	0.5	94 0	04	3.0
Iron oxide & iron	0.5	0	0	10	0.5	0	0	0.5	0.5	0.5	3	5	1.7
Silicates	21	59	41	40	42	65	24	11	10	26	3	8	29.2
Wood fibres	0	0	0	40	42 0	0	0	0	8	0	0	0	0.7
Wood char	0	0	0	0	0	0	0	0	0	0	0	0	0.0
Carbonates	0	0	0	0	0	0	6	0.5	0	0	0	0	0.5
Biological debris	0	0	0	0	37	28	21	0.5	17	0	0	0	8.6
Vegetation fibres/chips	0	0	0	0	0	0	0	0	0	0	0	0	0
Paint chips	0	0	0	0	0	0	0	0	0	0	0	0	0
Loading(g/m2/30d)	0.7	0.5	1.1	3.4	2.6	4.1	3.6	2.7	1.9	1.3	0.8	0.5	U
Loading(g/m2/300)	0.7	0.5	1.1	5.4	∠.0	7.1	5.0	4.1	1.7	1.3	0.0	0.5	

Site 71081 (Bahweting School, Sault Ste. Marie Michigan)

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