# GROUND-LEVEL OZONE IN ALBERTA





# GROUND-LEVEL OZONE IN ALBERTA

### Prepared for:

Science and Technology Branch Environmental Sciences Division Alberta Environmental Protection 9820 – 106 Street Edmonton, Alberta T5K 2J6

by:

Dr. H.S. (Harby) Sandhu

Atmospheric Science and Management Associates 2446 – 78 Street Edmonton, Alberta T6K 3W4

**April, 1999** 

Pub. T/453

ISBN: 0-7785-0620-7

Although prepared with funding from Alberta Environmental Protection (AEP), the contents of this report do not necessarily reflect the views or policies of AEP, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Any comment, questions or suggestions regarding the content of this document may be directed to:

Science and Technology Branch Environmental Sciences Division Alberta Environmental Protection 4<sup>th</sup> Floor, 9820 – 106 Street Edmonton, Alberta T5K 2J6

Telephone: (780) 427-5883

The report may be cited as:

Sandhu, H.S., 1999. Ground-level ozone in Alberta. Report prepared for Science and Technology Branch, Alberta Environmental Protection, No. 1494-A9901, Edmonton, Alberta.

### SUMMARY

At higher concentrations, ground-level ozone has adverse human health effects, and is one of the most damaging air pollutants to vegetation. In Canada, federal, provincial and territorial governments are in the process of reviewing ambient national objectives as well as setting new Canada-Wide standards for ozone. Available ambient ozone monitoring information from Alberta has been reviewed, and government agencies, industries and associations involved in monitoring ozone and its precursors have been identified. Also, published literature from Alberta after 1980 has been reviewed.

The cities of Edmonton and Calgary most often act as sinks of ozone, due to removal reactions with nitric oxide emitted from transportation sources. These chemical reactions give rise to other secondary air pollutants like peroxyacetyl nitrate, nitric acid and particulate nitrate. A good urban database on ambient ozone concentrations exists in Alberta. This information is reliable and is well recognized in the international scientific literature. To improve the database further, monitoring strategies recommended by the Alberta Clean Air Strategic Alliance should be implemented.

Considering the current Canadian and Alberta objective of one-hour maximum ozone concentration of 82 ppb, there are no major concerns of meeting this objective in the cities of Edmonton and Calgary, except a few exceedances during the last five years. However, rural ozone concentrations are high compared with urban centres. The 24-hour Alberta objective for ozone is often exceeded in rural Alberta. Based on the scientific and monitoring evidence to date, it is recommended that the 24-hour objective of 25 ppb be eliminated immediately, as was done for eliminating the annual objective for ozone in the 1980s. However, a new objective for ozone to protect vegetation should be considered.

A revised objectives document for ozone was drafted by the Federal-Provincial Working Group on Air Quality Objectives and Guidelines. This work has now been taken over by the Canada-Wide Standards Development Committee for Particulate Matter and Ozone, formed under the Canadian Council of Ministers of the Environment. Before accepting any new reference levels, ambient objectives or standards, current Alberta information should be used to assess the relevance and impact of these proposed objectives and standards. For example, the proposed SUM60 index, the sum of hourly ozone values at or above 60 ppb to protect vegetation, should first be evaluated for Alberta crops and vegetation, and then considered for adoption.

Measured ground-level ozone concentrations are the net result of atmospheric formation, transport and destruction processes. There are still differences in viewpoints within the Alberta scientific community as to the relative importance of contributions to ground-level ozone from intrusion of ozone from the stratosphere, mixing from the upper troposphere, local photochemistry and the medium and long-range transport. Time dependent modelling and field measurements of meteorology, ozone, its precursors, and products at strategic rural and urban locations can resolve this issue.

# **TABLE OF CONTENTS**

		P	age
SUM	IMARY		III
LIST	OF TA	BLES	VII
LIST	OF FI	GURES	IX
ACK	NOWL	EDGEMENTS	<b>XI</b>
1.0	INTR	ODUCTION	1
	1.1	Objectives of the Present Study	2
	1.2	Air Quality Framework	3
	1.3	Format	4
2.0	PREC	CURSORS AND PRODUCTS	5
	2.1	Photochemical Smog	5
	2.2	Nitrogen Oxides	6
	2.3	Volatile Organic Compounds	6
	2.4	Products	7
3.0	CHE	MISTRY, METEOROLOGY AND MODELS	9
	3.1	Chemistry	
	3.1.1	Hydroxyl Radicals	9
	3.1.2	Nitrogen Oxides	10
	3.1.3	Volatile Organic Compounds	11
	3.2	Meteorology	13
	3.2.1	Atmospheric Processes	13
	3.2.2	Meteorological Parameters	
	3.3	Models	15
	3.3.1	Grid-Based Models	16
	3.3.2	Lagrangian (Trajectory) Models	16
	3.3.3	Modelling in Alberta	17
4.0	MEA	SUREMENTS AND RESULTS	19
	4.1	Monitoring in Alberta	19
	4.2	Results	
	4.2.1	Hourly Mean Concentrations	
	4.2.2	Daily, Monthly and Annual Mean Concentrations	
	4.2.3	Peroxyacetyl Nitrate (PAN), Nitric Acid (HNO <sub>3</sub> ) and Particulate Nitrate (PN).	20
5.0	DISC	USSION	
	5.1	Hourly Mean Ozone Concentrations	35
	5.1.1	Urban	35
	5.1.2	Rural	
	5.1.3	Daily Mean and Maximum Ozone Concentrations	
	5.1.4	Monthly Mean and Hourly Maximum Ozone Concentrations	
	5.1.5	Annual Mean Ozone Concentrations	
	5.2	Peroxyacetyl Nitrate (PAN), Nitric Acid(HNO <sub>3</sub> ) and Particulate Nitrate (PN)	43

5.3	Human and Environmental Health Effects	47
5.4	Proposed National Ambient Objectives and Canada-Wide Standards	50
5.4.1	Materials	50
5.4.2	Vegetation	50
5.4.3	=	
5.4.4	Canada-Wide Standards	51
5.5	Alberta Situation	52
CON	CLUSION	57
REFI	ERENCES	59
APPE	NDICES	A1
I	Monitoring methods and air quality and precipitation quality monitoring stations of Alberta Environmental Protection (1997).	A3
II	Locations, parameters and time period of monitoring by Alberta	Δ7
	Environmental Protection, industry and Associations	A /
III	Monitoring results for NO, NO <sub>2</sub> , total hydrocarbons and volatile organic	
	compounds (ppb) for Calgary Central (June and December) and Edmonton	
	Central (June) in 1997. Ozone data for Calgary Central and Edmonton	
		A13
IV	Summary and comparison of peroxyacetyl nitrate measurements for Albert	ล
1 4	• • • • • • • • • • • • • • • • • • • •	
	5.4 5.4.1 5.4.2 5.4.3 5.4.4 5.5 CON REFI APPE	5.4 Proposed National Ambient Objectives and Canada-Wide Standards. 5.4.1 Materials

# **LIST OF TABLES**

	I	Page
Table 1	Emissions of nitrogen oxides and volatile organic compounds (tonnes) for Alberta. Also listed are the total Canadian emissions	7
Table 2	Typical hourly mean ozone data (ppb) for the Calgary Central location for June 1997.	
Table 3	Typical hourly mean ozone data (ppb) for the Edmonton Central location for June 1997.	23
Table 4	Typical hourly mean ozone data (ppb) for the Fort Saskatchewan location for June 1997.	
Table 5	Typical hourly mean ozone data (ppb) for the Hightower Ridge location for June 1997.	
Table 6	Typical hourly mean ozone data (ppb) for the Tomahawk location for June 1997	
Table 7	Daily mean and hourly maximum ozone concentrations (ppb) at different locations for the month of June 1997.	27
Table 8	Daily mean and hourly maximum ozone concentrations (ppb) at different locations for the month of December 1997.	28
Table 9	Range of daily maximum ozone concentrations in the Northern Hemisphere	42
Table 10	Ozone/PAN ratios on selected days at the University of Calgary and downtown Calgary.	
Table 11	Monthly mean concentrations of NO, NO <sub>2</sub> , PAN, PN and HNO <sub>3</sub> in the Edmonton atmosphere, calculated as the equivalent $\mu g \text{ m}^{-3}$ of NO <sub>3</sub> , and the fractional conversion ( $F_n$ ).	
Table 12	Options for form of ozone CWS.	
Table 13	Number of 1-hour ozone objective (82 ppb) exceedances at nine stations from 1993 to 1997.	
Table 14	Monthly mean and hourly maximum ozone concentrations (ppb) at two rural background monitoring sites during 1997.	
Table AII.1	Ozone (O <sub>3</sub> ), nitric oxide (NO), nitrogen dioxide (NO <sub>2</sub> ), nitrogen oxides (NO <sub>x</sub> ), total hydrocarbons (THC) and volatile organic compounds (VOCs) monitoring by Alberta Environmental Protection.	
Table AII.2	Short term monitoring of ozone $(O_3)$ , nitric oxide $(NO)$ , nitrogen dioxide $(NO_2)$ , nitrogen oxides $(NO_x)$ , and total hydrocarbons $(THC)$ by Alberta	
Table AII.3	Environmental Protection	
Table AII.4	Ozone, nitrogen oxides, total hydrocarbons and volatile organic compounds monitoring by Associations during 1998.	
Table AII.5	Station, type and elevation (m ASL) of monitoring stations whose data is referenced in this report	
Table AIII.1	Hourly mean nitric oxide data (ppb) for Calgary Central for June 1997	
Table AIII.2 Table AIII.3	Hourly mean nitrogen dioxide data (ppb) for Calgary Central for June 1997 Hourly mean total hydrocarbons data (ppb x10 <sup>2</sup> ) for Calgary Central for	
1 4010 1 1111.0	June 1997.	A16

Table AIII.4	Daily mean volatile organic compounds data (ppb) for Calgary Central for	
	June and December, 1997.	A17
Table AIII.5	Hourly mean ozone data (ppb) for Calgary Central for December 1997	A18
Table AIII.6	Hourly mean nitric oxide data (ppb) for Calgary Central for December 1997	A19
Table AIII.7	Hourly mean nitrogen dioxide data (ppb) for Calgary Central for December	
	1997	A20
Table AIII.8	Hourly mean total hydrocarbon data (ppb x10 <sup>2</sup> ) for Calgary Central for	
	December 1997.	A21
Table AIII.9	Hourly mean nitric oxide data (ppb) for Edmonton Central for June 1997	A22
Table AIII.10	Hourly mean nitrogen dioxide data (ppb) for Edmonton Central for June	
	1997	A23
Table AIII.11	Hourly mean total hydrocarbon data (ppb $x10^2$ ) for Edmonton Central for	
	June 1997	A24
Table AIII.12	Daily mean volatile organic compounds data (ppb) for Edmonton Central for	
	June and December, 1997.	A25
Table AIII.13	Hourly mean ozone data (ppb) for Edmonton Central for December 1997	A26
Table AIV.1	Summary of measurements of peroxyacetyl nitrate and peroxypropionyl	
	nitrate in urban areas.	A28
Table AIV.2	Summary of measurements of peroxyacetyl nitrate and peroxypropionyl	
	nitrate in rural areas.	A29

# **LIST OF FIGURES**

	J	Page
Figure 1	The cyclic reactions of nitrogen oxides and methane oxidation	12
Figure 2	Simplified air quality management system	18
Figure 3	Alberta Environmental Protection monitoring locations for ozone, nitrogen oxides and total hydrocarbons (continuous monitoring), and volatile organic	21
T: 4	compounds (intermittent monitoring).	21
Figure 4	Monthly mean ozone concentrations (ppb) at nine Alberta monitoring stations for 1997.	29
Figure 5	Monthly hourly maximum ozone concentrations (ppb) at nine Alberta monitoring stations for 1997.	30
Figure 6	Annual mean ozone concentrations (ppb) at nine Alberta monitoring stations from 1982 to 1997.	
Figure 7	Hourly ozone and PAN concentrations recorded on August 4, 1983 in Edmonton	
Figure 8	Monthly average of PAN, PN and HNO <sub>3</sub> concentrations in Edmonton	
Figure 9	Diurnal variation of ozone concentrations at urban (Edmonton) and rural stations in summer	
Figure 10	Diurnal variation of ozone concentrations at urban (Edmonton) and rural stations during winter	
Figure 11	Diurnal variation of hourly ozone concentrations over the period 1 November 1985 – 31 October 1987	•
Figure 12	Diurnal O <sub>3</sub> profiles on episode versus non-episode days at Fortress Mountain The vertical bars represent standard deviation of the mean for each hour	•
Figure 13	A schematic diagram of the idealized variations in $O_3$ concentrations at remote locations	
Figure A1	Alberta Environmental Protection air quality and precipitation quality monitoring stations (1997).	

### **ACKNOWLEDGEMENTS**

Many individuals have contributed and helped in one form or another in getting this report completed. For providing information, I thank George Murphy, Dennis Stokes, Dave Slubik and Chow-Seng Liu of Alberta Environmental Protection; Karen McDonald of Environment Canada; Bob Scotten of Wood Buffalo Environmental Association; Henry Bertram of Alberta Research Council; Peter Bieman of Strathcona Industrial Association, and Rob McIntosh and Dan Smith of the Pembina Institute.

Special thanks are due to Long Fu, Randy Angle, Lawrence Cheng and Ken Foster of Alberta Environmental Protection; Allan Legge of Biosphere Solutions; Douglas Leahey of Jacques Whitford and Associates, and Eric Peake of Alberta Research Council for useful scientific discussions on numerous occasions either in person or by telephone. They were very kind to accommodate my telephone calls at odd hours.

I express my thanks to Ms. Yayne Aklilu and Mr. Bob Myrick of Alberta Environmental Protection for spending a lot of time in providing data in the requested format. Without their dedicated help, this report would not have been completed within the agreed upon time. Also, I thank Ms. Lynn Lockhart for her patience and word processing skills in preparing and finalizing the report. Funding of this project from Alberta Environmental Protection is gratefully acknowledged.

### 1.0 INTRODUCTION

Primary air pollutants are released to the environment from both natural and human-made sources. Natural sources include volcanoes, dust storms, forest fires, vegetative decaying processes and evaporation from large bodies of water. Human-made emissions are generated by burning of fossil fuels in motor vehicles, home furnaces, industrial facilities and thermal power plants. Once in the air, many primary pollutants, such as nitrogen oxides (NO<sub>x</sub>), volatile organic compounds (VOCs), and sulphur dioxide (SO<sub>2</sub>), undergo chemical transformations resulting in the formation of secondary pollutants like ozone (O<sub>3</sub>), nitric acid (HNO<sub>3</sub>), sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and aerosols. The concentration of primary pollutants in the atmosphere depends upon their emission rate, transport, dispersion, chemical transformation and removal rates. However, the situation with secondary pollutants like ozone is much more complex (Leighton, 1961; Finlayson-Pitts and Pitts, 1986; Seinfeld, 1986). It is more difficult to relate ambient concentrations of secondary pollutants like O<sub>3</sub> to sources of precursor emissions than it is to identify the sources of primary pollutants.

Earth's atmosphere is composed of different types of layers. Only the troposphere, stratosphere and the boundary between them, the tropopause, are of importance in the present context. The troposphere extends from the earth's surface to the tropopause, approximately 10 to 18 km in altitude, depending upon latitude and season. The temperature and pressure in the troposphere decreases with increasing altitude. The stratosphere extends from the tropopause to an altitude of approximately 50 km. In the stratosphere, the temperature increases with increasing altitude, whereas pressure decreases with increasing altitude. As mentioned above, temperature generally decreases with increasing altitude in the troposphere. However, the lowest 1 to 2 km of troposphere are influenced by the planetary boundary layer (PBL) and by temperature inversion layers at certain places. The atmosphere above inversion and boundary layers is called the "free" troposphere. Both inversion and boundary layers prevent vertical mixing of air constituents into the free troposphere.

Ozone is an important natural chemical component of the atmosphere and its concentration is highly variable. Ozone, an oxidizing agent, co-exists with other air pollutants. As ground-level ozone concentrations are affected by many human and natural factors, it is difficult to determine natural background levels. Altshuller (1986) has noted that ground-level ozone formation can be influenced by:

- transport of stratospheric ozone into the free troposphere and the subsequent transport into PRI.
- photochemical ozone formation within the free troposphere and the clean PBL;
- photochemical ozone formation within the polluted PBL, especially during the passage of warm high pressure systems, and
- ozone formation within single or superimposed plumes.

Thus, the ground-level ozone is determined by formation, transport and destruction processes. Lefohn et al. (1990) have reported ground-level ozone exposures measured at clean locations around the world.

Numerous scientific publications and reports, prepared after the mid-1940s, have documented the occurrence of high levels of ozone and other photochemical oxidants, as well as their impacts on human health and the environment in different parts of the world. Over the years these publications have been reviewed and assessed by different national environmental protection agencies while preparing the scientific criteria documents for setting their national standards and objectives for ozone and other photochemical oxidants. In 1996, United States Environmental Protection Agency (USEPA) published three volumes on the Air Quality Criteria for Ozone and Related Photochemical Oxidants, which includes extensive internationally published literature (USEPA, 1996). In the same year, the Canadian Multistakeholder NO<sub>x</sub>/VOC Science Program published eight science assessment reports (EC, 1996 a-h). This was a response to science initiatives contained in the Canadian Council of Ministers of the Environment (CCME) 1990 NO<sub>x</sub>/VOC Management Plan.

It should be noted that CCME adopted this plan because of strong concerns about the effects of ozone in Canada and because of Canadian international commitments to reduce  $NO_x$  and VOCs. Any additional review of the science and related information from the international and national perspective is beyond the scope of the present report. Alberta's information on photochemical air pollution prior to 1980 has been summarized in earlier publications (Sandhu, 1975, 1977; Bottenheim et al., 1977; 1980), and published information from Alberta after the 1980s is discussed in later chapters.

Canadian national air quality objectives (maximum acceptable levels) for ozone are 82 ppb for the one-hour average, 25 ppb for the 24-hour average, and 15 ppb for the annual average. The Alberta ambient air quality guidelines are 82 ppb for one-hour and 25 ppb for 24-hour, respectively. In July 1997, United States Environmental Protection Agency (USEPA) announced the revised National Ambient Air Quality Standards for ozone. The new standard is an 8-hour standard at a level of 0.08 parts per million (ppm) with a form based on the 3-year average of the annual fourth-highest daily maximum 8-hour average  $O_3$  concentrations measured at each monitor within an area (USEPA, 1997).

In Canada, the Federal-Provincial Working Group on Air Quality Objectives and Guidelines, set up under the Canadian Environmental Protection Act, has published "A protocol for the development of national ambient air quality objectives. Part I: Science assessment document and derivation of the reference level(s)" (WGAQOG, 1996). This group has also drafted the science assessment document for ground-level ozone (WGAQOG, 1998). The Canada-Wide Standards Development Committee has drafted an options paper for ozone and particulates (CCME, 1998 c). Alberta Environmental Protection is a long-standing member and active participant of this Working Group.

### 1.1 Objectives of the Present Study

- 1. Identify agencies, industries and associations that are collecting data on ambient ozone and its precursors, NO<sub>x</sub> and VOC, in Alberta;
- 2. Compile a list of study reports, published papers and other relevant information from Alberta on ambient ozone, ozone precursors and related photochemical products starting from the year 1980;

- 3. Provide a literature review on all papers and reports produced for Alberta;
- 4. Review and assess the information compiled. Relate Alberta information to the national scene wherever possible. Compare ambient ozone levels in Alberta to the proposed reference levels and Canada-Wide Standards (CWS) options for ground-level ozone, and
- 5. Prepare a report including written text, tables, figures and references for review.

### 1.2 Air Quality Framework

Alberta is the largest supplier of hydrocarbon energy resources in Canada. The environmental consequences of energy production and use have long been recognized as an important element in economic development in Alberta. Therefore, the existing air quality management system used by the Alberta government, has evolved over years (Lack, 1980, Macdonald and Bietz, 1996). The key components of the system include ambient guidelines, source emission standards, plume dispersion modelling, ambient and source emissions monitoring, environmental reporting, emission inventories, approvals, inspections, abatement, enforcement and research. This system was designed to ensure that emissions are minimized through the use of Best Available Demonstrated Technology (BADT), and to ensure that ambient air quality meets Alberta's objectives. Quantitative relationships between emissions of interest from sources and ambient concentrations are obtained by means of mathematical models that simulate the transport and diffusion of the emitted substances and their chemical transformations. Such models yield both concentrations in the air and deposition levels of both primary and secondary pollutants (Cheng et al., 1995).

In the late 1980s, the Government of Alberta recognized new local and global challenges on air issues and launched the development of a Clean Air Strategy for Alberta (CASA). Subsequently, the government endorsed a clean air vision for Alberta (CASA, 1991; Legge et al., 1992):

"The air will be odourless, tasteless, look clear and have no measurable short- or long-term adverse effects on people, animals or the environment."

In 1994, Clean Air Strategic Alliance of Alberta (also CASA) was formed and incorporated with representatives from government, industry and non-government organizations. The overarching goal of the Alliance is to develop an air quality management system for Alberta with the specific mandate of: 1) clearly identify the most important air quality issues; 2) prioritize specific problems; 3) allocate and coordinate resources; 4) develop solution oriented action plans, and 5) evaluate results. CASA provides an excellent forum for multistakeholder consultations on air issues. The 1996 annual report of the Clean Air Strategic Alliance provides a good overview of the Alliance activities (CASA, 1997). CASA has provided leadership in setting up various zones for air quality management in Alberta. The zones are outlined in the 1996 report, which contains a strategic plan for air quality monitoring in Alberta, including ozone. Once the strategic plan for air quality was adopted by the CASA Board in November 1995, an Implementation Team was struck to implement the plan. Phase I focussed on technical details, ecological effects monitoring, zone coordination, administration and management, and data management. Details of the implementation process have been reported (Teal and Angle, 1997).

### 1.3 Format

Within the objectives of this study, every effort was made to make this document as a "stand alone" report. To do so, inclusion of a brief background on precursor emissions, chemistry, meteorology, and models on ozone and related photochemical oxidants became essential. Because extensive published literature is available on the ground-level ozone in the national and international context, only selected literature references from outside Alberta are quoted. Two main criteria considered to cite such references are: 1) that they further the understanding of the subject matter under discussion, and 2) that the reported values from these references are compared with Alberta information.

An integrated air quality management framework approach was followed in preparing this report. Ambient air quality data in general, including data on ozone, is one of the many elements that constitute the air quality management framework as mentioned in the previous section. This report has eight sections: 1) Introduction; 2) Precursors and Products; 3) Chemistry, Meteorology and Models; 4) Measurements and Results; 5) Discussion; 6) Conclusion; 7) References, and 8) Appendices. Sections 4, 7 and 8 address objectives 1 and 2, whereas sections 1, 2, 3, 5 and 6 address objectives 3 and 4. Submission of this final report takes care of the last objective. Words "mean" and "average", as well as "maximum" and "peak" are used interchangeably in the text. "Human-made" and "anthropogenic" words are also used interchangeably. "Median" denotes the 50<sup>th</sup> percentile of a distribution. Mass units are micrograms per cubic meter of air (µg m<sup>-3</sup>). Concentrations are given in parts per billion of air by volume (ppb).

Some of the references use "mixing ratios" for ozone instead of concentrations. In simple terms, the ozone mixing ratio is defined as the ratio of ozone in molecules per cubic centimeter to that of air in molecules per cubic centimeter. Throughout the report only "concentrations" or "levels" are used instead of mixing ratios. Two other numbers on ozone 1-hour ambient objectives of "82" and "80" have been quoted in different references. They refer to the same objective. A value of 82 ppb is used in the present text.

### 2.0 PRECURSORS AND PRODUCTS

Ozone is not directly emitted into the atmosphere from human-made sources. It is formed photochemically in the stratosphere and transported downward, resulting in the presence of ozone in the natural or "free" troposphere. Though the presence of  $O_3$  at low concentrations is an integral part of the troposphere, its presence at higher concentrations is detrimental. In the lower atmosphere, especially close to earth's surface, ozone and other photochemical oxidants are formed through a complex sequence of reactions of precursors, mainly nitrogen oxides and volatile organic compounds, in the presence of sunlight. An overview of photochemical smog, precursors of  $O_3$ , and their emissions from Alberta in the context of Canadian emissions is presented here. Products of  $O_3$  reactions are mentioned but main aspects of chemistry and meteorology of  $O_3$  are given in the next chapter.

### 2.1 Photochemical Smog

Leighton's (1961) monumental book and two other recent books give an excellent account of the chemical characteristics of photochemical smog (Finlayson-Pitts and Pitts, 1986; Seinfeld, 1986). A brief description of "smog" has been published recently (Sandhu, 1999). The word "smog" is derived from the words smoke and fog. Two other words which have been used are "smaze" and "smist", resulting from the combination of smoke and haze, and smoke and mist, respectively. Many episodes of the "killer fog" or "smog" have been recorded in the 20<sup>th</sup> century. In recent years smog has extended to refer to any chemical "soup" that is visible, such as the common brownish-yellow haze over urban areas, sometimes including suburban and rural areas. Two types of smog have been quoted in the scientific literature: 1) coal sulphur, sulphurous, reducing-type or London-type smog, and 2) photochemical, which is frequently referred to as Los Angeles or oxidizing-type smog (Leighton, 1961).

The great London, England fog of December 1952 contained high concentrations of smoke particles and sulphur dioxide. This type of smog occurs in winter, caused by an accumulation of products resulting from the combustion of fossil fuels in home heating, industry and power stations under light winds and temperature inversions. Los Angeles-type smog was first observed in North America in 1944. This type of smog is more a haze than a fog, and is characteristic of a low humidity aerosol, which originates through photochemical processes involving primary pollutants such as nitrogen oxides and hydrocarbons, emitted from automobiles, petroleum industries and other sources. Because sunlight is a key factor in producing oxidizing type smog, ozone is the main component of this smog and has the highest concentration on hot summer days. One important minor component is peroxyacetyl nitrate (PAN).

Published literature and Alberta data on photochemical air pollutants and meteorological variables was examined in the mid-1970s (Sandhu, 1975). Comparison between the observed and calculated values of ozone revealed that photochemical reactions do occur in the airsheds of Edmonton and Calgary during summer months. The observed net concentrations of ozone are the end result of chemistry and meteorology of the air. Forest fire enhanced photochemical air pollution from Alberta has been reported recently (Cheng et al., 1998).

### 2.2 Nitrogen Oxides

When air is heated to high temperatures, nitric oxide (NO), nitrogen dioxide (NO<sub>2</sub>) and other higher oxides of nitrogen are produced. Human-made sources of nitrogen oxides (NO<sub>x</sub>) are associated with combustion processes. NO<sub>x</sub> includes NO, NO<sub>2</sub> and higher oxides of nitrogen. The main primary pollutant is NO. Burning of fossil fuels containing nitrogen also results in the formation of NO<sub>x</sub>. Major categories of NO<sub>x</sub> sources include transportation, stationary source fuel combustion, industrial processes, solid waste disposal and other fossil fuel combustion-related activities. Emissions in different categories are generally quantified using emission factors and the level of activity. Table 1 shows the NO<sub>x</sub> emission estimates from Alberta for the years 1990 and 1995, along with the total Canadian emissions (EC, 1996; Slubik, 1998). It is important to remember that sources of error are associated with the emissions estimation process and values shown in this table are the best estimates.

Natural sources of  $NO_x$  include lightning, soils, wildfires, stratospheric intrusion and the oceans. Of these, lightning and soil are the major sources. Because of the large forested areas in Alberta and Canada,  $NO_x$  emissions from large wildfires can be significant on a local or regional scale in the fire season. Uncertainties in the estimation of natural emissions are even higher than the uncertainties in the human-made emissions.  $NO_x$  emissions in Alberta, from open sources such as forest fires, were estimated at 1,498 tonnes in 1990 (Table 1). Though nitrous oxide ( $N_2O$ ) is produced naturally by soils, oceans and other processes, its contribution to ground-level ozone formation is negligible. It is one of the greenhouse gases.

### 2.3 Volatile Organic Compounds

Man-made volatile organic compounds are emitted into the atmosphere by evaporative and combustion processes in the form of hundreds of chemical species. The species commonly associated with O<sub>3</sub> production contains 2 to 12 carbon atoms and hydrogen only, or functional groups having oxygen and halogen atoms. The atmospheric oxidation rate of methane is very slow compared with higher hydrocarbons, making methane (CH<sub>4</sub>) least important in O<sub>3</sub> formation. However, CH<sub>4</sub> emissions are extremely important as the greenhouse gas. Major sectors contributing to VOCs are industrial processes, transportation, fuel combustion, incineration and miscellaneous sources. Alberta emissions of VOCs for 1990 and 1995 are also shown in Table 1, along with the Canadian emissions. Alberta emissions of VOCs are about one quarter of the national emissions.

Biogenic emissions of VOCs are significant and contribute to O<sub>3</sub> production in both urban and rural areas. Vegetation emits significant quantities of reactive VOCs into the atmosphere. The VOC emissions of primary interest are isoprenes and the monoterpenes, which are hydrocarbons. Most biogenic VOC emissions from vegetation increase exponentially with temperature. Isoprene emissions are light-dependent, being minimal at night and increasing with solar intensity during the day. Other things being equal, isoprene is emitted at a much higher rate than the monoterpenes. Estimated biogenic emissions of VOCs for Alberta and Canada are also shown in Table 1. It is worth noting that biogenic emissions are larger than the anthropogenic emissions by a factor of more than 2, whereas Canadian biogenic emissions are greater than Canadian anthropogenic emissions by a factor of more than 5.

Table 1 Emissions of nitrogen oxides and volatile organic compounds (tonnes) for Alberta. Also listed are the total Canadian emissions.\*

Sector		N	O <sub>x</sub>	voc					
		1990	1995**	1990	1995**				
	Industrial Process	179,716	327,444	458,030	497,497				
	Fuel Combustion	98,058	103,211	3,516	24,838				
genic	Transportation	208,582	206,326	108,589	107,946				
Anthropogenic	Incineration	344	15	1,896	1,071				
Anth	Miscellaneous	13	0	65,622	50,840				
	Alberta	486,713	636,996	637,653	682,192				
	Canada	2,062,297	2,288,354	2,579,051	3,189,475				
Open	Alberta	1,498	16,323	56,687	67,473				
Op	Canada	103,735	216,578	446,908	936,871				
enic	Alberta	NA	NA	1,476,331	NA				
Biogenic	Canada	NA	NA	14,197,000	NA				

<sup>\*</sup> Taken from reference EC, 1996.

NA Not Available

### 2.4 Products

Ozone is present in the atmosphere, even in the absence of human activities, due to the photochemistry of oxygen in the stratosphere. It is a potent oxidizing agent and its reactions with different precursors yield a variety of products which may be photochemically reactive themselves. Product identification and quantification of yield, in both laboratory and ambient air, are helpful in the verification of chemical mechanisms used in model calculations, as well as in further research on the synergistic effects of  $O_3$  in the presence of other pollutants. Chemistry of  $O_3$  is discussed briefly in the next chapter. The main reactive species in the lower atmosphere is the hydroxyl (OH) radical, which is responsible for initiating reactions of almost all VOCs and

<sup>\*\*</sup> These are preliminary estimates (Slubik, 1998)

 $CH_4$ . The oxygen atom produced by the ultraviolet photolysis of ozone in the upper atmosphere reacts with water vapour to form the OH radicals. Generally, the water vapour concentration decreases with increasing altitude and the  $O_3$  concentration increases with increasing altitude in the lower atmosphere. These opposing forces result in OH radical concentrations that are reasonably independent of altitude.

In the air, initially emitted nitric oxide (NO) is converted to nitrogen oxides (NO<sub>x</sub>) (NO + NO<sub>2</sub>). Furthermore, reactions of O<sub>3</sub> and OH with NO<sub>x</sub> and VOCs yields nitric acid (HNO<sub>3</sub>) and nitrous acid (HNO<sub>2</sub>), peroxyacetyl nitrate (PAN) and its homologues, organic nitrates, and particulate nitrates. These reservoirs and termination products are referred to as NO<sub>z</sub>. The term "NO<sub>y</sub>" refers to the total amount of nitrogen, with  $NO_v = (NO_x + NO_z)$ . Attempts have been made to correlate O<sub>3</sub> levels with NO<sub>x</sub>, NO<sub>y</sub> and NO<sub>z</sub>. It was noted that, in rural areas in the eastern United States, there is a good correlation between O<sub>3</sub> levels and NO<sub>y</sub> (USEPA, 1996). It has been shown also that ambient O<sub>3</sub> levels correlate even better with NO<sub>2</sub> than with NO<sub>3</sub>, as may be expected because NO<sub>z</sub> quantifies the amount of initially emitted NO that has been processed photochemically, forming O<sub>3</sub> in the process. Intermediate products of OH radicals with CH<sub>4</sub> include methyl (CH<sub>3</sub>), methoxy (CH<sub>3</sub>O), methyl peroxy (CH<sub>3</sub>O<sub>2</sub>) and methyl hydroperoxide (CH<sub>3</sub>OOH) radicals. Through complex sequence of reaction these radicals terminate yielding formaldehyde (HCHO) and ultimately CO<sub>2</sub>, the major greenhouse gas. Numerous compounds are formed by reactions of VOCs and O<sub>3</sub>, OH and NO<sub>3</sub>. Calculated lifetimes in the troposphere of selected VOCs, due to photolysis and reactions with O3, OH and NO3, have been discussed (USEPA, 1996).

### 3.0 CHEMISTRY, METEOROLOGY AND MODELS

Excellent reviews and books on the atmospheric chemistry, meteorology and modelling of ozone are now available (Leighton 1961; Finlayson-Pitts and Pitts, 1986; Seinfeld, 1986; USEPA, 1996; EC, 1997a-h). The only attempt in this chapter is to introduce the reader to general aspects.

### 3.1 Chemistry

Human activities lead to the emissions of  $NO_x$ ,  $CH_4$  and non-methane organic compounds (NMOC) or VOCs. In addition to the anthropogenic emissions, large quantities of biogenic VOCs are emitted, both in polluted and non-polluted areas, from vegetation (Table 1). The major tropospheric process for the removal of  $CH_4$  is by reaction with OH radicals and is relatively slow compared with reactions of VOCs. Because of the importance of OH radicals in the atmosphere, the chemistry of OH formation is briefly described first, and then the reactions of  $NO_x$  and hydrocarbons (RH) or VOCs are presented.

### 3.1.1 Hydroxyl Radicals

The key reactive species in the troposphere is the OH radical, which is responsible for initiating the degradation reactions of almost all VOCs. In the presence of NO, these OH radical reactions with VOCs lead to the formation of  $O_3$  and, hence to  $O_3$  concentrations above those encountered in the free troposphere. In the upper atmosphere, the OH radical is produced from ultraviolet photolysis of  $O_3$ . Ozone photolyses to generate the electronically excited  $O^*$  atom and  $O_2$  molecule:

$$O_3 + h\nu \text{ (sunlight)} \rightarrow O_2 + O^*$$

The O\* atoms are either deactivated or they react with water vapour to form the OH radical:

$$O^* + H_2O \rightarrow 2 OH$$

Hydroxyl radical production from the above two reactions is balanced by reactions of OH radicals with CO and CH<sub>4</sub>. Because the water vapour concentration decreases with increasing altitude in the troposphere, and O<sub>3</sub> concentration generally increases with increasing altitude, the OH concentration is expected to be reasonably independent of the altitude.

It has been shown from the modelling of a generalized photochemical air pollution system, that lower rates of product formation like PAN, under winter conditions in Alberta, are due to solar altitude or intensity rather than temperature (Bottenheim et al., 1977). The rate of primary formation of major radicals, HO, HO<sub>2</sub> and RO<sub>2</sub>, together with their participation in several reactions, are the driving forces in these systems. Primary formation of these radicals is largely unaffected by temperature. Reaction chain lengths are dependent upon the activation energies, which are generally small, thus temperature has little influence. Conversely, solar attitude is expected to have a much greater effect since these radicals are produced primarily by photochemical reactions.

### 3.1.2 Nitrogen Oxides

The basic process leading to the photochemical formation of  $O_3$  in the lower troposphere and the polluted urban atmosphere involves the photolysis of  $NO_2$  to yield NO and a ground-state O atom. Ozone is formed and destroyed in a series of reactions involving NO and  $NO_2$ . These three compounds are inter-related by the following reaction scheme:

$$NO + O_3 \rightarrow NO_2 + O_2$$
 R1

$$NO_2 + hv \rightarrow NO + O$$
 R2

$$O + O_2 + M \rightarrow O_3 + M$$
 R3

where M denotes a third body like a nitrogen or oxygen molecule. In the absence of other chemical species, these three reactions govern  $O_3$  concentration. Thus, under steady-state conditions, the ozone concentration  $[O_3]$  is given by:

$$[O_3] = \frac{J_2 [NO_2]}{k_1 [NO]}$$
 [1]

where  $k_1$  is the reaction rate constants for reaction R1. Typical value of  $k_1 = 26.6$  ppm<sup>-1</sup> min<sup>-1</sup> at 25°C.  $J_2$  is the photodissociation rate constant of  $NO_2$ . In theory, it is a time-dependent function which is determined by the position of the sum, atmospheric conditions and the absorptive and photodissociative properties of nitrogen dioxide. Procedures for its estimation have been developed. Approximate  $J_2$  value is 0.5 min<sup>-1</sup> during midday in summer (Seinfeld, 1986). One of the main important reactions involving  $NO_x$  is the reaction of  $NO_2$  with  $O_3$  giving rise to  $NO_3$  radical,

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$
 R4

which, in the lower atmosphere, is in equilibrium with  $N_2O_5$ :

$$NO_3 + NO_2 \stackrel{\longleftarrow}{\longrightarrow} N_2O_5$$
 R5

Removal processes for  $NO_x$  involve the daytime reaction of  $NO_2$  with OH radical and the nighttime wet and dry deposition of  $N_2O_5$  to produce  $HNO_3$ .

$$NO_2 + OH \rightarrow HNO_3$$
 R6

$$N_2O_5 + H_2O \rightarrow 2HNO_3$$
 R7

The gas-phase reaction of the OH radical with NO<sub>2</sub> is the major and ultimate removal process for NO<sub>x</sub>. This reaction removes radicals (OH and NO<sub>2</sub>) and competes with the reactions of the OH radical with VOCs. HNO<sub>3</sub> formed undergoes wet and dry deposition, including combination with ammonia (NH<sub>3</sub>) to form particulate phase ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>). The cyclic nature

of reactions of nitrogen oxides is shown in Figure 1. It should be noted that OH radicals can react with NO to produce nitrous acid (HNO<sub>2</sub>):

$$OH + NO \xrightarrow{M} HNO_2$$
 R8

Nitrous acid can become an important photochemical source of OH radicals during the early morning hours, leading to the rapid initiation of photochemical activity. Major termination species for  $NO_x$  are PAN (peroxyacetyl nitrate) and its homologues, organic nitrates,  $HNO_3$  and particulate nitrate.

### 3.1.3 Volatile Organic Compounds

The major classes of VOCs are alkanes, alkenes, aromatic hydrocarbons, carbonyl compounds, alcohols and ethers. The chemical loss processes of VOCs include photolysis and chemical reactions with the OH radical during daylight hours, reaction with the  $NO_3$  radical during night, and reaction with  $O_3$ , which often is present throughout day and night. If RH denotes a hydrocarbon compound, then the major loss process of alkanes like  $CH_4$  or  $C_2H_6$  is the abstraction reaction with OH.

$$OH + RH \rightarrow H_2O + R$$
 R9

Then, R attaches to  $O_2$  to form an alkyl peroxy radical (RO<sub>2</sub>),

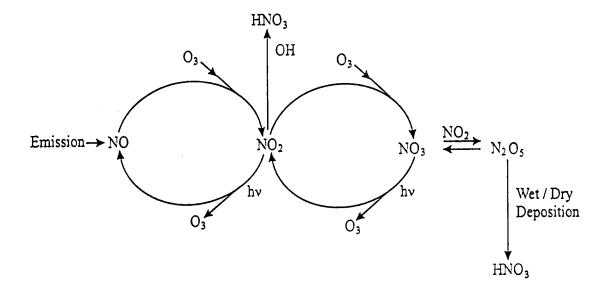
$$R + O_2 + M \rightarrow RO_2 + M$$
 R10

Aklyl peroxy radicals can react with NO, NO<sub>2</sub> and HO<sub>2</sub> radicals

$RO_2 + NO \rightarrow RO + NO_2$	R11
$RO_2 + NO_2 \iff ROONO_2$	R12
$RO_2 + HO_2 \rightarrow ROOH + O_2$	R13
$RO_2 + NO \rightarrow RONO_2$	R14

All these organic peroxy radicals react with each other to terminate the chain and give rise to products. A diagram showing cyclic reactions of methane oxidation is given in Figure 1.

The alkenes, like ethylene (C<sub>2</sub>H<sub>4</sub>), react with OH and NO<sub>3</sub> radicals and O<sub>3</sub>. These three reactions are important transformation processes. The initial process is the addition to the double bond in alkenes to form radicals whose reactions are very similar to reactions R8 to R12. The chemistry of aromatic hydrocarbons is not well understood. The most abundant aromatic hydrocarbons in urban atmospheres are benzene, toluene, xylenes and trimethyl benzenes (Grosjean and Fung, 1984). The reactions of OH radicals with aromatics proceed either by H-atom abstraction or OH radical addition to the aromatic ring leading to new radicals. As noted above, the OH radical



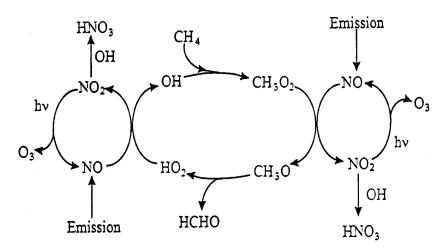


Figure 1 The cyclic reactions of nitrogen oxides and methane oxidation (USEPA, 1996).

reactions with the alkanes, alkenes and aromatic hydrocarbons, lead to the formation of carbonyl compounds.

Also, carbonyls are formed during the reactions of NO<sub>3</sub> and O<sub>3</sub> with alkenes. The major loss process of the carbonyls formed is either due to photolysis or reactions with OH. The end products of these carbonyl reactions are organic nitrates, like peroxyacetyl nitrate (PAN), and particulate nitrate.

It has been noted that the transport of PAN out of urban areas into colder air masses leads to PAN becoming a temporary reservoir of  $NO_x$ , allowing the long-range transport of  $NO_x$  to less polluted areas. Release of  $NO_2$  in these less polluted areas via reaction R-15,

$$CH_3C(O)OO + NO_2 + M \stackrel{\longleftarrow}{\hookrightarrow} CH_3C(O)OONO_2$$
 R15, R-15

with subsequent photolysis of  $NO_2$ , then leads to  $O_3$  formation and pollution of remote areas (USEPA, 1996). Different alcohols and ethers are used in gasoline and alternative fuels. Again, OH radical reactions are dominant in the atmospheric chemistry of alcohols and ethers. Addition of VOC reactions with  $O_3$  and OH to reaction scheme R1 to R3 make the steady-state concentration equation [1] more complex and dictates using complex reaction schemes in modelling studies to predict  $O_3$  concentrations.

### 3.2 Meteorology

The province of Alberta lies between the 49<sup>th</sup> and 60<sup>th</sup> parallels of latitude, which places it in the central belt of the northern cool temperate zone. The Rocky Mountains, immediately to the west, prevent any sustained influence of the Pacific Ocean and lead to a continental climate with long, cold winters and short, warm summers. Prevailing upper level winds are west-northwest. Daylight ranges from about 7.5 h in the winter to 17 h in the summer. Much of the available solar energy in winter is reflected by snow cover. Because mechanisms governing O<sub>3</sub> concentrations are dependent upon climatic variables, it might be expected that O<sub>3</sub> concentrations measured in Alberta would exhibit different characteristics from those measured in more moderate, southerly climates. Day-to-day variability in O<sub>3</sub> concentrations, to a first approximation, is the result of day-to-day variations in meteorological conditions. Thus, many atmospheric processes and parameters affect the concentrations of O<sub>3</sub> and other photochemical oxidants. The list of processes includes the vertical structure and dynamics of the planetary boundary layer (PBL); transport processes, including thermally-driven mesoscale circulations such as lake breeze circulations; complex terrain effects on transport and dispersion; vertical exchange processes; deposition and scavenging, and meteorological controls on biogenic emissions and dry deposition.

### 3.2.1 Atmospheric Processes

Knowledge of the surface energy budget is fundamental to an understanding of the dynamics of the PBL. The PBL is directly influenced by the characteristics of the earth's surface. In combination with synoptic winds, it provides the forces for the vertical fluxes of heat, mass and momentum. The accounting of energy inputs and outputs provides a valuable check on modelled

PBL. The global annual average surface energy budget has been assumed at zero, though continuing debate on climate change has questioned this assumption. On a day-to-day basis, the surface heat budget causes changes in surface temperature. Clouds, for example, reduce the amount of radiation reaching earth's surface, which in turn modifies the outgoing components. Similarly, albedo of the surface will modify the outgoing radiation. For a place like Alberta, which is covered with snow in winter, albedo plays a significant role in the photochemistry of air pollution (Angle et al., 1992). The concentration of an air pollutant depends on the degree of mixing that occurs between the time a pollutant or its precursors are emitted and the arrival of the pollutant at the receptor. Atmospheric mixing is the result of either mechanical turbulence or thermal turbulence. The potential for thermal turbulence can be characterized by atmospheric stability.

When air moves vertically through the atmosphere its temperature decreases with height as a result of adiabatic cooling. Those layers of the atmosphere where temperature increases with height (inversion layers) are the most stable, as air, cooling as it rises, becomes more dense than its new, warmer environment. Thus, mixing of air is faster in an unstable layer compared with the mixing in a stable air. A stable layer can also act as a trap for air pollutants laying beneath it. On the other hand, if pollutants are emitted into a stable layer aloft, the lack of turbulence will keep the contaminants from reaching the ground while the inversion persists. Traditionally, atmospheric mixing has been treated through the use of a mixing height, which is defined as the base of an elevated inversion layer. Concerns have been expressed that the strict use of mixing height unduly simplifies the complex atmospheric processes that redistribute pollutants in urban areas. Seasonal mixing heights and inversions at Edmonton have been reported (Myrick, et al., 1994). Cloud venting and stratospheric-tropospheric ozone exchange processes are important in understanding the ozone distribution at earth's surface. The intrusion of stratospheric ozone into the troposphere has been examined by many authors and is well documented in the literature. Recent estimates of  $O_3$ , which originates from the stratosphere, are 5-15 ppb to the daily maximum hourly mean O<sub>3</sub> concentrations during the summer season (USEPA, 1996).

### 3.2.2 Meteorological Parameters

Ground-level ozone concentrations are influenced by meteorological parameters like sunlight, temperature, wind speed, atmospheric mixing, transport and surface scavenging. Longer-term trend analysis requires that meteorological fluctuations from the observed data should be filtered out, however, this is not easy. Solar radiation plays a key role in initiating the photochemical process that leads to ozone formation. Sunlight intensity varies with season and latitude. The importance of photochemistry to the formation of ozone and time of the year has been linked. During the summer, the UV intensity is fairly constant throughout the contiguous United States and Southern Canada, and only the duration of the solar day varies with latitude. The effects of light intensity on the atmospheric chemistry and overall oxidant formation processes have been studied and summarized in standard books and reviews. It was shown that the effect of light intensity varies with initial reactant concentrations. Most important was the observation that VOC/NO<sub>x</sub> systems showed different oxidant-forming potential depending on whether studies of these systems were conducted using constant or diurnal light.

An association between ground-level ozone concentration and temperature has been demonstrated from measurements in outdoor smog chambers and from measurements in ambient air. Episodes of high temperature have been linked to seasonally high ozone values. An upper-bound on ozone concentrations that increases with temperature has been noted at number of urban and rural locations. This showed that, at a given temperature, there is a wide range of possible ozone concentrations because other factors like cloudiness, precipitation and wind speed can reduce the ozone production. The upper-bound presumably represents the maximum ozone concentration achieved under the most favourable conditions. The role of temperature on ozone formation, regarding its photochemistry, thermal decomposition of PAN, increased anthropogenic and natural emissions, and correlation with stagnation, has been discussed (USEPA, 1996). Wind speed influences ozone levels because lower wind speeds lead to reduced ventilation and the potential for greater buildup of ozone and its precursors. Abnormally high temperatures are frequently associated with pressure, stagnant circulation and suppressed vertical mixing, all of which may contribute to elevated ozone levels. The effect of wind speed and direction on ozone levels varies from place to place.

It is well accepted now that at a local level, ozone and other oxidants result from a complex sequence of reactions. Therefore, it is important to understand the concept of an "air mass", or "chemical air mass". These are created when air becomes stagnant over a "source region", with or without emissions, and subsequently takes on the characteristics of the source region, such as temperature, humidity and stability. Meteorological processes play an important role in determining the amount of "accumulation" of ozone and its precursors that occur under such stagnant conditions. The areas of ozone accumulation are characterized by synoptic-scale subsidence of air in the free troposphere, resulting in development of an elevated inversion layer, with low wind speeds, lack of cloudiness and high temperatures. Considerable progress in understanding the transport of photochemical ozone, other oxidants and their precursors by weather systems using modelling has been made over the years.

### 3.3 Models

It always becomes necessary to predict how ambient ozone concentrations will change when emissions of its precursors change as a result of a new development or a control on the existing sources. A model is a set of mathematical relationships, based on scientific principles that relate chemical emissions to the resulting ambient concentrations (Angle and Sakiyama, 1991). Models are the ultimate integrators of our knowledge of the comprehensive chemistry and physics of the atmosphere. They are an indispensable tool for understanding the complex interactions of transport, transformation and removal in the atmosphere. The model can be used as an experiment that can not be run in the atmosphere. Models are useful in the design of field measurements like ambient monitoring and are essential in the interpretation of data. Air quality models in general, including ozone, operate on sets of input data that characterize the emissions, topography, meteorology and chemistry of a region and produce outputs that describe air quality in that region. Mathematical models for photochemical air pollution were first developed in the early 1970s and have been refined over time.

### 3.3.1 Grid-Based Models

The basis for grid-based air quality models is the atmospheric diffusion equation that expresses the conservation of mass of each pollutant in a turbulent fluid in which chemical reactions occur (Seinfeld, 1986). The region to be modelled is bordered on the bottom by ground, on the top by some height that characterizes the maximum extent of vertical mixing, and on the sides by east-west and north-south boundaries. The region of interest to be modelled is divided into a three dimensional array of grid cells. The horizontal dimensions of each cell are usually a few kilometers for urban applications and up to tens of kilometers for regional applications. Some older grid-based models assumed only a single, well-mixed vertical cell extending from the ground to the inversion base. However, current models subdivide the region into layers.

There are practical and theoretical limits to the minimum horizontal grid cell size. Increasing the number of cells increases computing and data acquisition efforts and costs, as well as better resolution of input data. Thus, the spatial resolution of the concentrations predicted by a grid-based model corresponds to the size of the grid cell. Ozone predictions are sensitive to the choice of grid cell size. It has been noted that the coarse grid models tend to predict higher ozone concentrations and lower NO<sub>2</sub> than the finer grid models. On the other hand, the coarse grid tends to transport O<sub>3</sub> + NO<sub>2</sub> more in the form of O<sub>3</sub>, whereas the finer grid tends to transport the O<sub>3</sub> + NO<sub>2</sub> more in the form of NO<sub>2</sub>. Several grid-based photochemical air quality models have been developed to simulate ozone production in urban areas or in larger regions. They differ primarily in their treatment of specific atmospheric processes, such as chemistry, and in the numerical procedure used to solve the governing system of equations. Some examples of grid-based models are Urban Airshed Model (UAM), Acid Deposition and Oxidant Model (ADOM), Regional Acid Deposition Model (RADM) and Regional Oxidant Model (ROM).

### 3.3.2 Lagrangian (Trajectory) Models

In this approach, a hypothetical air parcel moves through the area of interest along a path calculated from wind trajectories. Emissions are injected into the air parcel and undergo mixing and chemical transformations. The data requirements for these models include: 1) initial concentrations of all relevant pollutants and species; 2) rates of emissions of  $NO_x$  and VOC precursors into the parcel along its trajectory; 3) meteorological characteristics, such as wind speed and direction, to define the path of the air parcel through the region; 4) mixing depth; 5) horizontal expansion rates, and 6) solar ultraviolet radiation.

The key assumption inherent in these models is that a hypothetical air parcel maintains its integrity along the trajectory. Trajectory models provide a dynamic description of atmospheric source-receptor relationships that is simpler and less expensive to derive than that obtained from grid models. Simple models in this class are based on the use of a simple one cell moving box model. As the box moves downwind, it encounters emissions of NO<sub>x</sub> and VOCs that are assumed to be uniformly mixed within the box. The height of the box is allowed to expand to account for the breakup of the nocturnal inversion layer. A simple trajectory model was used in the Empirical Kinetic Modelling Approach. (EKMA). The EKMA-based method of determining control strategies has some limitations (USEPA, 1996).

### 3.3.3 Modelling in Alberta

In Alberta, air quality models are an essential component of an air quality management system (Lack, 1980; Macdonald and Bietz, 1996; AEP, 1997). Modelling is used to relate the resulting ambient air quality to the air quality objectives or to develop new or revised ambient air quality objectives. Figure 2 is a schematic diagram of this approach (Cheng et al., 1995). A quantitative relationship between emission of interest from sources and ambient levels is obtained by means of a mathematical model that simulates the transport and diffusion of the emitted substances and the chemical transformation into secondary products. Such models yield the concentration in the air and deposition levels. These predicted values become inputs both to the objective setting process and thereafter become a management tool for limiting sources to meet the ambient objective and guidelines, exploring future industrial development and choosing locations for industrial activities. This air quality management framework allows industrial facilities to operate while protecting the environment, an early approach to environmentally sustainable economic development. Alberta Environmental Protection uses air quality model predictions in a wide variety of air quality management decisions, including determining appropriateness of facility location, monitoring network design, and stack design (AEP, 1997). Models for ozone prediction have been identified by the Department for performing assessments for regulatory applications. Modelling related to ozone from Alberta is discussed in chapter 5.

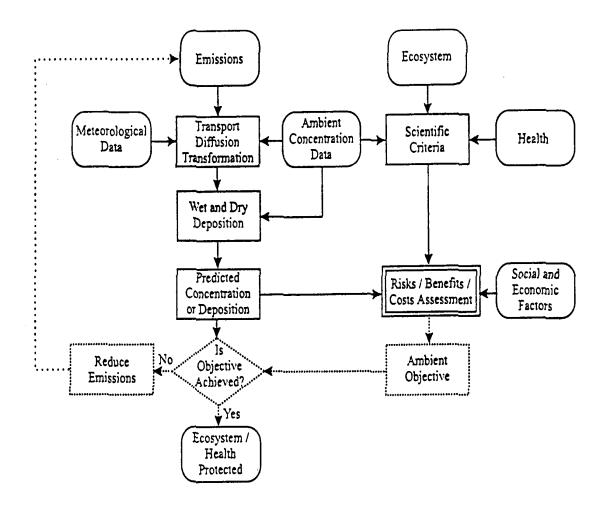


Figure 2 Simplified air quality management system (generalized from Cheng et al., 1995).

### 4.0 MEASUREMENTS AND RESULTS

Ambient air quality monitoring is an essential component of the air quality management framework in Alberta as described in section 1.2. Over the years, different methods have been used to measure  $O_3$ ,  $NO_4$ ,  $NO_5$ ,  $NO_8$ , total hydrocarbons (THC) and volatile organic compounds.  $NO_8$  is simply a sum of  $NO_8$ . Monitoring agencies adopted new techniques as the new instrumentation became available commercially. Measurement methods used by Alberta Environmental Protection are briefly outlined in Appendix I, which also gives a brief description of total air quality monitoring network of Alberta Environmental Protection.

### 4.1 Monitoring in Alberta

Routine monitoring of air pollutants in Alberta started in the early 1960s. Governments, industry and associations are all involved in monitoring of ambient  $O_3$ ,  $NO_x$ , THC and VOCs, both on long- and short-term bases. Governments have been monitoring ambient air for the longest time. As part of Environment Canada's National Air Pollution Surveillance (NAPS) network, Alberta Environmental Protection has been routinely monitoring ambient concentrations of ozone and other criteria pollutants at three locations in Edmonton and three locations in Calgary. Industry is also involved in making measurements of  $O_3$  or its precursors, either as a formal or informal requirement, by Alberta Environmental Protection. Four associations, Strathcona Industrial Association; West Central Airshed Society; Fort Saskatchewan Regional Industrial Association and Wood Buffalo Environmental Association are involved in air quality monitoring. The Alberta Government-Industry Acid Deposition Research Program (ADRP) also monitored ozone and its precursors (Legge and Krupa, 1990). Locations and facilities for which short- and long-term observations have become available are listed in Appendix II.

It is worth noting that Alberta Environmental Protection (formerly Alberta Environment) uses five types of names for their monitoring stations: (1) continuous stations; (2) intermittent stations; (3) static networks; (4) precipitation quality stations; and (5) mobile monitoring. Continuous stations measure hourly concentrations of air contaminants, including dust and smoke and inhalable particles, while intermittent stations report 24-hour measurement of particulates and other chemicals. Stations that monitor monthly or tri-monthly loadings are called static networks. Weekly rain and snow samples are collected at precipitation quality stations. Mobile monitoring is carried out using a Mobile Air Monitoring Laboratory (MAML). This is a special vehicle that has been designed to measure the air quality at any location in Alberta. A detailed description of the MAML is available from Alberta Environmental Protection.

### 4.2 Results

### **4.2.1** Hourly Mean Concentrations

Over the years, a large body of hourly data on O<sub>3</sub>, NO, NO<sub>2</sub>, VOCs and total hydrocarbons has been collected by Alberta Environmental Protection (AEP) either solely or in cooperation with Environment Canada. All these data have been published in annual reports (AEP, different years; Myrick et al., 1992 to 1996). In the early 1990's, three types of annual documents on air

quality were published: (1) Summary Report; (2) Detailed Report; and (3) Data Report. Locations, parameters monitored and the time period of data collections are given in Appendix II. Continuous monitoring locations are shown in Figure 3.

A typical set of hourly ozone data for Calgary and Edmonton downtown sites, Fort Saskatchewan, and Hightower Ridge for June, 1997 is given in Tables 2, 3, 4 and 5. The months of June and December were selected because summer and winter solstices occur in these months and the solar day has the maximum and minimum number of sunshine hours at this time. Ozone is not emitted directly into the atmosphere from anthropogenic sources. It is the natural components of the air and is also produced by photochemical reactions of precursors like NO<sub>x</sub> and VOC. Therefore, a typical set of data on NO, NO<sub>2</sub>, THC and VOC for Calgary and Edmonton are given in Appendix III. These data are given so that others interested in this subject can do their calculations and further their understanding. Environment Canada measures ozone and other air quality parameters at Esther.

Industrial facilities that monitor ozone or its precursors (Appendix II) use the same or equivalent monitoring protocols as developed by Alberta Environmental Protection. Only a couple of industries are required by the government to monitor ambient ozone around their facilities. Monitoring information from associations is also given in Appendix II. Like industry, associations use the same or equivalent monitoring protocols as developed by Alberta Environmental Protection. Typical monitoring results from Tomahawk, one of the sites of the West Central Airshed Society, for the month of June, 1997 are shown in Table 6. Strathcona Industrial Association does not monitor  $O_3$  at their sites. Wood Buffalo Environmental Association started operating in 1997. Fort Saskatchewan Regional Industrial Association is not involved in ambient monitoring as an association. Instead, they rely on the monitoring information provided by Association's member industries.

### 4.2.2 Daily, Monthly and Annual Mean Concentrations

Daily mean and hourly maximum O<sub>3</sub> concentrations for June and December, 1997 for Edmonton Central, Calgary Central, Fort Saskatchewan, Fort McMurray and Hightower Ridge, are given in Tables 7 and 8. Monthly mean and hourly maximum O<sub>3</sub> concentrations are shown in Figures 4 and 5. Annual mean concentrations of ozone are given in Figure 6. Variations and trends in these values are discussed in the next chapter.

### 4.2.3 Peroxyacetyl Nitrate (PAN), Nitric Acid (HNO<sub>3</sub>) and Particulate Nitrate (PN)

Between 1980 and 1984, secondary air pollutants concentrations of PAN, HNO<sub>3</sub> and PN were recorded under a variety of meteorological conditions at urban and rural locations in Alberta. The PAN measurements were the first in Alberta (Peake and Sandhu, 1983a; Peake et al., 1983b, 1985; Peake et al., 1986, 1988a,b). Urban monitoring included the cities of Edmonton and Calgary. Typical hourly PAN and O<sub>3</sub> concentrations recorded on August 4, 1983 in Edmonton are shown in Figure 7. Typical monthly averages of PAN, PN and HNO<sub>3</sub> concentrations for Edmonton are shown in Figure 8. It was noted that PAN concentrations showed seasonal

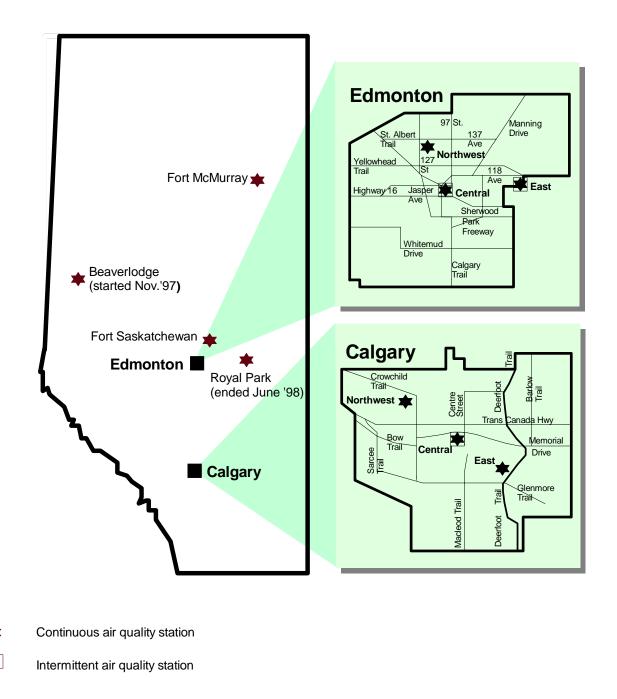


Figure 3 Alberta Environmental Protection monitoring locations for ozone, nitrogen oxides and total hydrocarbons (continuous monitoring), and volatile organic compounds (intermittent monitoring).

Table 2 Typical hourly mean ozone data (ppb) for the Calgary Central location for June 1997.

HOUR/ DAY	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	25	23	26	35	40	34	33	33	36	37	41	47	47	47	45	45	47	42	39	35	23	23	22	19
2	21	28	30	31	25	12	5	12	29	33	36	41	41	42	38	37	32	32	29	24	17	9	14	22
3	20	23	15	11	9	5	2	4	4	13	25	30	32	34	34	30	28	27	27	23	24	16	13	18
4	19	10	16	21	18	10	7	3	2	2	3	7	12	10	8	6	12	21	22	19	11	9	7	5
5	0	0	0	0	0	1	0	1	0	1	2	9	14	23	29	19	12	15	18	14	11	13	21	24
6	23	25	24	21	16	5	3	3	11	14	16	20	0	23	18	19	18	21	16	34	30	20	15	3
7	1	7	11	11	8	9	9	7	9	23	28	38	39	41	35	37	41	37	37	30	24	19	23	28
8	31	29	28	22	18	10	6	9	16	33	47	51	54	52	50	49	46	47	45	40	27	19	18	22
9	28	32	34	31	24	18	13	10	17	20	23	32	37	39	37	35	35	39	43	41	29	26	26	28
10	25	20	17	11	5	6	4	4	4	10	19	30	34	37	32	28	29	31	37	32	20	14	13	20
11	16	19	20	14	1	5	4	7	16	25	28	28	14	10	12	10	6	8	16	14	15	19	23	26
12	22	32	39	34	34	21	6	8	6	8	10	16	26	40	40	32	33	20	20	18	16	12	12	17
13	8	11	8	10	12	4	5	7	17	24	23	29	36	41	43	37	40	43	37	30	20	14	18	19
14	23	31	31	31	29	27	23	19	21	27	29	29	29	33	36	38	43	38	34	41	38	26	17	23
15	32	15	13	13	10	9	9	10	18	34	38	33	36	39	35	39	43	36	31	24	17	13	17	15
16	11	23	22	21	25	21	16	19	25	26	31	34	37	28	14	21	18	28	39	33	26	16	14	16
17	17	2	6	8	7	3	2	1	2	4	12	18	19	23	18	17	17	14	19	20	13	10	7	10
18	23	32	40	39	38	27	17	22	27	25	21	17	21	19	29	24	25	31	30	28	26	23	27	21
19	20	26	17	18	17	8	8	8	20	22	24	29	26	28	26	25	23	28	28	24	14	8	6	10
20	13	12	9	6	6	2	2	5	10	10	18	16	16	19	16	12	13	12	15	12	12	11	12	15
21	14	15	19	20	17	18	16	15	16	18	18	19	20	22	20	26	18	20	16	24	24	20	20	22
22	21	20	21	20	21	24	24	30	33	37	35	40	37	36	34	36	34	35	29	26	18	21	20	22
23	22	21	13	14	16	5	8	14	18	24	26	29	31	26	18	8	12	12	21	24	21	17	20	24
24	21	19	19	20	21	10	6	8	11	12	11	12	15	18	17	18	20	22	22	15	8	2	1	2
25	2	4	8	7	2	2	2	2	4	12	23	25	29	29	24	24	20	23	22	14	14	21	21	13
26	11	9	4	6	5	1	2	4	12	27	31	34	40	43	41	27	24	32	34	27	25	29	25	21
27	15	9	14	25	16	2	3	9	23	32	30	27	31	31	29	23	25	32	30	25	20	17	16	16
28	15	17	18	16	13	7	13	16	19	23	30	32	36	39	36	29	18	20	22	20	13	10	8	9
29	9	10	12	13	15	12	9	10	10	10	8	5	4	5	7	6	3	4	4	4	5	3	3	10
30	14	12	14	16	10	7	5	4	8	9	10	9	11	9	7	3	4	9	6	11	8	6	5	4

Table 3 Typical hourly mean ozone data (ppb) for the Edmonton Central location for June 1997.

HOUR/ DAY	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	22	25	17	23	25	21	19	9	18	35	36	37	42	41	40	40	39	38	36	33	21	12	4	16
2	31	31	19	22	15	14	7	3	17	26	27	29	33	35	36	31	33	31	35	40	29	29	17	17
3	24	29	24	15	5	5	5	7	20	29	35	38	36	36	38	33	29	39	43	40	32	34	32	33
4	36	36	34	30	22	13	9	4	4	7	8	8	5	6	4	3	4	5	18	26	35	35	38	42
5	42	38	22	25	11	8	3	1	3	9	10	6	7	10	11	11	14	20	21	18	11	4	NA	NA
6	NA	NA	6	12	3	2	1	2	5	11	13	9	16	18	20	22	30	30	35	36	19	12	7	2
7	4	15	28	36	30	28	27	23	29	36	36	37	43	45	47	48	48	49	50	46	39	30	35	35
8	39	43	34	28	23	29	25	25	23	27	25	29	36	41	38	40	40	38	38	38	33	22	17	17
9	14	NA	7	2	3	3	3	6	13	27	30	35	35	34	35	32	35	43	48	39	29	20	8	20
10	32	40	33	28	30	17	7	16	24	23	39	38	41	49	40	39	36	37	45	39	31	9	12	13
11	17	19	30	11	5	12	2	6	15	30	36	44	27	32	9	19	18	19	13	21	22	13	8	22
12	32	34	32	19	14	9	6	10	16	18	23	18	25	35	37	32	25	32	17	12	3	1	17	28
13	24	17	20	14	29	11	8	14	22	29	26	21	24	31	31	32	33	34	31	33	31	25	22	16
14	19	16	17	19	18	19	21	17	24	26	29	30	32	33	34	33	33	36	35	32	27	20	13	13
15	10	14	20	21	10	19	13	20	25	25	24	24	25	27	26	24	23	23	26	27	21	19	23	13
16	10	16	16	17	13	10	4	4	9	13	21	20	28	29	31	28	29	31	37	38	32	25	23	16
17	11	NA	3	1	2	2	2	4	11	17	19	24	34	35	30	27	31	37	31	26	19	18	27	28
18	27	34	34	30	27	26	15	6	7	10	14	18	24	28	29	25	22	22	23	24	21	15	18	22
19	25	25	23	21	19	21	17	18	22	23	23	23	22	20	21	18	18	21	19	19	20	18	18	19
20	20	22	21	19	16	13	9	5	5	4	6	9	7	10	9	8	6	10	7	9	9	2	5	4
21	8	10	9	12	13	12	12	10	12	6	13	13	10	11	10	12	10	9	12	13	4	3	3	3
22	5	6	7	7	7	8	8	9	9	9	9	7	8	13	18	11	12	12	25	27	24	28	13	32
23	33	25	33	19	13	6	3	7	17	23	25	30	25	17	21	26	27	25	22	23	22	20	20	15
24	17	17	18	18	14	9	7	8	14	17	19	22	24	23	23	15	12	10	8	13	14	13	7	10
25	12	17	15	14	9	5	3	3	4	8	19	27	33	31	34	34	36	44	38	39	23	21	29	37
26	39	35	34	22	21	10	9	15	15	21	31	40	38	26	15	25	27	30	27	33	26	14	9	16
27	18	25	27	32	25	16	11	10	16	18	19	18	20	21	21	21	23	26	21	18	14	8	3	4
28	4	2	4	6	8	10	8	7	4	6	12	16	13	15	15	15	16	15	15	14	11	6	1	1
29	1	1	1	1	1	2	4	10	19	21	21	20	21	18	24	25	23	18	18	17	14	10	6	5
30	2	1	2	1	1	3	6	8	12	16	19	25	19	24	24	19	18	21	18	19	18	17	14	16

NA Not Available

Table 4 Typical hourly mean ozone data (ppb) for the Fort Saskatchewan location for June 1997.

HOUR/	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
DAY 1	28	30	23	27	27	26	24	22	22	39	39	39	41	41	40	38	38	38	38	30	17	9	7	11
2	7	9	9	15	8	15	14	18	22	31	37	38	40	42	42	39	42	42	40	35	27	31	20	14
3	, 12	11	16	12	2	6	13	24	29	37	45	48	50	49	49	49	46	48	47	40	37	35	35	34
4	35	32	30	27	29	24	21	23	26	26	26	24	22	16	18	17	24	22	30	38	39	37	41	41
<u>-</u> 5	41	39	31	29	14	11	2	15	21	15	14	13	19	19	20	22	24	27	27	24	21	5	3	0
6	0	8	7	3	0	1	1	5	15	21	27	33	34	28	30	32	35	41	42	38	24	12	8	0
7	1	2	7	22	10	18	18	31	34	36	43	50	52	48	53	56	55	53	50	44	29	27	31	25
8	25	27	27	33	17	19	27	31	33	35	36	40	41	44	44	39	41	41	40	39	33	20	11	13
9	10	4	4	1	2	2	7	13	18	25	33	40	42	43	46	47	47	48	50	41	28	23	22	27
10	28	28	27	32	28	22	26	31	38	39	37	47	0	0	0	51	51	51	51	46	36	21	13	16
11	21	17	11	5	5	5	10	19	17	32	40	47	51	50	42	44	35	38	34	35	28	22	25	24
12	24	22	21	23	23	16	18	23	25	31	33	34	36	40	46	43	39	40	39	38	33	30	21	23
13	22	18	12	8	9	5	12	18	19	27	39	42	39	50	49	49	47	45	44	45	39	26	34	32
14	26	29	25	21	17	17	20	26	28	30	32	33	36	35	37	38	37	40	39	36	23	15	17	17
15	21	23	24	24	22	21	21	22	24	26	26	27	28	29	30	31	31	30	29	26	16	15	20	20
16	16	15	13	12	14	13	11	11	18	25	29	31	36	39	39	37	38	39	38	36	29	19	3	1
17	3	11	10	6	0	3	10	18	28	37	42	44	45	44	47	49	47	45	40	34	28	29	23	23
18	27	22	31	35	24	27	32	24	23	19	20	25	27	31	34	34	32	29	30	28	20	22	26	24
19	22	27	26	24	22	22	24	26	28	27	26	26	25	25	25	24	23	23	22	21	21	21	20	20
20	20	20	20	18	15	14	12	11	14	14	14	16	17	19	19	21	19	19	21	20	18	14	15	16
21	14	14	14	16	12	11	13	13	12	16	19	18	17	21	21	22	20	21	23	22	17	12	11	13
22	14	15	15	13	9	10	12	14	16	18	17	18	18	18	29	36	28	21	30	35	44	43	30	36
23	41	41	32	29	18	14	6	14	23	27	25	26	31	35	38	26	16	29	30	30	29	28	24	21
24	20	20	20	19	17	12	13	18	21	23	25	27	27	23	23	20	22	15	4	13	13	7	11	10
25	4	0	0	0	0	0	2	7	11	20	23	34	38	43	44	45	46	50	52	49	14	19	38	38
26	43	40	24	18	24	16	21	26	23	29	36	42	44	33	37	36	42	37	32	31	27	23	17	7
27	4	26	24	22	11	16	15	20	26	28	31	33	32	31	29	28	29	27	22	19	15	11	9	10
28	6	0	0	0	0	0	3	3	8	8	22	17	15	17	18	18	18	19	17	18	16	5	1	1
29	1	0	0	0	0	1	2	7	15	18	23	27	26	26	26	30	32	28	22	18	11	6	5	3
30	5	3	2	0	0	1	1	7	14	20	26	29	29	28	28	29	29	29	27	23	18	18	22	15

Typical hourly mean ozone data (ppb) for the Hightower Ridge location for June 1997.\* Table 5

HOUR/	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
DAY	-		Ū	·	Ū	Ů	-	•	Ů						.0			.0	.0					
1	NA	43	44	46	45	45	45	47	51	53	53	53	50	48	45	45	45	43	45	46	46	47	48	49
2	NA	50	48	46	44	45	42	42	44	45	44	44	44	44	44	44	44	44	45	45	42	40	41	40
3	NA	44	43	43	43	42	40	39	39	43	44	NA	NA	NA	50	52	54	55	60	57	53	55	55	53
4	NA	52	50	48	46	45	43	41	41	40	42	44	44	43	40	38	39	38	36	35	32	29	31	33
5	NA	27	24	24	18	19	26	28	32	38	43	45	43	42	44	46	43	41	39	40	44	44	47	50
6	NA	51	51	43	46	48	47	49	48	47	47	48	48	48	50	50	51	50	48	48	47	45	45	46
7	NA	47	48	47	48	49	47	49	48	49	50	50	49	49	52	52	51	51	53	54	54	51	50	46
8	NA	39	41	42	39	41	39	37	37	40	47	46	48	48	47	44	42	42	43	38	36	39	38	39
9	NA	43	45	45	44	44	40	40	40	43	43	42	44	43	45	51	54	55	55	55	53	45	42	44
10	NA	40	42	42	42	42	41	41	41	42	42	44	46	48	50	52	52	53	54	59	64	63	62	62
11	NA	65	68	66	61	56	51	50	55	57	58	58	58	58	58	59	61	60	58	57	55	54	53	50
12	NA	45	43	41	42	39	38	37	37	42	46	48	48	50	48	45	40	37	37	36	33	29	37	27
13	NA	42	41	40	50	45	41	37	40	45	45	42	46	44	43	35	31	37	36	36	36	36	36	38
14	NA	42	41	42	41	42	44	44	48	50	50	51	53	56	59	53	47	42	38	36	35	34	34	32
15	NA	34	33	34	31	31	29	25	21	21	23	25	29	32	34	35	35	33	32	39	30	31	38	38
16	NA	38	40	38	37	41	37	42	46	52	54	55	55	53	52	51	52	51	50	48	46	43	43	43
17	NA	41	39	38	37	33	35	36	33	28	27	29	31	34	36	38	37	33	37	41	38	35	33	33
18	NA	27	38	34	34	39	39	37	39	38	38	38	38	37	37	41	40	37	36	35	33	33	33	34
19	NA	32	31	32	32	31	32	33	33	34	34	NA	NA	NA	NA	NA	40	40	39	39	38	39	39	38
20	NA	38	37	38	38	37	36	35	35	34	34	33	34	35	35	35	33	32	32	31	30	31	28	29
21	NA	25	24	24	26	25	23	25	27	26	28	30	32	33	34	44	43	40	36	34	36	34	35	35
22	NA	35	33	34	32	29	29	31	34	35	32	35	36	34	34	41	42	40	38	37	39	40	42	41
23	NA	39	39	40	38	36	36	41	40	40	37	33	34	37	38	40	41	40	39	42	40	42	42	40
24	NA	43	41	39	35	38	37	37	39	40	40	41	39	39	38	36	39	41	42	41	37	34	39	41
25	NA	38	38	38	30	29	30	32	38	40	42	42	44	47	48	47	47	49	46	47	45	44	41	44
26	NA	41	43	44	41	36	34	40	41	48	49	51	54	52	54	53	51	51	51	49	49	48	48	48
27	NA	46	45	43	42	41	42	43	43	42	42	41	40	43	48	NA	52	52	45	34	33	35	31	28
28	NA	24	25	24	30	34	24	26	28	32	30	27	25	25	24	23	28	26	26	25	23	23	21	16
29	NA	21	24	25	26	25	22	25	27	30	32	35	37	39	40	41	40	42	39	40	38	35	34	32
30	NA	31	31	31	31	30	27	26	33	39	42	43	42	38	41	44	46	45	42	41	38	37	36	34

<sup>\*</sup> Station operated by West Central Airshed Society
NA Not Available

Table 6 Typical hourly mean ozone data (ppb) for the Tomahawk location for June 1997.\*

HOUR/ DAY	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	29	NA	30	25	19	18	24	30	34	37	41	42	42	45	45	45	44	43	40	38	39	36	35	34
2	36	NA	37	35	34	33	32	29	29	37	39	40	40	40	41	41	41	39	39	34	29	29	31	31
3	31	NA	16	11	19	19	15	23	32	39	48	49	50	50	49	48	48	47	45	43	42	39	37	34
4	36	NA	30	31	28	25	24	25	25	24	24	24	22	22	24	22	21	21	16	14	12	12	13	15
5	16	NA	16	14	11	9	10	12	16	19	27	28	37	37	34	31	34	34	33	28	24	26	22	18
6	13	NA	9	11	12	12	26	29	32	39	43	***	48	48	50	51	38	48	52	49	45	51	51	52
7	52	NA	45	33	27	28	39	44	42	45	47	51	52	53	54	53	53	53	58	56	53	52	51	51
8	49	NA	45	37	38	34	31	36	39	33	39	44	47	49	49	48	47	48	48	46	41	43	44	32
9	21	NA	19	26	13	8	8	15	34	41	47	49	51	56	58	58	58	58	56	52	47	45	43	43
10	51	NA	32	22	21	24	32	40	41	38	41	51	60	64	66	68	71	74	72	67	62	62	55	47
11	41	NA	34	32	26	20	29	34	39	47	54	56	57	59	59	59	58	55	45	38	46	43	44	39
12	43	NA	35	35	35	30	25	22	21	25	31	37	26	29	46	52	52	53	38	37	30	31	26	24
13	26	NA	18	20	16	30	28	25	25	29	32	34	37	36	32	34	42	46	41	41	35	30	25	21
14	19	NA	21	20	22	21	28	31	34	36	36	39	42	44	45	45	45	44	42	40	35	29	39	34
15	32	NA	20	19	19	17	20	25	28	28	29	29	28	27	27	28	29	30	32	30	29	30	26	19
16	16	NA	11	12	11	10	19	25	27	33	35	36	37	38	39	39	41	41	42	43	38	26	31	21
17	25	NA	23	21	19	14	16	20	24	33	36	37	42	40	38	34	35	35	34	27	31	32	37	40
18	38	NA	29	24	20	19	17	20	24	28	33	33	35	36	37	36	37	36	36	34	31	29	32	33
19	26	NA	24	20	20	21	23	27	30	30	30	30	29	29	28	27	26	26	28	29	29	28	29	28
20	29	NA	27	26	24	24	24	24	23	23	22	21	22	22	24	25	24	25	29	26	22	21	19	20
21	19	NA	18	16	15	14	15	17	21	22	23	18	23	21	25	29	31	29	24	20	22	20	23	20
22	18	NA	12	13	14	15	13	14	17	15	16	26	37	41	44	41	40	45	30	26	30	31	28	26
23	20	NA	29	23	16	13	20	36	39	34	35	35	33	33	37	38	35	35	33	27	23	22	22	22
24	21	NA	15	14	14	9	17	22	25	27	28	29	31	30	27	28	28	28	26	22	18	20	17	17
25	16	NA	15	14	12	7	9	14	23	29	32	33	34	35	38	39	36	34	31	32	34	35	35	26
26	22	NA	20	18	15	6	12	18	23	31	38	38	33	34	40	41	38	37	32	31	32	34	32	31
27	34	NA	29	27	25	19	18	24	28	NA	NA	NA	NA	35	37	36	35	33	32	30	27	22	20	15
28	14	NA	13	10	7	5	9	14	19	21	23	18	18	19	20	21	21	21	20	17	17	16	16	11
29	9	NA	9	10	8	5	9	15	19	24	26	25	22	21	22	24	23	21	21	22	17	17	11	3
30	10	NA	9	8	12	13	16	22	26	28	29	29	30	30	29	29	30	29	28	27	20	22	26	27

<sup>\*</sup> Station operated by West Central Airshed Society NA Not Available

Table 7 Daily mean and hourly maximum ozone concentrations (ppb) at different locations for the month of June 1997.

Date	Edmo Cen	onton itral	Calç Cen	gary itral	Fo Saskato		Fo McM	rt urray	High: Ric	tower dge
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
1	27	42	35	47	29	41	17	27	47	53
2	25	40	27	42	27	42	21	39	44	50
3	28	43	19	34	32	50	23	44	48	60
4	18	42	11	22	28	41	20	37	40	52
5	13	42	9	29	19	41	13	27	37	50
6	13	36	17	34	19	42	14	37	48	51
7	35	50	23	41	33	56	24	45	50	54
8	31	43	32	54	32	44	18	34	41	48
9	22	48	29	43	26	50	24	38	46	55
10	30	49	20	37	30	51	21	34	49	64
11	19	44	15	28	27	51	23	44	58	68
12	21	37	22	40	30	46	19	35	40	50
13	24	34	22	43	30	50	12	22	40	50
14	25	36	30	43	28	40	25	38	44	59
15	21	27	24	43	24	31	27	39	31	39
16	21	38	24	39	23	39	17	28	46	55
17	18	37	11	23	28	49	16	32	35	41
18	22	34	26	40	27	35	24	36	36	41
19	21	25	19	29	24	28	23	34	35	40
20	10	22	11	19	17	21	17	25	34	38
21	10	13	19	26	16	23	17	27	31	44
22	13	32	28	40	22	44	19	38	36	42
23	21	33	19	31	26	41	15	27	39	42
24	15	24	14	22	18	27	19	33	39	43
25	22	44	14	29	24	52	17	29	41	49
26	24	40	21	43	30	44	21	34	47	54
27	18	32	21	32	22	33	18	25	41	52
28	9	16	20	39	10	22	17	28	26	34
29	13	25	8	15	14	32	17	37	33	42
30	13	25	8	16	17	29	16	38	37	46

Table 8 Daily mean and hourly maximum ozone concentrations (ppb) at different locations for the month of December 1997.

Date		onton ntral		gary Itral	Fo Saskato			ort urray		tower Ige
20	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
1	11	24	8	24	16	33	NA	NA	52	55
2	5	10	4	11	2	6	1	4	54	58
3	4	6	6	16	2	4	9	23	NA	NA
4	6	11	2	4	11	19	12	24	55	59
5	6	9	2	4	9	16	8	12	55	58
6	5	11	4	6	8	16	11	20	56	59
7	10	15	5	6	14	21	8	18	53	60
8	8	17	3	4	11	20	3	10	52	57
9	4	8	6	17	4	22	2	11	49	53
10	10	17	7	13	4	15	0	2	52	54
11	10	24	18	30	2	6	13	28	50	52
12	10	23	12	28	2	6	19	29	54	55
13	14	30	9	22	6	19	3	9	58	64
14	17	35	23	38	9	31	1	5	51	59
15	16	29	15	36	19	38	16	32	47	49
16	5	16	3	4	8	24	9	20	42	46
17	9	22	14	28	14	30	6	22	50	53
18	12	24	7	20	18	31	20	27	48	49
19	4	6	4	14	6	15	7	10	47	50
20	3	8	7	22	1	2	2	6	45	50
21	22	31	17	25	23	31	14	26	45	48
22	11	27	6	27	9	26	5	10	47	48
23	16	32	20	35	24	37	21	29	48	50
24	18	26	12	22	16	29	NA	NA	48	51
25	25	37	13	23	26	36	NA	NA	51	53
26	12	28	20	31	6	13	NA	NA	50	52
27	21	35	19	31	27	35	NA	NA	49	50
28	23	32	20	34	23	35	NA	NA	48	81
29	22	34	8	22	27	40	NA	NA	48	51
30	8	23	4	22	11	29	NA	NA	48	52
31	10	23	9	28	10	27	NA	NA	38	49

NA Not Available

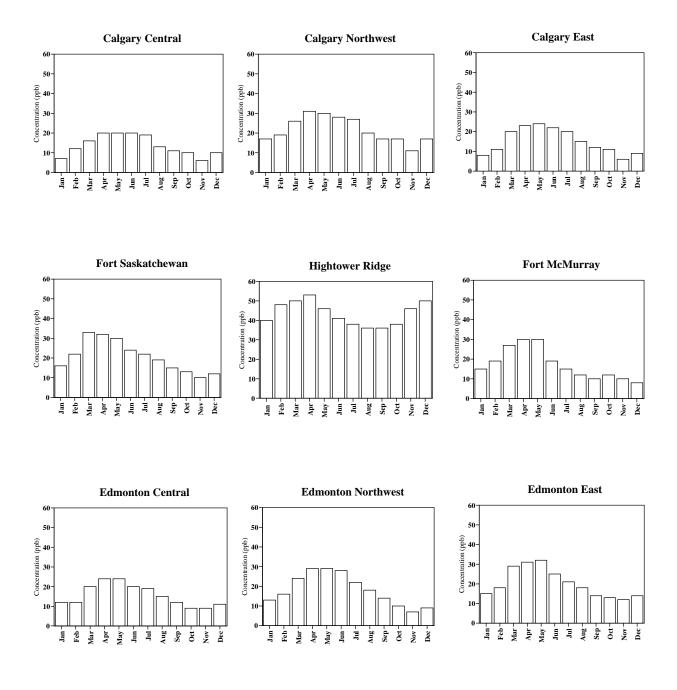


Figure 4 Monthly mean ozone concentrations (ppb) at nine Alberta monitoring stations for 1997.

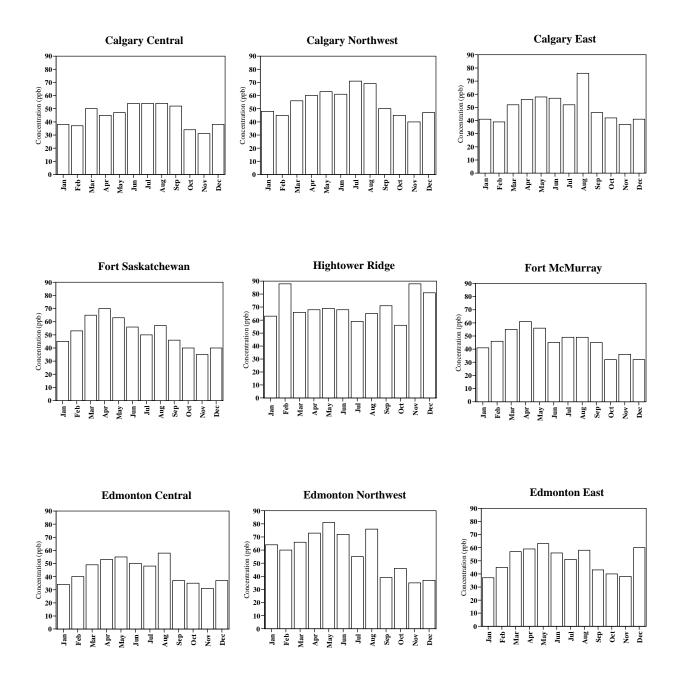


Figure 5 Monthly hourly maximum ozone concentrations (ppb) at nine Alberta monitoring stations for 1997.

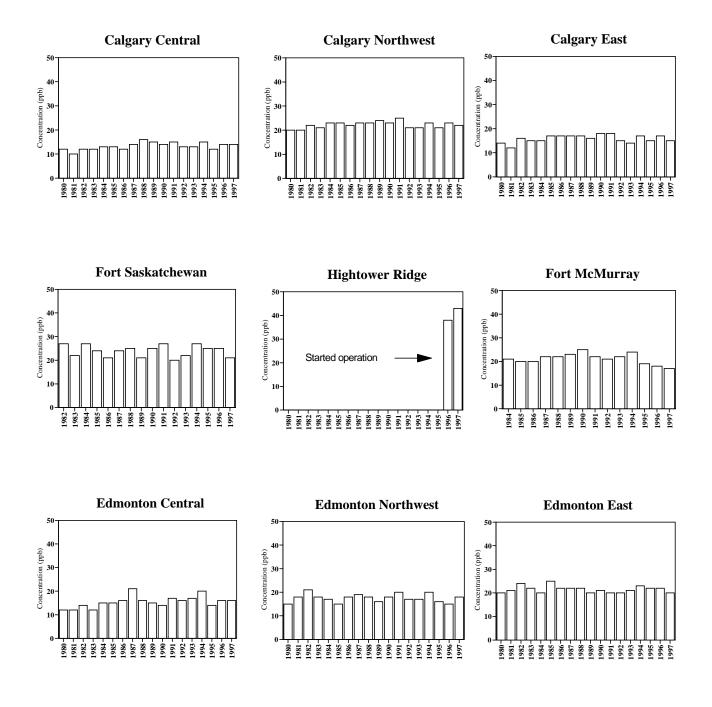


Figure 6 Annual mean ozone concentrations (ppb) at nine Alberta monitoring stations from 1982 to 1997.

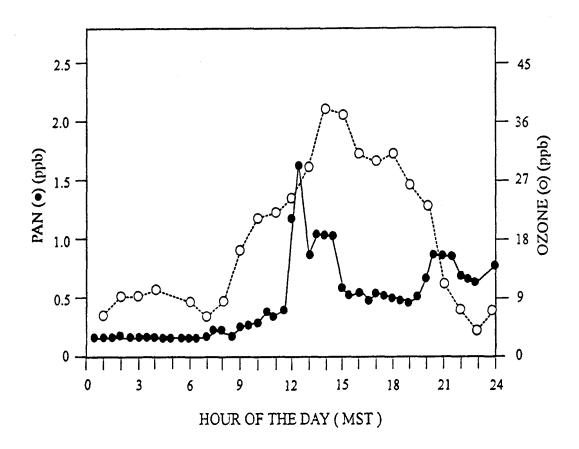


Figure 7 Hourly ozone and PAN concentrations recorded on August 4, 1983 in Edmonton (Peake et al., 1986).

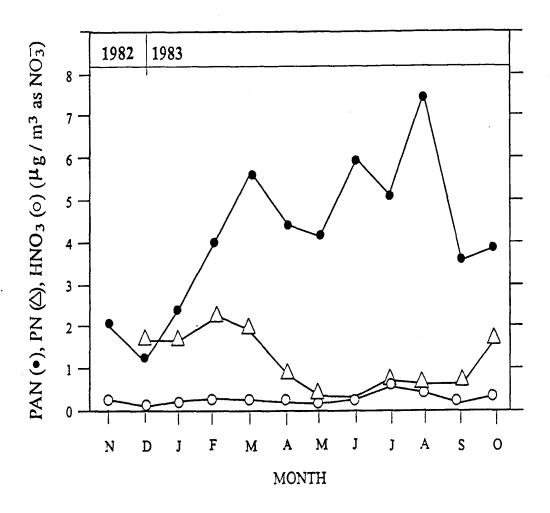


Figure 8 Monthly average of PAN, PN and HNO<sub>3</sub> concentrations in Edmonton (Peake et al., 1986).

variations and were limited in the winter months by lack of solar radiation and by low temperatures, and in the summer by low concentrations of primary pollutants. PAN concentrations were highly correlated with the presence of anticyclonic synoptic conditions aloft. Surface synoptic conditions varied, but weak pressure gradients were common to all episodes. PAN:HNO3:PN ratios indicate that PAN is the major product of NO<sub>x</sub> reactions in the atmosphere under dry, cold continental climatic conditions of Alberta. Mean HNO3 and PN concentrations in Edmonton were 0.30 and 1.22  $\mu$ g m<sup>-3</sup>, respectively. Both showed strong seasonal variations in concentrations with the highest daily value of 2.4  $\mu$ g m<sup>-3</sup> being recorded in July, 1983 and highest PN concentration, 8.1  $\mu$ g m<sup>-3</sup>, in December, 1982. The mean for the combined months of June, July and August 1983 in Edmonton was 1.1  $\mu$ g m<sup>-3</sup>, as compared with the 0.51  $\mu$ g m<sup>-3</sup> found in Calgary for the same period in 1982. A report on the ambient particulate matter in Alberta has been published (Sandhu, 1998).

# 5.0 DISCUSSION

Ozone is an important natural chemical component of the atmosphere. It is difficult to determine whether any geographic location on Earth is free from human influences (Furlayson-Pitts and Pitts, 1986). Its ground-level concentration is highly variable because of natural and human activities. Most of the long-term information on ozone and its precursors in Alberta comes from the two major urban centres of Edmonton and Calgary. However, during the last two decades, a number of special monitoring programs have generated scientific information from rural areas in a variety of settings. These places are listed in Appendix II.

# **5.1** Hourly Mean Ozone Concentrations

Modern instruments can record concentrations at minute intervals. Historically, most air pollutant concentrations are reported as hourly means. In certain cases, downwind from point sources, pollutant episodes may occur for periods much shorter than one hour. Under these conditions, computations of hourly means can provide distorted expressions of the actual episodes or exposure regimes. Since the ambient ozone objective is based on average 1-hour values and routine monitoring values are published also on an hourly basis, only hourly mean concentrations are reported.

### **5.1.1** Urban

Ambient hourly concentrations of O<sub>3</sub> for the month of June, 1997 for Calgary Central and Edmonton Central stations are given in Tables 2 and 3. Ozone is at a maximum around noon and a minimum at night. Overnight, O<sub>3</sub> is decreased in the cities by scavenging reactions. A diurnal trend in NO<sub>2</sub> levels is evident from the hourly data given in Appendix III. NO and NO<sub>2</sub> values are at a minimum in the early morning hours, with their concentrations increasing in the morning rush hour and again in the afternoon rush hour. Maximum concentrations generally occur during the morning and afternoon rush hours. Concentrations begin to drop again at about midnight. This diurnal trend is more pronounced during the winter months. Significant diurnal trends of THCs are noted at all urban monitoring stations located close to major traffic arteries and city centres. These diurnal trends are more pronounced in winter months.

VOCs monitoring in June and December, 1997 for 20 dominant specifies is shown in Appendix III for Edmonton and Calgary. It is obvious from these tables that concentrations of VOCs are higher in winter than summer. Some of the VOCs observed and listed in these tables are air toxics and carcinogens. Because of the lower mixing heights in winter (Myrick et al., 1994), these VOCs get concentrated and give rise to other photochemical products like PAN, HNO<sub>3</sub>, particulate nitrate and other unknown compounds. Analysis of VOC information from Edmonton has been reported (Cheng, et al., 1997).

A comprehensive analysis of urban ozone concentrations in Alberta cities has been published (Angle and Sandhu, 1989). It was reported that ozone concentrations in Alberta cities typically exhibit a maximum in May (up to 35 ppb) and a minimum in November (as low as 4 ppb). Variations of hourly O<sub>3</sub> concentrations throughout the day in winter (December, January and February) and summer situations (June, July and August) were somewhat different

(Figures 9 and 10). It was concluded that Alberta cities act as  $O_3$  sinks throughout the year. The destruction of rural  $O_3$  in cities is more pronounced during winter when stable air and shallow mixing depths lead to high concentrations of  $NO_x$ . In summer, net destruction of  $O_3$  occurs at all urban stations overnight and daytime, from the upwind edge to the city centre. Further downwind, net destruction is replaced by net production, under favorable meteorological conditions, and afternoon  $O_3$  production leads to  $O_3$  concentrations above the advected rural values. It was suggested that details of the balance between production and destruction reactions can only be understood by the application of time dependent models.

Leahey and Hanson (1990) have published the observational evidence of ozone depletion by nitric oxide at 40 km downwind of Calgary. The data collection was part of the Acid Deposition Research Program jointly sponsored by Alberta Government and Industry. The data consistently showed evidence of ozone depletion. Mean levels of depletion were, as required by scavenging theory, highly correlated with similar levels of nitrogen dioxide creation. Only about 3 percent of the data showed depletion to be less than that which would have been expected on the basis of nitrogen oxide scavenging. These data were collected during afternoon periods and might indicate a tendency for ozone creation attributable to photo-chemical reaction. Leahey has argued that ozone creation in Alberta is not a problem because the meteorology relating to high temperatures and shallow mixing depths necessary for ozone formation does not exist. In consequence, there has been no evidence of net ozone creation (Leahey, 1998).

In 1991, Gladstone et al. published the results of a modelling study that investigated the nature of periods of elevated oxidant production (episodes) in the atmospheres of Edmonton and Calgary. The box model was used to simulate concentration profiles of  $O_3$  and PAN as they would be observed within a stagnant air parcel. It was concluded that the combination of a stagnant air mass with urban VOCs and  $NO_x$  inputs and radiation flux at this latitude (> 51°N) can lead to substantial oxidant production near the urban source and elevated concentrations in the rural downwind air mass.

It was pointed out in section 3.2.1 that albedo is a fundamental parameter in the energy budget equations used to estimate environmental quantities affected by solar radiation. Air pollution models require surface albedo values as an input to determine the magnitude of photochemical reaction rate constants. Eight years of albedo measurements at Edmonton yielded average monthly surface albedo values ranging from 0.17 in summer to 0.69 in winter (Angle et al., 1992). The pattern of variation throughout the day over a snow surface differed from that over a grass surface. It was concluded that surface albedo makes a major contribution to the photochemical rate constants in the snow-covered winter months.

#### **5.1.2** Rural

Long- and short-term monitoring sites in rural Alberta from which the data has become available are classified into three categories: (1) rural-background sites, (2) rural-industrial sites, and (3) rural-influenced sites. Rural-background sites generate information that can be considered a regional background for that area. This category of sites includes location of Birch Mountain, Bitumont, Fortress Mountain, Hightower Ridge and Esther. More than four years of data are available from these sites. All the sites operated by industry (Table AII.3) for O<sub>3</sub> and its

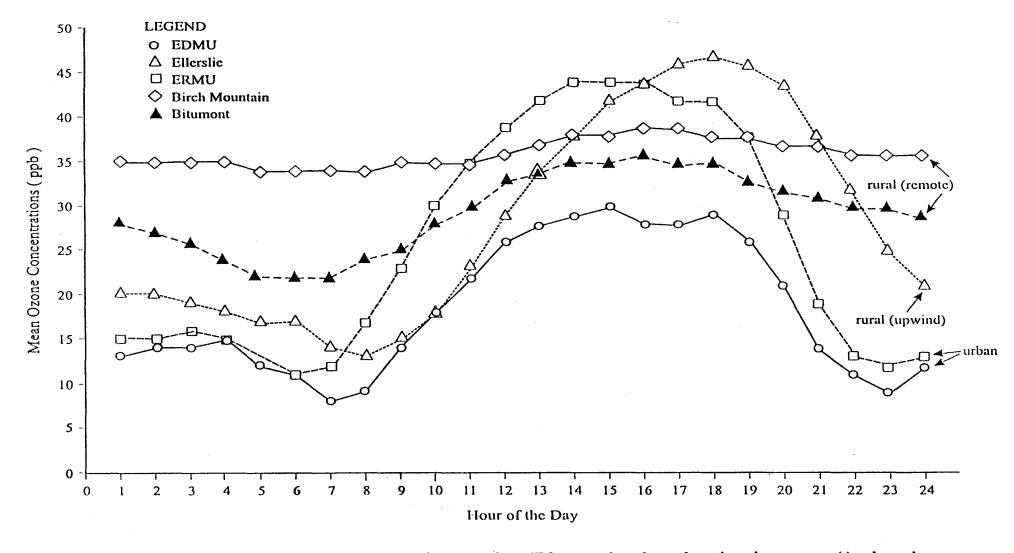


Figure 9 Diurnal variation of ozone concentrations at urban (Edmonton) and rural stations in summer (Angle and Sandhu, 1989).

Ground-Level Ozone in Alberta

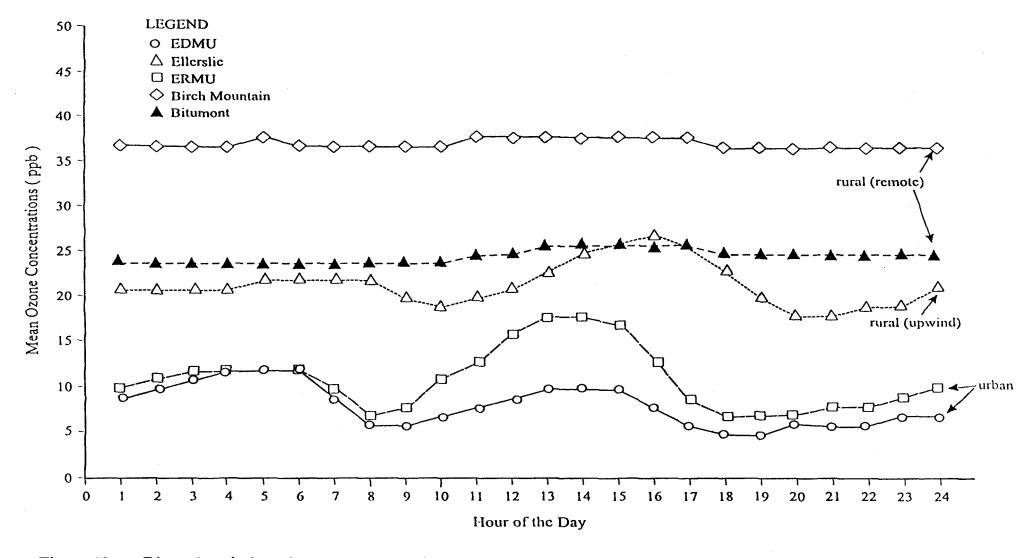


Figure 10 Diurnal variation of ozone concentrations at urban (Edmonton) and rural stations during winter (Angle and Sandhu, 1989).

Ground-Level Ozone in Alberta 38

precursors are the rural-industrial sites. These sites are operated mainly for compliance purposes. Rural-influenced sites are those sites which are affected, to some degree, either by agricultural and other human practices, or by transport of air pollutants. The data for hourly mean concentrations for winter and summer for Birch Mountain and Bitumont are given in Figures 9 and 10. For Hightower Ridge, daily mean and maximum O<sub>3</sub> values are given in Tables 7 and 8 for June and December, 1997.

Analysis of data from the rural background sites of Birch Mountain and Bitumont has been reported (Angle and Sandhu, 1986). One of the best sets of data on background ozone and other air pollutants from Alberta has been published by Legge et al. (1988), from the Alberta Government Industry Acid Deposition Research Program. Ozone was monitored at the Fortress Mountain remote site (background) and two regional sites, Crossfield East and Crossfield West. Monitoring for O<sub>3</sub> was carried out from November 1, 1985 to October 31, 1987. A detailed description of the program, sites, summary of air quality and meteorology, and measurement methodology has been published (Legge and Krupa, 1990, and Peake and Fong, 1990). Diurnal variations of hourly ozone concentrations for the monitoring period are given in Figure 11.

The average hourly O<sub>3</sub> concentration at this site was 43.4 ppb. It was also noted that the Canadian air quality objective of an 82 ppb hourly average was exceeded 1.5% of the time. The diurnal variation in O<sub>3</sub> concentrations was small - 2.9 ppb, indicative of a remote location, above the nocturnal inversion and not greatly influenced by local emissions. During the period when O<sub>3</sub> concentrations were highest, winds were generally from the southwest, suggestive of the long-range transport of anthropogenic pollutants from distant sources rather than the generation of O<sub>3</sub> from local emissions. In contrast, hourly O<sub>3</sub> concentrations at two regional air quality monitoring sites showed an average diurnal variation of 14 ppb. Only two hourly averages exceeded 82 ppb during the two years, and the mean O<sub>3</sub> concentration was 26 ppb. When these regional sites were within the urban plume from Calgary, the O<sub>3</sub> concentrations were depressed to a mean of 18 ppb. Ozone concentrations in downtown Calgary averaged 13 ppb. It was concluded that under Alberta climatological and meteorological conditions, hourly O<sub>3</sub> objectives are most likely to be exceeded in remote areas rather than in cities, or in areas under the direct influence of urban emissions.

It was observed at the Fortress Mountain monitoring location (elev. 2103 m MSL), both on episode and non-episode days (Figure 12), that O<sub>3</sub> profiles were not typical of the known patterns at lower elevation sites (Legge and Krupa, 1990; Legge et al., 1990). While during the daytime high O<sub>3</sub> concentrations occurred between roughly 1100 and 1500 h, after a decrease during the subsequent hours, O<sub>3</sub> concentrations increased again sharply into the nighttime hours on episode days. Such a pattern was also observed on non-episode days but with a lag time. The nighttime high O<sub>3</sub> concentrations may also be due to the presence of the mixed layer at an altitude lower than the elevation of the monitoring site. To explain the results it was suggested that neither stratospheric intrusion nor local photochemistry could satisfactorily account for O<sub>3</sub> episodes at Fortress Mountain. In order to determine whether long-range transport of O<sub>3</sub> and/or its precursors can explain the occurrence of O<sub>3</sub> episodes, air mass trajectory analysis was undertaken. These analyses indicated that the high O<sub>3</sub> concentrations at Fortress Mountain were generally associated with air masses from the west and northwest, and attributed O<sub>3</sub> episodes at

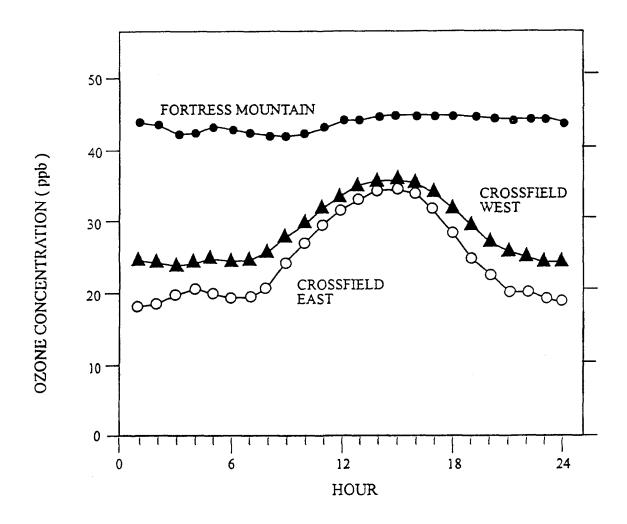


Figure 11 Diurnal variation of hourly ozone concentrations over the period 1 November 1985 – 31 October 1987 (Peake and Fong, 1990).

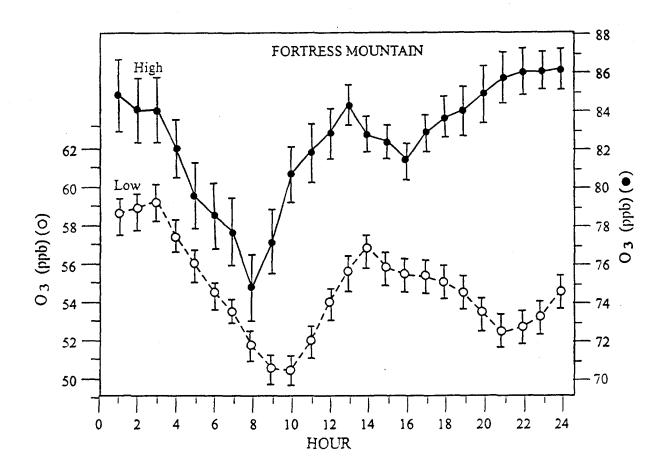


Figure 12 Diurnal O<sub>3</sub> profiles on episode versus non-episode days at Fortress Mountain. The vertical bars represent standard deviation of the mean for each hour (Legge and Krupa, 1990).

Fortress Mountain to mainly long-range transport coupled with some contribution from the local tropospheric chemistry.

# **5.1.3 Daily Mean and Maximum Ozone Concentrations**

Daily mean and maximum O<sub>3</sub> concentrations from five stations for June and December, 1997 are given in Tables 7 and 8. Edmonton Central and Calgary Central mean concentrations for June, 1997 range from 9 - 35 and 8 - 35 ppb, respectively. At Fort Saskatchewan, O<sub>3</sub> concentrations range from 10 - 33 ppb whereas Fort McMurray concentrations are in the range of 12 - 27 ppb. The Hightower Ridge station registers concentrations of daily mean O<sub>3</sub> in the range of 31 - 58 ppb. Maximum O<sub>3</sub> concentrations have a higher range at all these stations, including Esther (Table 14). These values and previously published literature from Alberta on daily mean and maximum O<sub>3</sub> concentrations demonstrate that Alberta's daily average concentration objective of 25 ppb should be eliminated as it is exceeded at most rural sites during summer and winter months (Peake et al., 1983; Angle and Sandhu, 1986, 1989; Legge and Krupa, 1990; Peake and Fong, 1990). Comparison of average daily maximum ozone concentrations range in the Northern Hemisphere is shown in Table 9 (EC, 1997b). Alberta's values fall in the range observed at other places.

Table 9 Range of daily maximum ozone concentrations in the Northern Hemisphere.\*

Reference	Location	Range of Daily Maximum Ozone (ppb)
Angle and Sandhu, 1986	Northern Alberta, Canada	27 – 66
Altshuller and Lefohn, 1996	Western U.S., summertime	50 – 78
Colbeck and Harrison, 1985	Stodday, U.K.	41.5 - 50.6
Evans et al., 1983	U.S. National Forests	33 – 49
Kelly et al., 1982	South Dakota, U.S.	34 – 36
Legge et al., 1991	Rocky Mountains, Alberta, Canada	3 – 122**
	Continental U.S.	17 – 75
Singh et al., 1978	Hawaii, U.S.	30 – 59
	Germany	18 - 52

<sup>\*</sup> Taken from EC, 1997b.

## **5.1.4** Monthly Mean and Hourly Maximum Ozone Concentrations

Monthly mean and hourly maximum O<sub>3</sub> concentrations from nine Alberta monitoring stations are given in Figures 4 and 5. The monthly variations are very typical of urban and rural sites in North America. From an Alberta perspective, Legge and Krupa (1990) have discussed background monthly O<sub>3</sub> concentrations. Singh (1978) has discussed background concentrations of O<sub>3</sub> observed in a number of locations around the world. To explain the behavior of O<sub>3</sub> in remote locations, Singh et al. (1978) developed a schematic representation of the variations in

<sup>\*\*</sup> This is hourly maximum range and was changed after consultation with Dr. A. Legge.

the  $O_3$  concentrations at the surface and in the free troposphere, as well as variations in  $O_3$  concentrations by season. Idealized seasonal variations in  $O_3$  are shown in Figure 13, where natural  $O_3$  effects (curve A) are expected to be at maximum in the early spring. Perturbations in  $O_3$  levels due to localized  $O_3$  production and transport from urban centres, both resulting from photochemical processes, are depicted by curves B and C. Monthly ozone values from Alberta for 1997 and other years should be viewed in the light of curves A, B and C. The behavior of monthly means and maximums from urban centres and rural areas, especially in summer months, is different. Further research and analysis, are needed to sort out the complex chemistry and meteorology occurring at these Alberta locations.

### **5.1.5** Annual Mean Ozone Concentrations

Annual mean concentrations are displayed in Figure 6 for the period 1982 to 1997. No trend is apparent from this figure. It has been noted in the literature that as the old cars are replaced by new cars with tighter emission controls,  $NO_x$  and VOC will decrease in urban centres, which might affect  $O_3$  concentrations in the upward direction. Calgary Central and Edmonton Central are the stations which will show those trends first if the population and number of cars do not increase.

# 5.2 Peroxyacetyl Nitrate (PAN), Nitric Acid(HNO<sub>3</sub>) and Particulate Nitrate (PN)

As mentioned earlier, PAN and  $O_3$  are the two important secondary photochemical air pollutants found in the urban atmospheres. Of the two, PAN is a more useful indicator of photochemical reactions in polluted air as, unlike ozone, it appears to have no large natural source. The formation of PAN is initiated by the photo-oxidation of hydrocarbons, leading to aldehydes and, subsequently, peroxy radicals (Figure 1). These peroxyradicals then react with  $NO_x$  to form PAN and its higher lomologues. It must be remembered that the concentrations of all secondary pollutants like PAN and  $O_3$  are influenced not only by solar radiation and temperature, but also by the magnitude of primary pollutant emissions and other meteorological parameters like mixing volumes, wind speeds and ventilation rates. Some comments on PAN and  $O_3$  relationships are in order here. Both PAN and ozone are generated by related photochemical processes in Alberta, each usually reaching maximum concentrations simultaneously in the early afternoon (Peake and Sandhu, 1983). The peak afternoon concentration of PAN is much less than the corresponding ozone maximum. During episodes of photochemical smog in Los Angeles or in Japan, ozone/PAN ratios of 10 have been reported.

In downtown Calgary, ratios as low as one were measured (Table 10). Such low ratios occurred when the background concentration of ozone was first suppressed by nitrogen oxides followed by photochemical ozone and PAN formation. Ozone/PAN ratios at the University in northwest Calgary were generally higher than downtown. On August 14, the day of maximum PAN concentrations at both downtown and the University, the ratio was 33 at the University compared with 9 downtown. The mean ratio for 14 days when PAN was measured both at the University and downtown was 65 at the University and 21 downtown. Overall ozone concentrations are higher at the University than downtown (means for 1981 of 18.3 ppb and 10.3 ppb respectively), reflecting the University location upwind of the major transportation sources of nitrogen oxides. Downtown Calgary ozone concentrations are suppressed by nitric oxide emissions. On days of

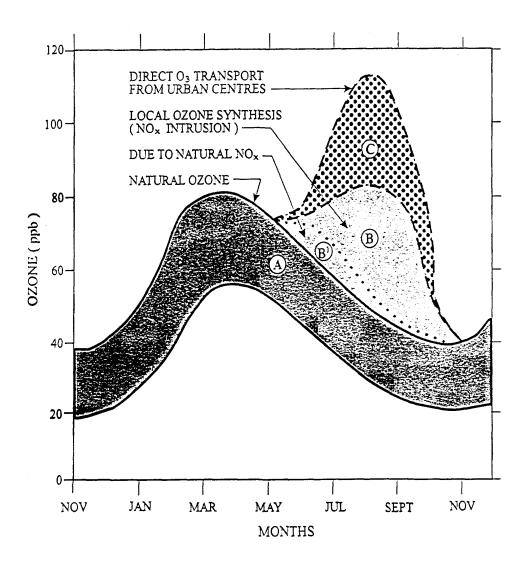


Figure 13 A schematic diagram of the idealized variations in O<sub>3</sub> concentrations at remote locations (Singh et al., 1978).

Table 10 Ozone/PAN ratios on selected days at the University of Calgary and downtown Calgary (Peake and Sandhu 1983).

Day	University	Downtown
Jan. 2, 1981	38	NA
Jan. 27, 1981	4	NA
Jul. 29, 1981	35	12
Aug. 6, 1981	43	17
Aug. 14, 1981	33	9
Aug. 25, 1981	120	31
Jan. 25, 1982	NA	1
Feb. 15, 1982	NA	7

NA Not Available

relatively high pollution during the winter months, low ozone/PAN ratios may result, even at the University, from suppression of ozone by nitric oxide rather than from high PAN concentrations. For example, on January 27, a ratio of 4 was measured at the University. The PAN concentration was 2.3 ppb, while the ozone concentration was only 10 ppb.

Comparison of the primary pollutant concentrations with the corresponding ozone and PAN concentrations, showed the generation of ozone and PAN after a decline in the overall concentration of nitrogen oxides, which corresponded to the conversion of NO to NO<sub>2</sub>. In some cases, however, PAN maximum occurred coincident with maximum concentrations of the primary pollutants. On January 27, 1981, high nitrogen oxide concentrations were recorded at the University, and the maximum PAN concentration of 2.3 ppb occurred simultaneously with a maximum of 410 ppb nitrogen oxides, both NO and NO<sub>2</sub> reaching a maximum at that time. Comparison of Alberta values of PAN with the published literature values for urban and rural areas is given in Appendix IV. Ambient concentrations from Alberta compare favourably with similar geographical and population places (USEPA, 1996).

Peake et al. (1988a) converted the monthly mean concentrations of  $NO_x$ , PAN, HNO<sub>3</sub> and PN to equivalents of  $NO_3$  to allow direct comparison of the abundance of each chemical species (Table 11). The primary pollutant NO was the most abundant of these nitrogen compounds, with a mean concentration over a 12-month period of 110  $\mu g$  m<sup>-3</sup>. Nitrogen dioxide, the initial oxidation product of NO, was also abundant with a 12-month mean concentration of 80  $\mu g$  m<sup>-3</sup>. The secondary pollutants, PAN, PN and HNO<sub>3</sub>, were far less abundant. PAN, rather than PN or HNO<sub>3</sub>, was the major product of photochemical conversion of  $NO_x$  observed in the Edmonton atmosphere. The mean PAN concentration was 42  $\mu g$  m<sup>-3</sup> compared with 0.30  $\mu g$  m<sup>-3</sup> HNO<sub>3</sub> and 1.22  $\mu g$  m<sup>-3</sup> PN, calculated as  $NO_3$ . Table 11 clearly shows that seasonal variations in the concentrations of PAN and HNO<sub>3</sub> occurred during the summer months, whereas the highest concentrations of NO,  $NO_2$  and PN occurred in the winter. Nitric acid concentrations were highest in July, with a mean of 0.67  $\mu g$  m<sup>-3</sup>, and lowest in December, with a mean of

 $0.14~\mu g~m^{-3}$ . PAN concentrations were highest in August at  $7.6~\mu g~m^{-3}$  (as  $NO_3$  equivalents) and lowest in December at  $1.2~\mu g~m^{-3}$ . These seasonal variations in PAN and HNO<sub>3</sub> are due to the influence of solar radiation, temperature and meteorology. In winter, lower wind speeds and shallower mixing depths tend to concentrate pollutants, resulting in higher NO and  $NO_2$  concentrations. The seasonal variation in PN reflects this variation in  $NO_x$ .

The fractional conversion  $(F_n)$  of  $NO_x$  to reaction products has been calculated as:

$$F_{n} = \frac{HNO_{3} + PAN + PN}{NO + NO_{2} + HNO_{3} + PAN + PN}$$

Table 11 Monthly mean concentrations of NO, NO<sub>2</sub>, PAN, PN and HNO<sub>3</sub> in the Edmonton atmosphere, calculated as the equivalent  $\mu$ g m<sup>-3</sup> of NO<sub>3</sub><sup>-</sup>, and the fractional conversion  $(F_n)$ .\*

	Date	NO	$NO_2$	PAN	PN	HNO <sub>3</sub>	$F_{\rm n}$
Nov.	1982	140	80	-	1.52	0.23	0.010
Dec.	1982	170	110	1.2	1.63	0.14	0.008
Jan.	1983	220	110	2.4	1.68	0.19	0.013
Feb.	1983	170	80	4.0	2.28	0.23	0.025
Mar.	1983	110	80	5.7	1.98	0.28	0.040
Apr.	1983	80	80	4.5	0.91	0.23	0.034
May	1983	60	50	4.2	0.39	0.22	0.042
Jun.	1983	60	50	6.0	0.34	0.28	0.057
Jul.	1983	60	60	5.2	0.81	0.67	0.057
Aug.	1983	80	80	7.6	0.71	0.50	0.059
Sep.	1983	80	60	3.6	0.66	0.28	0.031
Oct.	1983	140	80	3.9	1.73	0.39	0.027
12 mo	nths	110	80	4.2	1.22	0.30	0.034

<sup>\*</sup> Taken from Peake et al., 1988a.

The monthly  $F_n$  values are also given in Table 11. The  $F_n$  value for the 12-month period based on all data collected was 0.034, indicating a very low conversion rate of  $NO_x$  to secondary pollutants on a yearly basis. The summer (June, July and August) mean was 0.06. This compares with values of 0.11 downwind of Los Angeles. In Calgary, the mean  $F_n$  value for 14 days in July and August of 1982 was also low, 0.08 (Peake et al., 1983a,b). Measurements in Calgary were made only 6 km downwind of the city centre. In Edmonton, measurements were

made downtown, thus the time available for conversion of  $NO_x$  to PAN. Nitric acid (HNO<sub>3</sub>) and PN in both cities would generally be short, accounting for the low conversion factors.

#### 5.3 Human and Environmental Health Effects

Studies from Alberta on health effects of ozone are almost non-existent (AH, 1997). From Canada, Burnett et al. (1994) have published the results of effects of low ambient levels of ozone. Associations between ozone and health effects have been noted. Also, ozone is one of the most damaging air pollutants to vegetation. Ozone has been studied the most over the years and its effects are understood better than those of other photochemically derived oxidants. On the basis of concentration, PAN is more toxic to vegetation than O<sub>3</sub>, but the concentration of PANs are much smaller than O<sub>3</sub> and are distributed less widely. Numerous studies have been published on the effects of O<sub>3</sub> on humans, animals and the environment. Recent reviews have documented that scientific information (USEPA, 1996; EC 1997f,g; WGAQOG, 1998). The nature of effects as summarized in the NO<sub>x</sub>/VOC Management plan and by the Health and Vegetation Objectives Working Group are outlined below.

In 1990, the Canadian Council of Environment Ministers concluded that over 50% of the Canadian population was routinely exposed in summer to ozone levels above the 82 ppb target, which was used to design ozone management programs (CCME, 1990). Epidemiological and statistical evidence have indicated that the target level of 82 ppb was not protective of human health. Observations of adverse effects at very low levels and the absence of any apparent lower threshold suggested that a much greater percentage of the population was being exposed to ozone levels that adversely affect health, and that new lower management targets should be set. Consideration should be given to whether measures need to be taken to reduce ozone levels where there are elevated levels due to human activity, not just in the areas where the highest ambient levels occur. There are few toxicological studies from Canada on this subject.

The CCME also noted that ground-level ozone is the most damaging of all air pollutants to vegetation. Acute symptoms, such as damage to leaves or needles, result from short term, high level exposures. Chronic effects, such as changes in plant growth and productivity, occur as a result of exposure to frequent, low, hourly ozone concentrations with periodic, intermittent peaks. Visible foliar injury has been observed in crops grown in British Columbia, Ontario, Quebec, and New Brunswick, providing empirical evidence that crops are being affected at ozone concentrations currently experienced in Canada. There have not been sufficient investigations in other provinces. There is also considerable evidence that many natural and ornamental species (e.g. trees and grasses) common to Canada are sensitive to ozone, and that current ambient concentrations have the potential to cause both foliar injury and growth reductions.

During the early 1990's, two national working groups were formed to review the latest scientific research on the effects of ozone on health and vegetation, and recommend revised air quality objectives for ozone. These groups have produced consensus reports. It is worth repeating here, for the benefit of the reader, the final conclusions and recommendations of the Health Objectives Working Group (HOWG) and the Vegetation Objectives Working Group (VOWG) on the effects

of O<sub>3</sub>. The following is taken from the "Summary for Policy Makers" document (EC, 1997h) on effects:

"1. The HOWG recommends that the form of a health guideline should be from as short as one hour to as long as eight hours.

With respect to the form of a guideline, the epidemiological and clinical study findings indicate the selection of averaging times from as short as one hour to as long as eight hours. Both are very highly correlated in results from epidemiological studies, and both give almost the same degree of association with ozone-related health effects. The clinical studies indicate that the shorter averaging times would be preferable and would protect against adverse respiratory effects noted after peaks of one to three hours of exposure. While a 24-hour averaging time might be preferable from the statistical point of view, by lowering the variance observed, it tends to obscure the effect of real-world strong diurnal peaks in ambient ozone.

2. The HOWG concludes that there is no level of a health guideline that will protect all Canadians.

With respect to the level of a guideline that might be suggested, based on the sum of the evidence, researchers can discern no clear level that would be protective of human health for all segments of the population. The data from the epidemiological studies demonstrate a monotonically increasing relationship between ozone concentration and adverse health effects without any strong evidence of threshold, thus precluding the establishment of a No Observable Adverse Effect Level (NOAEL) or a Lowest Observable Adverse Effect Level (LOAEL).

3. A strategy for ozone management from the human health perspective should focus on continuous improvement reflecting the nature of the health endpoints data (i.e. a continuum of effects throughout the current exposure range for the general population).

The apparent continuum of adverse health effects indicates that any improvements in ambient ozone concentrations are expected to result in public health benefits.

- 4. The HOWG recommends that interested members of the health community should be involved in the development of strategies for continuous improvement in ambient ozone so as to accurately represent the health data.
- 5. Because of the rapidly evolving human health database and improvements in relevant methodologies, Health Canada and stakeholders should review the information on which this report is based within five years.

6. Members of the HOWG recommend that further health research be conducted in a number of areas.

Health researchers should undertake further method development to isolate the effects of ozone from the chemical mixture and from other climatic factors. Health researchers should undertake research to more clearly understand the nature of the affected population with respect to the part played by previously compromised and susceptible populations. Health researchers should pursue further epidemiological studies on the chronic effects of ozone.

7. Environment Canada should pursue harmonization with the U.S. form of an ozone air-quality standard to improve coordination of research and monitoring activities in both countries.

The current (September 1997) Canadian ground-level ozone objective is 82 ppb averaged over one hour. The current U.S. ground-level ozone standard is 120 ppb averaged over one hour. Both countries are in the process of reviewing their respective ozone objective/standard, with consideration being given to the health and ecosystem benefits of lower concentrations and longer averaging periods. Risk assessment and management criteria will be factored into the final decisions made in each country.\*

- 8. The Vegetation Objective Working Group recommends that the scientific basis of the form and level of a ground-level ozone air-quality objective should be the SUM60 (sum of ozone hourly values at or above 60 ppb) method, with the following parameters.
  - a) a rolling three-month, 12-hour (0800-1959) maximum SUM60 not to be exceeded in any year from April 1 to September 30 at a level of either:
    - 6,600 ppb-h for protection of 95% of crops, trees and natural unmanaged vegetation, or
    - 7,400 ppb-h for protection of 90% of crops, trees and natural unmanaged vegetation;
  - b) a rolling three-day, 12-hour (0800-1959) maximum SUM60 not to be exceeded in any one year from April 1 to September 30 at a level of 700 ppb-h to protect against foliar injury in excess of 5 to 10% on sensitive plants, or
  - a one-day, 12-hour (0800-1959) maximum SUM60 not to be exceeded in any one year from April 1 to September 30 at a level of 500 ppb-h, to protect against foliar injury in excess of 5 to 10% on sensitive plants.

Given the cumulative nature of crop and forest tree response to ozone, over single or multiple seasons, any reductions in the (mid to high) range of ozone concentrations (i.e., greater than 60 ppb) should result in decreased risk of plant

<sup>\*</sup> United States changed their standard for ozone in July, 1997. The new standard is an 8-hour standard at a level of 80 ppb, with a form based on the 3-year average of the annual fourth-highest daily maximum 8-hour average ozone concentrations measured at each monitor within an area (USEPA, 1997).

damage and increased benefits to Canadian crop and tree producers. Crop damage (productivity loss) is routinely observed over large areas of the Windsor-Quebec City Corridor and Lower Fraser Valley, and severe foliar injury/plant mortality to sensitive bio-indicators are observed regularly, early in the season, in the Southern Atlantic Region. Ozone-like foliar symptoms on white pine trees are occurring within the Windsor-Quebec City corridor and Southern Atlantic Region. Forest declines are occurring on some species within these regions, but the role of ozone as a causal agent remains uncertain."

## 5.4 Proposed National Ambient Objectives and Canada-Wide Standards

For the last few years, the Working Group on Air Quality Objectives and Guidelines set up under the Canadian Environmental Protection Act (CEPA), has concluded that two-tier approach be used for setting national objectives for air pollutants. Two-tiers are defined as:

The Reference Level: A level above which there are demonstrated effects on human health and/or environment. It provides a basis for establishing goals for air quality management.

The Air Quality Objective: Represents the air quality management goal for the protection f the general public and the environment in Canada. It is a level based upon consideration of scientific, social, economic and technological factors.

The Working Group has drafted a document entitled "National Ambient Air Quality Objectives for Ground-Level Ozone - Science Assessment" (WGAQOG, 1998). The Working Group relied heavily on the recently published reviews from Canada and U.S. (EC, 1997a-h; USEPA, 1996). The main purpose of this draft was to lay the foundation and present the rationale for setting the reference level. It is not the intention to review the information from this report here but to present the final recommendations. Reference levels for three receptors were considered as given below.

#### 5.4.1 Materials

It was recommended that no reference level be identified for O<sub>3</sub> impact on materials given the lack of broadly based applicable quantitative concentration-response relationship.

### **5.4.2** Vegetation

A number of different "exposure indices" are used frequently now to define the ozone "dose", which a given plant receives during exposure to atmosphere O<sub>3</sub> concentrations. The SUM60 index was identified by the Vegetation Objectives Working Group (EC, 1997g) as being a preferred index on which to have air quality "standards" compared to other indices. The SUM60 index is the sum of hourly mean ozone concentrations equal to or greater than 60 ppb. Considering many factors, the Working Group recommended that a peak-weight cumulative SUM60 index be selected as the form of a Reference Level to provide long- and short-term protection of crops and trees in Canada from ozone exposure. The numeric values of the reference levels are conservatively set to provide protection to vegetation at the lowest level of scientific certainty, which is 10% yield or biomass loss, for 95% of the experimentally evaluated

crop/tree species. For the protection of vegetation, the following two reference levels were recommended:

Maximum 3-month 12-hour (0800-1959) SUM60 not to be exceeded during April-September in any year:	6600 (ppb-h)
Maximum 3-day 12-hour (0800-1959) SUM60 not to be exceeded during April-September in any year:	700 (ppb-h)

#### **5.4.3** Human Health

The recommended reference level is based on epidemiological and statistical associations between ozone, and both total mortality and respiratory hospital admissions, as well as other such factors that pertain to certain populations. Because very little toxicological data is available on the effects of ozone on animals and humans, it was not possible to establish a direct doseresponse relationship. To protect human heath, the Working Group recommended a reference level of a daily, one-hour maximum average level of 15 ppb. It was noted that the proposed reference level was an estimate of the lowest ambient ozone level at which statistically significant increases in health responses could be detected.

### 5.4.4 Canada-Wide Standards

The Canadian Council of Ministers of Environment signed a Canada-Wide Accord on Environmental Harmonization in different areas of environmental management in 1998 (CCME, 1998a). The Sub-Agreement on Canada-Wide Standards was a part of that document (CCME, 1998b). It sets out principles for governments to jointly agree on priorities, to develop standards, and to prepare complementary workplans to achieve those standards, based on the unique responsibilities and legislation of each government. Public input will be a key feature in their development. Canada-Wide Standards (CWSs) can include qualitative or quantitative standards, guidelines, objectives, and criteria for protecting the environment and reducing the risk to human health. CWSs presented to Ministers for endorsement will include a numeric limit (for example, ambient, discharge, or product standard), a commitment and timetable for attainment, a list of preliminary actions to attain the standard, and a framework for reporting to the public.

The focus of the Standards Sub-Agreement is on ambient standards. Ambient standards can be described as levels of environmental quality for specific media (for example, air, water, soil, or sediment). The Sub-Agreement also anticipates standards for products, discharge limits, and emission reductions where such standards represent the best strategy for achieving the desired outcome. Product and discharge standards may include specifications on the quantity or quality of a release of a specific type or source of pollution (such as waste specifications for a substance), or the content and use of a commercial product. Generally, CWSs are being developed using a risk-based approach. The draft conceptual risk-based framework outlines the scientific, technical, and socio-economic factors involved in developing and implementing CWSs (CCME, 1998c). This draft framework is being tested, adapted, and modified as necessary during the development of the current CWSs.

Ozone is one of the air pollutants chosen for establishing a Canada-Wide Standard. A national committee, comprising of representatives from federal, provincial and territorial environment and health departments has been established to develop CWSs on ozone for Ministers by the fall of 1999. For moving the process forward, a workshop was held on September 25, 1998. Various options for an O<sub>3</sub> standard were outlined in a background document prepared for the workshop, and are given in Table 12 (CWS, 1998). Each option is further discussed in the background document. The final outcome from this workshop is not known yet. All these options will have some consequences for Alberta. A clear Alberta position on each option needs to be developed.

#### 5.5 Alberta Situation

Alberta has a population of about 3 million, which is about one tenth of the Canadian population. It ranks fourth in population as compared to the population base of Ontario, Quebec and British Columbia. However, the anthropogenic emissions of  $NO_x$  and VOC, major precursors of ozone, are the second highest in Canada when compared to the other Canadian provinces. This is due to the industrial base of Alberta that is rooted in oil, gas and coal. One of the key industrial sectors which generate  $NO_x$  and VOC emissions involves oil and gas developments and their operations. These facilities are scattered around the province and their emissions of ozone precursors may contribute to enhancing downwind rural and regional levels of ozone. Relative contribution of such processes to rural ozone concentration in Alberta has not been determined yet. It should be noted that estimated natural or biogenic emissions of VOCs from Alberta are larger than the anthropogenic emissions by a factor of more than two.

A good urban database on ambient O<sub>3</sub> concentrations now exists in Alberta. This information is reliable and is well recognized in the international scientific literature. Most of the time, Alberta cities act as sinks of ozone because of reactions with nitrogen oxides emitted mainly from transportation sources. Reactions of ozone with nitrogen oxides and volatile compounds, in the absence and presence of sunlight, give rise to other products like PAN, HNO<sub>3</sub> and particulate nitrate. A few episodes of elevated ozone levels above Alberta's hourly mean ozone objective (82 ppb) have been observed in urban centres in the last five years (Table 13).

These exceedances only occur in summer months when chemistry, meteorology and precursor emissions are optimum to generate higher levels of ozone. Rural background hourly and daily mean  $O_3$  concentrations are relatively high in Alberta. High elevation monitoring stations record higher  $O_3$  levels compared with low elevation stations, as expected. Exceedances of hourly mean ozone concentrations above Alberta's one-hour objective of 82 ppb have also been observed at rural background sites.

Alberta adopted three tier-objectives for  $O_3$  in the 1960s: (1) mean one-hour maximum concentration of 50 ppb, (2) mean 24-hour maximum concentration of 25 ppb, and (3) mean annual concentration of 15 ppb. These values were based on the recommendations from a Canadian federal and provincial advisory committee on air quality (FPAC, 1976). Consideration of research findings in the late 1970s and ambient monitoring from Alberta data led to the elimination of the annual ambient  $O_3$  objective, and changing the one-hour objective from 50 ppb to 82 ppb. Though a recommendation was made to eliminate the 24-hour objective,

Table 12 Options for form of ozone CWS.\*

Table 12 Option	s for form of ozone CWS.*
Form	Considerations
Option 1: Ambient Concentration Limit (ppb, [8 hr] [1 hr]	<ul> <li>Simple, easy to understand, easy comparison with daily ambient levels</li> <li>Same level of protection everywhere, consistent with Accord/Sub-Agreement</li> <li>an 8-hr limit would be same form as U.S. NAAQSs for ozone allowing easier cross-border comparisons and joint program development</li> <li>regional feasibility analyses could lead to lowest common denominator selection</li> </ul>
Option 2: Cumulative Exposure Index (Human Exposure) (ppb-hours above a specified ambient level, over 30 days)	<ul> <li>same level of protection everywhere, consistent with Accord/Sub-Agreement</li> <li>directly linked to human health effects</li> <li>directs control efforts to cumulative exposure rather than episode management</li> <li>difficult for the public to understand</li> <li>cannot relate to current daily air quality conditions, therefore no guidance for managing episodes</li> <li>not well suited for issuing daily air quality advisories</li> <li>can only determine whether CWS is being met after 30 days</li> </ul>
Option 3: Additional Cumulative Exposure Index (Vegetation Protection) (ppb-hours above 60 ppb, over 3 days and 3 months)	<ul> <li>provides a vegetation-based target to supplement the health-based target</li> <li>attempting to get agreement on a vegetation number may divert attention away from the primary driver: health; may make more sense to focus on health-based driver and achieve whatever supplemental vegetation benefits accrue by efforts to protection health.</li> </ul>
Option 4: Phased Percentage Reduction from Current Ambient Levels	<ul> <li>many different levels of protection in different parts of the country due to different baselines; difficult to explain to the public not consistent with Harmonization Accord</li> <li>difficult to set baseline levels and report on progress</li> <li>difficult to compare with the U.S.</li> <li>less precise/definitive commitment that U.S. NAAQSs</li> </ul>
Option 5: Phased Commitment Towards Long-Term Goal (ambient concentration or CEI long- term goal)	<ul> <li>provides a long-term science-based goal or beacon against which daily ambient levels can be compared</li> <li>any number above the Reference Levels may be hard to defend given no lower threshold</li> <li>difficult to determine feasibility of achieving goal everywhere, even in the long-term, therefore hard to meet conditions of Accord/Sub-Agreement</li> <li>less precise/definitive commitment than U.S. NAAQSs</li> </ul>
Option 5a: Phased Percentage Achievement of Long-Term Goal	<ul> <li>same level of protection everywhere, consistent with Accord/Sub-Agreement</li> <li>hard to explain to the public, e.g. that at 90% the goal is to still allow exceedances 36 days per year</li> <li>impossible to determine whether CWS is being met until year is over; therefore little incentive to manage episodes</li> </ul>
Option 5b: Phased Percentage Reduction in Exceedances of Long-Term Goal	<ul> <li>many different levels of protection in different part of the country due to different baselines; difficult to explain to the public not consistent with Harmonization Accord</li> <li>hard to explain to the public e.g. that at 90% the goal is to still allow exceedances 36 days per year</li> <li>impossible to determine whether CWS is being met until year is over; therefore little incentive to manage episodes</li> </ul>
Option 5c: Phased Percentage Reduction in Emissions Contributing to Ozone Towards Long-Term Goal	<ul> <li>maybe easier to measure and track than an ambient level target and ensure key pollutants contributing to poor air quality are reduced</li> <li>impossible to determine whether CWS is being met until year is over; therefore little incentive to manage episodes</li> <li>if same percentage everywhere, some of the reductions may not be necessary depending on the location; severity of the problem and contributing sources, therefore money wasted</li> <li>many different levels of protection in different parts of the country due to different baselines; difficult to the public not consistent with Harmonization Accord</li> </ul>

<sup>\*</sup> Taken from reference CWS, 1998

based on rural and urban ambient monitoring in Alberta, this objective was retained. Concentrations above this objective are observed at almost all of the monitoring stations in

Table 13 Number of 1-hour ozone objective (82 ppb) exceedances at nine stations from 1993 to 1997.

Stations	1993	1994	1995	1996	1997	Total
Calgary Central	0	0	0	0	0	0
Calgary East	0	0	0	0	0	0
Calgary Northwest	0	2	0	0	0	2
Edmonton Central	0	0	2	0	0	2
Edmonton East	1	1	0	0	0	2
Edmonton Northwest	0	2	2	2	0	6
Fort McMurray	2	0	0	0	0	2
Fort Saskatchewan	1	15	5	3	0	24
Hightower Ridge	NA	NA	NA	0	2	2
Total	4	20	9	5	2	40

NA Not Available

Alberta during the year. Therefore, the 24-hour objective of 25 ppb should be eliminated immediately as it has no sound scientific basis, as well as no relationship to the one-hour  $O_3$  objective. No air quality objective should be set below the natural background of an air pollutant if compliance is the intention, or "common sense" is the philosophy behind setting an air quality objective.

The one-hour ozone objective of 82 ppb has served Alberta well and should be retained for the time being, but immediate review should be taken in the light of recent scientific and monitoring information. As pointed out in the last section, the Working Group on Air Quality Objectives and Guidelines has proposed ambient air quality reference levels for vegetation and human health based on available scientific information from Canada, the United States and other countries. Before accepting any new reference levels, objectives or standards, current Alberta information should be used to assess the risks, costs and benefits of these new proposed objectives.

Hourly, daily, monthly, seasonal and annual mean concentrations of ozone reveal the complex nature of the chemistry, physics and meteorology of the air in Alberta. There are still differences in viewpoints in Alberta's scientific community as to the relative importance of contribution to surface  $O_3$  from intrusion of  $O_3$  from the stratosphere, mixing from free troposphere, local photochemistry, and medium and long-range transport of ozone and its precursors. Only time dependent modelling and field measurement, upwind and downwind of major urban centres and other industrial sources, can resolve this issue.

At present, no systematic efforts to study the effects of O<sub>3</sub> on vegetation, animals or humans, in the field or laboratory settings under Alberta climatic conditions, are in place in Alberta. Ozone

co-occurs with many other pollutants in the atmosphere and daily mean rural background  $O_3$  values are high - about 40 ppb (Table 14). It does not make "common sense" to accept a proposed human health reference level of 15 ppb, which is based on statistical associations alone and not on toxicological studies (section 5.4.3). Humans and animals have been surviving and coping with  $O_3$  levels above 15 ppb for centuries. More toxicological studies are needed to set a reference level for human health effects.

Table 14 Monthly mean and hourly maximum ozone concentrations (ppb) at two rural background monitoring sites during 1997.

Month	Esther* (Elevation 707 m ASL)		Hightower Ridge** (Elevation 1524 m ASL)	
	Mean	Maximum	Mean	Maximum
January	30	48	40	63
February	34	45	48	88
March	40	62	50	66
April	35	61	53	68
May	35	60	46	69
June	31	61	41	68
July	32	58	38	59
August	30	61	36	65
September	26	63	34	71
October	23	51	38	56
November	20	41	46	88
December	23	42	50	81

<sup>\*</sup> Operated by Environment Canada

As pointed out in section 5.4.2, the Working Group on Air Quality Objectives and Guidelines has recommended two reference levels: (1) Maximum 3-month 12-hour (0800-1959) SUM60 not to be exceeded during April-September in any year from 6600 ppb-h, and (2) maximum 3-day 12-hour (0800-1959) SUM60 not to be exceeded during April to September in any year from 700 ppb-h. It is important to note that the concept of using SUM60 is not founded in solid science (Legge, 1998). However, this was the approach recommended by the Vegetation Objective Working Group to protect vegetation. Most of the scientific data on crop yield, biomass loss and visible injury from eastern Canada, United States or Europe was used to derive SUM60 values for Canada. It is not certain whether crops and vegetation of economic importance to Alberta were considered in developing SUM60 for Canada. Ambient monitoring

<sup>\*\*</sup> Operated by West Central Airshed Society

data from Alberta is available to make a preliminary assessment of the proposed air quality objectives in the Alberta context (Tables 2, 3, 4, 5 and 14).

During the development of the Canadian Management Plan for  $NO_x$  and VOCs emissions to control ambient  $O_3$  concentrations, the Canadian Council of the Ministers of the Environment noted that Alberta and the Canadian prairies have no ozone problems (CCME, 1990). Alberta has endorsed the "Pollution Prevention" principles developed by the Canadian Council of Ministers of Environment (CCME, 1993). Continued commitment to these principles, and Alberta's clean air vision, will ensure that provincial ozone concentrations stay below Alberta's ozone objective.

## 6.0 CONCLUSION

The Alberta cities of Calgary and Edmonton mostly act as ozone sinks due to reactions with nitric oxide emitted from urban sources. These chemical reactions give rise to other secondary air pollutants like peroxyacetyl nitrate, nitric acid and particulate nitrate. A good urban database on ambient ozone concentrations exists in Alberta. This information is reliable and is well recognized in the international scientific literature. To improve the database further, monitoring strategies adopted by the Clean Air Strategic Alliance should be implemented. Considering the current Canadian and Alberta objective of one-hour maximum ozone concentration of 82 ppb, there are no concerns of meeting this objective in Alberta cities except a few exceedances during the last five years. Rural values of ozone concentrations are high compared with urban centres. The 24-hour Alberta objective for ozone is exceeded most of the time in rural Alberta compared with major cities. Based on the scientific and monitoring evidence to date, it is recommended that this 24-hour objective of 25 ppb be eliminated immediately, as was done for eliminating the annual objective for ozone in the 1980s. However, a new objective for ozone to protect vegetation should be considered. Relative importance of contributions to ground-level ozone from intrusion of ozone from the stratosphere, mixing from the upper troposphere, local photochemistry and the medium and long-range transport need to be determined under Alberta climatic conditions. Time dependant modelling and field measurements of the chemistry and meteorology of the rural and urban air can resolve this issue.

# 7.0 REFERENCES

- AH Alberta Health, 1997. The Alberta oil sands community exposure and health effects program report. Alberta Health, Edmonton, Alberta
- AEP Alberta Environmental Protection, different years. Air quality monitoring reports. Air Issues and Monitoring Branch, Edmonton, Alberta.
- AEP Alberta Environmental Protection, 1997. Air quality model guidelines. Air and Water Approvals Division, Edmonton, Alberta.
- Altshuller, A.P. 1986. The role of nitrogen oxides in non-urban ozone formation in the planetary boundary layer over North America, western Europe and adjacent areas of ocean. Atmospheric Environment **20**: 245-268.
- Altshuller, A.P. and A.S. Lefohn, 1996. Background ozone in the planetary boundary layer over the United States. Journal of Air and Waste Management Association **46**: 134-141.
- Angle, R.P. and H.S. Sandhu, 1986. Rural ozone concentrations in Alberta, Canada. Atmospheric Environment **20**: 1221-1228.
- Angle, R.P. and H.S. Sandhu, 1989. Urban and rural ozone concentrations in Alberta, Canada. Atmospheric Environment **23**: 215-221
- Angle, R.P., M. Brennand and H.S. Sandhu, 1992. Surface albedo measurements at 53°N latitude. Atmospheric Environment **26A**: 1545-1547.
- Angle, R.P. and S.K. Sakiyama, 1991. Plume dispersion in Alberta. Standards and Approvals Division, Alberta Environment, Edmonton, Alberta.
- Bottenheim, J.W., S.E. Braslavsky and O.P. Strausz, 1977. Modelling study of seasonal effect on air pollution at 60°N latitude. Environmental Science and Technology 11: 801-808.
- Bottenheim, J.W. and O.P. Strausz, 1980. Gas-phase chemistry of clean air at 55°N. Environmental Science and Technology **14:** 709-718.
- Buhr, M.P., D.D. Parrish, R.B. Norton, F.C. Fehsenfeld, R.E. Sievers, and J.M. Roberts, 1990. Contribution of organic nitrates to the total reactive nitrogen budget at a rural eastern U.S. Site. Journal of Geophysical research (Atmosphere) **95**: 9809-9816.
- Burnett, R.T., R.E. Dales, M.E. Raizene, D. Krewski, P.W. Summers, G.R. Roberts, M. Radd-Young, T. Dann and J. Brook, 1994. Effects of low ambient levels of ozone and sulfates on the frequency of respiratory admissions to Ontario hospitals. Environ. Res. **65**: 172-194.

- CCME Canadian Council of Ministers of the Environment, 1990. Management plan for nitrogen oxides (NO<sub>x</sub>) and volatile organic compounds (VOCs). Environment Canada, Ottawa.
- CCME Canadian Council of Ministers of the Environment, 1993. A national commitment to pollution prevention. CCME Secretariat, Winnipeg.
- CCME Canadian Council of Ministers of the Environment, 1998a. Canada-Wide accord on environmental harmonization. Environment Canada, Ottawa.
- CCME Canadian Council of Ministers of the Environment, 1998b. Canada-Wide Environmental Standards Sub-Agreement, Environment Canada, Ottawa.
- CCME Canadian Council of Ministers of the Environment, 1998c. (Draft) Risk-Based Framework Environment Canada, Ottawa.
- CASA Clean Air Strategy for Alberta, 1991. A report to the Ministers. Alberta Environment and Alberta Energy, Edmonton, Alberta. 90 pages.
- CASA Clean Air Strategic Alliance, 1997. Annual report 1996, Edmonton.
- Cheng, L., R.P. Angle, E. Peake and H.S. Sandhu, 1995. Effective acidity modelling to establish acidic deposition objectives and manage emissions. Atmospheric Environment **29:** 383-392.
- Cheng, L., L. Fu, R.P. Angle and H.S. Sandhu, 1997. Seasonal variations of volatile organic compounds in Edmonton, Alberta. Atmospheric Environment **31**: 239-246.
- Cheng, L., K.M. McDonald, R.P. Angle and H.S. Sandhu, 1998. Forest fire enhanced photochemical air pollution: a case study. Atmospheric Environment **32**: 673-681.
- Coleback, I. and R.M. Harrison, 1985. Dry deposition of ozone: Some measurements of deposition velocity and vertical profiles to 100 meters. Atmospheric Environment **19**: 1807-1818.
- Corkum, R., W.W. Giesbrecht, T. Bardsley and E.A. Cherniak, 1986. Peroxyacetyl nitrate (PAN) in the atmosphere at Simcoe, Canada. Atmospheric Environment **20**: 241-1248.
- CWS, 1998. Working discussion paper: options for Canada-Wide Standards for PM and ozone (Draft). Prepared by Canada-Wide Standards Development Committee for Particulate Matter and Ozone. Environment Canada, Ottawa.
- EC Environment Canada, 1997a. NO<sub>x</sub>/VOC management plan science program: Ground-level ozone precursor emissions. Report of the Emissions Inventory Working Group. Environment Canada, Ottawa.

- EC Environment Canada, 1997b. NO<sub>x</sub> /VOC management plan science program: Ground-level ozone and its precursors, 1980-1993. Report of the Data Analysis Working Group. Environment Canada, Ottawa.
- EC Environment Canada, 1997c. NO<sub>x</sub> /VOC management plan science program: Ground-level ozone and precursor monitoring guidelines and implementation plan. Report of the Ambient Air Monitoring Working Group. Environment Canada, Ottawa.
- EC Environment Canada, 1997d. NO<sub>x</sub> /VOC management plan science program: Modelling of ground-level ozone in the Windsor-Quebec City Corridor and in the Southern Atlantic Region. Report of the Windsor-Quebec City Corridor and Southern Atlantic Region Modelling and Measurement Working Group. Environment Canada, Ottawa.
- EC Environment Canada, 1997e. NO<sub>x</sub> /VOC management plan science program: Modelling of ground-level ozone in the Lower Fraser Valley. Report of the Lower Fraser Valley Modelling and Measurement Working Group. Environment Canada, Ottawa.
- EC Environment Canada, 1997f. NO<sub>x</sub> /VOC management plan science program: Report of the Health Objectives Working Group. Environment Canada, Ottawa.
- EC Environment Canada, 1997g. NO<sub>x</sub> /VOC management plan science program: Report of the Vegetation Objective Working Group, Environment Canada, Ottawa.
- EC Environment Canada, 1997h. NO<sub>x</sub> /VOC management plan science program: Summary for policy makers a synthesis of the key results of the NOx/VOC science program. Environment Canada, Ottawa.
- EC Environment Canada, 1996. Canadian emissions inventory of criteria air contaminants. Environment Canada, Ottawa.
- Evans, E.G., R.C. Rhodes, W.J. Mitchell and J.C. Puzak, 1985. Summary of precision of accuracy assessments for the state and local air monitoring networks: 1982. Research Triangle Park, NC: U.S.E.P.A. Report Number EPA-60014-85-031.
- Fahey, D.W., G. Hübler, D.D. Parrish, E.J. Williams, R.B. Norton, B.A. Ridley, H.B. Singh, S.C. Liu and F.C. Felsenfeld, 1986. Reactive nitrogen species in the troposphere: measurements of NO, NO<sub>2</sub>, HNO<sub>3</sub>, particulate nitrate, peroxyacetyl nitrate (PAN), O<sub>3</sub> and total reactive odd nitrogen at Niwot Ridge, Colorado. Journal of Geophysical Research (Atmos.) **91**: 9781–9793.
- FPCAP Federal Provincial Committee on Air Pollution, 1976. Criteria for national air quality objectives. Fisheries and Environment Canada, Ottawa.
- Finlayson-Pitts, B.J. and J.N. Pitts, 1986. Atmospheric chemistry: fundamentals and experimental techniques. John Wiley & Sons, New York.

- Gaffney, J.S., NA. Marley and E.W. Prestbow, 1993. Measurement of peroxyacetyl nitrate at a remote site in the southwestern United States: tropospheric implications. Environmental Science and Technology **27**: 1905-1910.
- Gladstone, K.P., H. Niki, P.B. Shepson, J.W. Bottenheim, H.I. Schiff and H.S. Sandhu, 1991. Photochemical oxidant concentrations in two Canadian prairie cities: model evaluation. Atmospheric Environment **25B**: 243-254.
- Grosjean, D. and K. Fung, 1984. Hydrocarbons and carbonyls in Los Angeles air. J. Air Pollut. Control Assoc. **34**: 537-543.
- Grosjean, D. and E.L. II Williams, 1992. Photochemical pollution at two southern California smog receptor sites. Journal of Air and Waste Management Association **42**: 805-809.
- Kelly, N.A., G.T. Wolff and M.A. Ferman, 1982. Background pollutant measurements in air masses affecting the eastern half of the United States I. Air masses arriving from the northwest. Atmospheric Environment **16**: 1077-1088.
- Lack, J.C., 1980. Development of an industrial oriented air pollution control program. In Processings of the 5<sup>th</sup> International Clean Air Congress, 20-25 October, Buenos Aires, Argentina.
- Leahey, D.M. and M.C. Hansen, 1990. Observational evidence of ozone depletion by nitric oxide at 40 km downwind of a medium size city. Atmospheric Environment **24A**: 2533-2540.
- Leahey, D.M., 1998. Jacques Whitford and Associates Limited, Calgary. Private Communication.
- Lefohn, A.S., S.V. Krupa and D. Winstanley, 1990. Surface ozone exposures measured at clean locations around the world. Environmental Pollution **63**: 189-224.
- Leighton, P.A., 1961. Photochemistry of air pollution. Academic Press, New York.
- Legge, A.H., 1988. The present and potential effects of acidic and acidifying air pollutants on Alberta's environment critical point I summary report. The Government-Industry Acid Deposition Research Program, Alberta Environment, Edmonton, Alberta.
- Legge, A.H. and S.V. Krupa, 1989. Air quality at a high elevation, remote site in western Canada. In Transactions Effects of air pollution on Western forests. Air and Waste Management Association, Pittsburgh.
- Legge, A.H. and S.V. Krupa (Eds.), 1990. Acid deposition: sulphur and nitrogen oxides. The Alberta Government-Industry Acid Deposition Research Program (ADRO). Lewis Publishers, Ann Arbor, Michigan.

- Legge, A.H., M. Nosal, G.E. McVehil and S.V. Krupa, 1991. Ozone and the clean troposphere: ecological implications. Environmental pollution **70**: 157-175.
- Legge, A.H., T. Guidotti, M. English and H.S. Sandhu, 1992. A vision of clean air. J. Air and Waste Management Assoc. **42**: 888-891.
- Legge, A.H., 1998. Biosphere Solutions, Calgary. Private Communication.
- Macdonald, W.S. and B.F. Bietz, 1996. Management of industrial sulphur dioxide and nitrogen oxides emissions in Alberta: description of the existing system. In Proceedings of the Acidifying Emissions Symposium, Clean Air Strategic Alliance (CASA), April 15-17, 1996, Red Deer, Alberta.
- Myrick, R.H. and D.M. Asquin, 1993 and 1992. Air quality monitoring in Alberta: 1991 and 1990 summary, detailed and data reports. Air Issues and Monitoring Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, Edmonton, Alberta.
- Myrick, R.H., S.K. Sakiyama, R.P. Angle and H.S. Sandhu, 1994. Seasonal mixing heights and inversions at Edmonton, Alberta. Atmospheric Environment **28**: 723-729.
- Myrick, R.H., 1996a, 1996b and 1995. Air quality monitoring in Alberta: 1995, 1994 and 1993 summary, detailed and data reports. Air Issues and Monitoring Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, Edmonton, Alberta.
- Myrick, R.H. and K. Hunt, 1998. Air quality monitoring in Alberta: 1996 summary, detailed and data reports. Air Issues and Monitoring Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, Edmonton, Alberta.
- Peake, E. and H.S. Sandhu, 1983a. The formation of ozone and peroxyacetyl nitrate (PAN) in the urban atmosphere of Alberta. Canadian Journal of Chemistry **61**: 927-935.
- Peake, E., M.A. MacLean and H.S. Sandhu, 1983b. Surface ozone and peroxyacetyl nitrate (PAN) observations at rural locations in Alberta, Canada. Journal of Air Pollution Control Association **33**: 881-883.
- Peake, E. M.A. MacLean and H.S. Sandhu, 1985. Total inorganic nitrate (particulate nitrate and nitric acid) observations in Calgary, Alberta. Journal of Air Pollution Control Association **35**: 250-253.
- Peake, E., M.A. MacLean, P.F. Lester and H.S. Sandhu, 1986. Secondary air pollutants (peroxyacetyl nitrate, nitric acid, particulate nitrate and ozone) in Alberta, Canada. In Proceedings 7<sup>th</sup> World Clean Air Congress, Sydney, Australia, August 25-29, 1986. Clean Air Society of Australia & New Zealand, Sydney.

- Peake, E., M.A. MacLean and H.S. Sandhu, 1988a. Total inorganic nitrate (particulate nitrate and nitric acid) in the atmosphere of Edmonton, Alberta, Canada. Atmospheric Environment 22: 2891-2893.
- Peake, E., M.A. MacLean, P.F. Lester and H.S. Sandhu, 1988b. Peroxyacetyl nitrate (PAN) in the atmosphere of Edmonton, Alberta, Canada. Atmospheric Environment 22: 973-981.
- Peake, E. and B.D. Fong, 1990. Ozone concentrations at a remote mountain site and two regional locations in Southwestern Alberta. Atmospheric Environment **24A**: 475.
- Ridley, B.A., J.D. Shaffer, J.G. Walega, S. Madvonich, C.M. Elsworth, F.E. Grahek, F.C. Fehsenfeld, R.B. Norton, D.D. Parish, G. Hübler, M. Buhr, E.J. Williams, E.J. Allwine and H.H. Westberg, 1990. The behaviour of some nitrates at Boulder and Niwot Ridge, Colorado. J. Geophys. Res. [Atmos.] **95**: 13,949-13,961.
- Ridley, B.A. 1991. Recent measurements of oxidized nitrogen compounds in the troposphere. Atmospheric Environment **25A**: 1905–1926.
- Sandhu, H.S., 1975. A study of photochemical air pollutants in the urban airsheds of Edmonton and Calgary. Alberta Environment, Edmonton, Alberta.
- Sandhu, H.S., 1977. Oxidant levels in Alberta airsheds. In Proceedings International Conference on Photochemical Oxidant Pollution and its Control. EPA 600/3-77-001a. United States Environmental Protection Agency, January, 1977, 299-305.
- Sandhu, H.S., 1998. Ambient particulate matter in Alberta. Report prepared for Science and Technology Branch, Alberta Environmental Protection. No. 1494-A-9805, Edmonton, Alberta.
- Sandhu, H.S., 1999. Smog. In Encyclopedia of Environmental Science, page 562. Kluwer Academic Publishers, Dordrecht, Netherlands.
- Seinfeld, J.H., 1986. Atmospheric chemistry and physics of air pollution. John Wiley & Sons, New York.
- SIA Strathcona Industrial Association, 1996. Ambient air monitoring network annual report. Edmonton, Alberta.
- Singh, H.B., F.L. Ludwig and W.B. Johnson, 1978. Tropospheric ozone: concentrations and variabilities in clean remote atmospheres. Atmospheric Environment **12**: 2185-2196.
- Singh, H.B. and L.J. Sales, 1989. Measurements of peroxyacetyl nitrate (PAN) and peroxyproprional nitrate (PPN) at selected urban, rural and remote sites. Atmospheric Environment 23: 231-238.
- Slubik, D., 1998. Alberta Environmental Protection, Private Communication.

- Tanner, R.L., A.H. Miguel, J.B. de Andrade, J.S. Gaffacy and G.E. Strait, 1988. Atmospheric chemistry of aldehydes: enhanced peroxyacetyl nitrate formation from ethanol-fueled vehicular emissions. Environmental Science and Technology **22**:1026-1034.
- Teal, A. and R. Angle, 1997. The Alberta ambient air quality monitoring system: seeing the provincial picture. In proceedings of the Emerging Air Issues for the 21<sup>st</sup> Century: The need for Multidisciplinary Management. Air and Waste Management Association, Pittsburg, U.S.A.
- Tsani-Bazaca, W.E., S. Gloves and H. Güsten, 1988. Peroxyacetyl nitrate (PAN) concentrations in Athens, Greece. Atmospheric Environment **22**: 2283–2286.
- Tsalkani, N., P. Perros, A.L. Dutot and G. Toupanca, 1991. One year measurement of PAN in the Paris basin: effect of meteorological parameters. Atmospheric Environment, **25A**: 1941–1949.
- USEPA United States Environmental Protection Agency. 1996. Air quality criteria for ozone and related photochemical oxidants Volume I, II & III. Office of Research and Development, Washington, DC. EPA/600/P-93/004aF, July 1996.
- USEPA United States Environmental Protection Agency. 1997. National ambient air quality standards for ozone, final rule. Federal Register, 40 CFR Part 50, [AD-FRL-5725-2], RIN 2060-AE66.
- WCAS West Central Airshed Society, 1996 and 1997. Annual reports. Drayton Valley, Alberta.
- Williams, E.L., II and D. Grosjean, 1990. Southern California air quality study: peroxyacetyl nitrate. Atmospheric Environment, **24A**: 2369–2377.
- Williams, E.L., II and D. Grosjean, 1991. Peroxyproponyl nitrate at a southern California mountain forest site. Environmental Science and Technology **25**: 653–659.
- Williams, E.L., II, E. Grosjean and D. Grosjean, 1993. Ambient levels of the peroxyacetyl nitrates (PAN), PPN and MPAN in Atlanta, Georgia.
- WGAQOG, 1996. A protocol for the development of national ambient air quality objectives. Part 1. Science assessment document and derivation of the reference level(s). CEPA/FPAC Working Group on Air Quality Objectives and Guidelines, Environment Canada, Ottawa.
- WGAQOG, 1998. National ambient air quality objectives for ground-level ozone science assessment document (Draft). CEPA/FPAC Working Group on Air Quality Objectives, Environment Canada, Ottawa.

# 8.0 APPENDICES

#### APPENDIX I

Monitoring methods and air quality and precipitation quality monitoring stations of Alberta Environmental Protection (1997).

# AI.1 Ozone $(O_3)$

Ozone is continuously monitored by either the chemiluminescence or ultra-violet (UV) photometry processes. The chemiluminescence process involves the reaction of  $O_3$  with ethylene, which produces light. The intensity of the light produced is proportional to the  $O_3$  concentration. The UV photometry process uses a mercury vapour lamp as a source of UV radiation, which is absorbed by  $O_3$ . The amount of UV radiation absorbed is proportional to the amount of  $O_3$  in the sample.

# AI.2 Oxides of Nitrogen (NO<sub>x</sub>)

 $NO_x$  are measured continuously by the principle of chemiluminescence. In this method, the air sample is split into two pathways; one to measure NO, and the other to measure total  $NO_x$ . In the first pathway, the sample is mixed with  $O_3$  and light is produced. The amount of light is proportional to the NO concentration. In the second pathway, a catalytic converter is used to change all the  $NO_2$  to NO, and the NO is measured again. The sum of the readings from the first and second pathways is equal to the total  $NO_x$ ; the different of the readings is the  $NO_2$  concentration.

#### AI.3 Total Hydrocarbons (THC)

Hydrocarbons are monitored continuously by a hydrogen flame ionization detector. When burned, carbon-hydrogen bonds break creating ions that conduct an electric current. This current is then measured by an electrometer to give a signal proportional to the number of ions.

### **AI.4** Volatile Organic Compounds (VOCs)

VOCs are monitored using a 6L stainless steel electropolished (SUMMA®) canister. Air samples are collected by drawing air into the canister at a constant rate (10 to 15 mL/min) for a 24-hour time period. These air samples are then analyzed by GC/FID and GC/MSD systems using a cryogenic preconcentration technique to quantify concentrations of over 150 hydrocarbon species. The SUMMA canisters are evacuated and cleaned prior to installation at the monitoring sites by the Environment Canada Environmental Technology Centre in Ottawa. Analysis of the VOC samples are also conducted by Environment Canada.

# AI.5 All air quality and precipitation quality monitoring stations operated by Alberta Environmental Protection in 1997 are shown in Figure A1. This monitoring program consisted of:

- 11 continuous stations that measured hourly concentrations of air chemicals such as carbon monoxide, carbon dioxide, dust and smoke (the coefficient of haze), hydrogen sulphide, oxides of nitrogen (including nitric oxide and nitrogen dioxide), ozone, sulphur dioxide, total hydrocarbons and inhalable particulates;
- 8 intermittent stations that collected 24-hour measurements of suspended particulates, polycyclic aromatic hydrocarbons, sulphates and nitrates;
- 2 static networks that monitored monthly loadings of total sulphation and hydrogen sulphide, and
- 11 precipitation quality stations that collected weekly rain and snow samples which were analyzed for pH and deposition of major cations and anions.

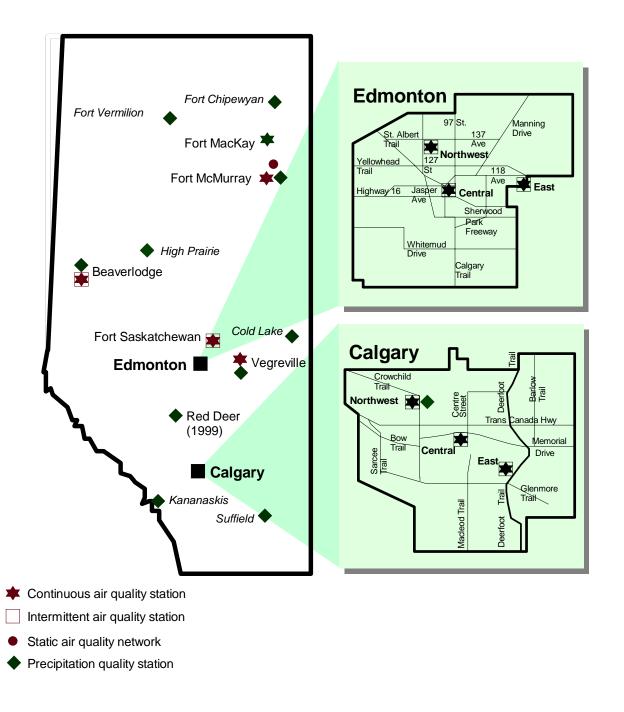


Figure A1. Alberta Environmental Protection air quality and precipitation quality monitoring stations (1997).

# **APPENDIX II**

Locations, parameters and time period of monitoring by Alberta Environmental Protection, Industry and Associations.

Table AII.1 Ozone  $(O_3)$ , nitric oxide (NO), nitrogen dioxide  $(NO_2)$ , nitrogen oxides  $(NO_x)$ , total hydrocarbons (THC) and volatile organic compounds (VOCs) monitoring by Alberta Environmental Protection.

Location	Parameter	Time Period
Decreadedes	$O_3$	1997-present
Beaverlodge	NO, NO <sub>2</sub> , NO <sub>x</sub>	1997-present
	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1976-present
Calgary Central	VOCs	1990-present
Calgary East	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1976-present
Calgary Northwest	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1976-present
Educates Control	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1976-present
Edmonton Central	VOCs	1991-present
Edmonton East	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1976-present
Edmonton East	VOCs	1990-present
Edmonton Northwest	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1976-present
E AMM	$O_3$	1984-present
Fort McMurray	NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1981-present
Fort Saskatchewan	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC	1981-present
Decret Devil	$O_3$	1993-1996
Royal Park	NO, NO <sub>2</sub> , NO <sub>x</sub>	1994-1996

Table AII.2 Short term monitoring of ozone  $(O_3)$ , nitric oxide (NO), nitrogen dioxide  $(NO_2)$ , nitrogen oxides  $(NO_x)$ , and total hydrocarbons (THC) by Alberta Environmental Protection.

Location	Parameter	Time Period
Bow Corridor	O <sub>3</sub> , NO <sub>x</sub> and THC	March 2-12, 1994
Caroline and Sundre Area	O <sub>3</sub> , NO <sub>x</sub> and THC	July 21 and 22, 1988; Spring and Summer 1997 Winter 1998
Cold Lake	O <sub>3</sub> , NO <sub>x</sub> and THC	June 1985 March 16-18, 1987
Drayton Valley, Edson and Hinton	O <sub>3</sub> , NO <sub>x</sub> and THC	May 5 and August 11, 1992
Drumheller Area	O <sub>3</sub> , NO <sub>x</sub> and THC	May 1 – June 5, 1986
East Calgary	$O_3$ , $NO_x$ and THC	March 1983 – February 1984
Exshaw	NO <sub>x</sub>	January 29 – October 31, 1993
Fort McVey	NO <sub>x</sub>	October 1983-1984; October 13-22, 1987
Fort McKay	O <sub>3</sub> , NO <sub>x</sub> and THC	Jan 19-27, 1988
Fort McMurray	O <sub>3</sub> , NO <sub>x</sub> and THC	July 1982 – January 1988; October 13-22, 1987; May 18-24,28,29, June 29, July 3,4, September 24-28, 1990; October 1991- June 1992
Fort Saskatchewan	O <sub>3</sub> , NO <sub>x</sub> and THC	November 1981 - December 1985; July 26 and 27, 1990
Goldbar, Edmonton	O <sub>3</sub> , NO <sub>x</sub> and THC	April-June 1981
Grande Prairie	O <sub>3</sub> , NO <sub>x</sub> and THC	June 7 and 9, 1994
Joffre Area	O <sub>3</sub> , NO <sub>x</sub> and THC	April – June 1980
Little Smoky Area	O <sub>3</sub> , NO <sub>x</sub> and THC	April –May 1983
Lloydminster	O <sub>3</sub> , NO <sub>x</sub> and THC	March 16-18 1987 June 14-16, 1994
Medicine Hat	O <sub>3</sub> , NO <sub>x</sub> and THC	November 1981 –March 1982
Nose Creek, Calgary	O <sub>3</sub> , NO <sub>x</sub> and THC	August 1980 – February 1981
Pincher Creek	O <sub>3</sub> , NO <sub>x</sub> and THC	March-May 1980; January-March 1981; January 30, 31, 1986
Primrose District	O <sub>3</sub> , NO <sub>x</sub> and THC	November – December 1981
Rainbow Valley Area	O <sub>3</sub> , NO <sub>x</sub> and THC	January – March 1981
Red Deer	O <sub>3</sub> , NO <sub>x</sub> and THC	November-March 1980; March 1981; July 1982; April 20, July 21, October 27, 1994; March 2, 1995; Winter 1996
Sherwood Park	O <sub>3</sub> , NO <sub>x</sub> and THC	Summer, Fall and Winter 1996; Spring, Summer and Fall 1997
South Calgary	O <sub>3</sub> , NO <sub>x</sub> and THC	March 1983 – February 1984
South East Calgary	O <sub>3</sub> , NO <sub>x</sub> and THC	April-October 1981 March- May 1984
St. Albert	O <sub>3</sub> , NO <sub>x</sub> and THC	April – August 1984 February 27,28 and March 7,8,11,12, 1987 January 29-February 1, 1991
Strathcona Industrial	O <sub>3</sub> , NO <sub>x</sub> and THC	Fall and Winter 1996 Spring, Summer and Fall 1997
Turner Valley	O <sub>3</sub> , NO <sub>x</sub> and THC	December 1979 - January 1980
West Central Alberta	O <sub>3</sub> , NO <sub>x</sub> and THC	September 21-29, 1993

Table AII.3 Ozone, nitrogen oxides, total hydrocarbons and volatile organic compounds monitoring by Industries during 1998.\*

Location	Facility	Parameter(s)	Number of Stations
Battle River	Alberta Power Ltd.	$NO_x$	2
Boyle	Alberta-Pacific Forest Industries	NO <sub>x</sub>	1
Caroline	Shell Canada	O <sub>3</sub> , NO <sub>x</sub> , THC, VOC	1
Carseland	Orica Canada Inc.	NO <sub>x</sub>	1
Carseland	Agrium Products Ltd.	NO <sub>x</sub>	1
Cold Lake	Imperial Oil Resources	NO <sub>x</sub> , THC	2
Drayton Valley	Weyerhaeuser Canada Ltd.	VOC	1
Edmonton	University of Alberta	NO <sub>x</sub>	1
Edmonton Clover Bar	Celanese Canada Ltd.	VOC	4
Edson OSB Plant	Weyerhaeuser Canada Ltd.	VOC	1
Fort McMurray	Suncor	THC	5
Fort McMurray	Syncrude Canada	NO <sub>x</sub> , THC	5
Fort Saskatchewan	Dow Chemical Canada	NO <sub>x</sub> , THC, VOC	2
Fort Saskatchewan	Sherritt International	$NO_x$	1
Fort Saskatchewan	Geon Canada Inc.	VOC	4
Genesee	Edmonton Power	NO <sub>x</sub>	1
H.R. Milner	Alberta Power Ltd.	NO <sub>x</sub>	1
Joffre	Nova Chemicals Ltd.	$NO_x$ , $C_2H_4$	1
Joffre	Agrium Products Ltd.	NO <sub>x</sub>	1
Keephills	TransAlta Utilities	NO <sub>x</sub>	1
May-Leming	Imperial Oil Resources	NO <sub>x</sub> , THC	1
Medicine Hat	City of Medicine Hat	NO <sub>x</sub>	1
Redwater	Agrium Products Inc.	NO <sub>x</sub>	1
Redwater	Sherritt International	NO <sub>x</sub>	1
Sheerness	Alberta Power Ltd.	NO <sub>x</sub>	1
Sundance	TransAlta Utilities	NO <sub>x</sub>	3
Wabamun	TransAlta Utilities	$NO_x$	2

<sup>\*</sup> These continuous and/or intermittent stations operate throughout the year.

Table AII.4 Ozone, nitrogen oxides, total hydrocarbons and volatile organic compounds monitoring by Associations during 1998.

Association	Station Location	Parameter(s)
	Clover Bar	NO, NO <sub>2</sub> , NO <sub>x</sub>
Strathagna Industrial Association (SIA)	Sherwood Park	THC
Strathcona Industrial Association (SIA)	Beverly	THC
	Forest Heights	NO, NO <sub>2</sub> , NO <sub>x</sub>
	Violet Grove	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC, VOC
	Hightower Ridge	$O_3$
West Central Airshed Society	Tomahawk	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub>
	Steeper	$O_3$
	Carrot Creek	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub>
	Fort McKay	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC, VOC
	Athabasca Valley	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC, VOC
Wood Buffalo Environmental Association	Patricia McInnes	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub> , THC, VOC
	Fort Chipewyan	O <sub>3</sub> , NO, NO <sub>2</sub> , NO <sub>x</sub>
	Buffalo View Point	THC
	Mannix	THC
	Mildred Lake	THC

Table AII.5 Station, type and elevation (m ASL) of monitoring stations whose data is referenced in this report.

Station	Туре	Elevation
Fort McMurray	Other – Influenced	260
Bitumont	Rural – Background	350
Fort Saskatchewan	Other – Industrial	625
Royal Park	Rural – Influenced	656
Edmonton Central	Urban – Downtown	663
Edmonton East	Urban – Industrial	679
Edmonton Northwest	Urban – Residential	679
Ellerslie	Other – Influenced	680
Esther	Rural – Background	707
Beaverlodge	Rural – Influenced	760
Tomahawk	Rural – Influenced	793
Birch Mountain	Rural – Background	850
Calgary East	Urban – Industrial	1028
Calgary Central	Urban – Downtown	1051
Crossfield East	Other – Influenced	1098
Calgary Northwest	Urban – Residential	1106
Crossfield West	Other – Influenced	1158
Hightower Ridge	Rural – Background	1524
Fortess Mountain	Rural – Background	2103

A DDENIDIY III	
APPENDIX III	
Monitoring results for NO, $NO_2$ , total hydrocarbons and volatile organic compounds (ppb for Calgary Central (June and December) and Edmonton Central (June) in 1997. Ozone data for Calgary Central and Edmonton Central for December, 1997 is also given.	)
Ground-Level Ozone in Alberta	Δ13

Table AIII.1 Hourly mean nitric oxide data (ppb) for Calgary Central for June 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	1	1	1	0	0	0	1	1	0	1	1	1	1	1	1	1	1	1	0	1	1	2	1	1
2	1	0	0	0	1	9	38	21	5	4	3	3	2	2	4	6	8	4	5	3	4	6	3	1
3	1	0	0	2	6	16	55	54	62	24	7	4	4	4	4	6	7	5	2	3	2	4	4	2
4	0	2	1	0	1	6	21	37	90	75	58	48	22	18	29	37	26	7	4	4	9	5	7	10
5	89	44	22	34	23	38	62	61	58	83	49	30	16	11	6	25	30	17	7	8	6	5	2	1
6	0	1	0	0	2	9	44	57	21	17	16	14	15	10	17	20	19	11	8	2	1	6	6	30
7	36	9	6	2	3	6	11	26	17	5	5	3	5	3	4	4	2	2	2	1	2	2	2	1
8	1	1	1	0	2	4	15	14	10	3	1	1	1	1	2	1	2	1	1	0	1	2	2	1
9	0	1	0	0	1	4	11	18	12	15	11	5	4	2	3	8	4	2	0	0	2	1	1	0
10	1	0	0	2	10	14	34	43	52	34	14	4	5	6	6	13	11	5	1	1	3	4	3	1
11	1	1	0	1	18	22	47	37	14	9	8	8	19	19	22	41	50	23	7	6	6	4	1	1
12	2	1	0	1	1	5	35	20	20	21	15	18	11	6	5	12	11	14	17	8	6	8	7	3
13	5	2	2	2	4	23	34	25	17	6	8	8	4	2	3	7	5	0	1	2	5	5	3	3
14	2	0	0	1	1	1	1	3	4	3	3	4	6	4	3	3	2	3	2	1	0	1	2	1
15	0	6	3	2	2	4	7	9	4	2	1	3	4	2	2	2	0	1	1	2	2	2	1	0
16	2	1	1	0	0	2	9	9	4	7	4	4	3	5	20	16	16	4	1	1	1	3	4	5
17	2	23	10	2	3	30	45	84	64	38	14	9	11	7	10	13	16	16	8	3	5	5	8	4
18	1	1	0	0	0	2	13	10	6	7	7	11	7	10	8	16	12	3	2	1	1	2	1	1
19	2	1	2	1	3	11	31	32	8	9	8	4	7	5	9	11	13	6	4	4	6	9	8	5
20	2	1	2	3	5	33	64	36	18	24	10	11	12	10	11	21	13	10	5	8	5	8	4	1
21	2	1	1	1	1	0	4	4	5	5	4	6	7	6	8	5	11	6	5	2	2	2	2	2
22	1	1	1	0	1	1	1	1	1	1	1	1	2	1	2	2	1	1	1	11	2	1	1	1
23	1	0	2	2	2	20	19	11	7	4	4	4	2	4	8	42	33	19	4	2	2	2	2	1
24	0	0	1	0	1	7	22	18	13	13	19	21	18	9	12	13	15	8	4	6	9	24	37	23
25	21	6	2	1	11	24	40	61	51	19	9	8	6	5	9	8	10	5	4	5	4	2	2	5
26	6	14	7	7	7	25	60	55	29	4	3	3	2	2	3	12	11	5	2	3	2	1	1	2
27	3	8	3	0	8	47	65	38	8	3	4	7	4	5	6	13	10	4	3	3	3	4	3	3
28	2	1	0	0	1	0	9	6	5	3	2	3	3	2	3	6	6	4	5	3	6	6	7	5
29	3	4	2	0	1	3	4	6	8	9	11	22	28	28	24	27	36	14	12	15	9	11	11	3
30	0	2	1	0	4	14	32	44	30	20	19	27	18	20	22	47	34	14	14	7	8	8	8	7

Table AIII.2 Hourly mean nitrogen dioxide data (ppb) for Calgary Central for June 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	12	13	9	5	5	8	11	12	12	14	14	12	13	13	13	14	11	14	13	13	22	19	18	18
2	16	11	12	11	18	30	41	37	26	23	20	17	13	13	18	21	24	24	31	31	37	43	27	19
3	22	15	21	23	23	24	30	32	44	44	24	21	18	18	20	26	28	29	26	28	25	32	33	24
4	21	31	23	15	18	28	34	38	47	49	47	40	31	29	35	43	40	28	24	25	29	24	23	24
5	32	26	22	22	21	20	21	22	24	26	24	27	31	28	25	42	51	43	33	28	23	18	17	12
6	10	8	9	10	13	20	25	27	22	26	25	27	29	28	36	39	38	34	36	25	31	41	46	53
7	48	38	30	22	21	22	25	29	31	24	27	23	26	24	25	25	18	21	20	24	26	29	22	17
8	15	20	17	15	17	22	25	24	28	20	14	14	12	12	14	14	17	16	18	17	22	25	23	18
9	13	8	8	9	20	29	38	44	42	40	32	24	21	17	21	30	27	20	14	13	23	23	19	13
10	13	14	12	17	25	26	30	31	40	50	44	23	25	27	35	43	41	35	24	26	38	48	45	34
11	30	22	20	22	34	34	40	43	36	31	30	31	44	46	46	50	53	46	35	35	34	28	22	17
12	25	18	13	16	18	26	44	42	39	37	33	32	30	27	31	42	37	43	44	37	31	34	33	27
13	31	27	26	23	21	30	35	34	32	29	32	35	25	22	24	31	26	17	21	25	34	35	28	27
14	18	10	8	5	6	9	14	17	18	14	17	20	23	19	16	15	13	20	25	16	18	28	34	25
15	14	26	21	15	18	18	18	20	19	15	13	18	17	13	14	13	12	16	20	23	28	29	20	21
16	23	9	4	5	7	12	21	21	22	25	20	18	17	24	37	39	40	28	16	19	23	29	28	26
17	23	38	31	26	24	33	36	38	39	32	27	20	22	20	20	25	27	31	29	18	18	22	27	25
18	14	7	4	5	10	20	34	29	24	25	26	32	28	31	24	32	28	14	13	12	15	20	19	21
19	22	16	22	21	22	30	35	34	24	25	23	16	20	17	23	26	29	21	18	18	25	29	26	19
20	14	15	16	19	17	22	27	28	25	26	21	23	23	20	20	25	21	20	16	17	17	19	16	15
21	15	14	9	6	8	9	11	12	13	12	13	14	16	15	18	16	25	23	25	22	30	23	25	23
22	22	22	19	21	13	11	12	9	8	6	11	7	10	9	12	8	10	9	13	15	21	15	16	13
23	11	11	14	16	17	28	31	29	21	16	17	16	13	16	22	36	32	31	19	16	20	21	16	11
24	12	10	7	7	8	18	24	28	26	26	31	31	26	22	26	29	31	24	20	24	28	31	29	28
25	26	22	13	11	16	18	20	23	28	29	24	24	21	19	23	24	26	21	17	20	26	20	20	29
26	28	27	28	25	23	26	29	35	31	17	16	15	13	12	17	34	30	18	13	17	17	14	16	21
27	26	32	27	14	26	38	42	41	27	17	18	23	15	16	19	27	27	20	21	24	25	24	18	17
28	16	13	11	10	14	21	23	21	19	16	13	17	20	17	20	28	23	18	16	16	21	18	17	15
29	15	14	11	11	8	12	15	15	15	16	16	19	21	22	22	25	25	19	21	21	21	23	24	16
30	11	13	11	9	20	25	30	35	30	29	27	27	22	21	22	27	26	21	24	19	22	23	23	23

Table AIII.3 Hourly mean total hydrocarbons data (ppb  $x10^2$ ) for Calgary Central for June 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
	40	40	40	40	40	40	40	20	20	20	200	200	200	20	200	200	200	20	20	20	20	20	04	24
2	18	19	19	18	18	19	19	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	21	21
3	21 20	20	20	20	21	21	21	21	20	20	20	20	20	20	20	19	19	19	20	20	20	20	20	20 21
4		21	21	21	20	22	23	23	24	24	22	22	21	21	21	21	21	21 NA	21	21	22	22	21	21
5	21 25	22 24	21 23	21 23	22 21	22 21	22 22	23 21	26 22	25 23	24 23	23 22	22 21	22 21	22 21	22 22	22 22	21	21 20	21 21	21 21	20 21	21 21	20
6	21	21	23	23	21	21	22	23	21	23	23	21	NA	21	22	22	22	21	21	20	21	21	21	23
7	24	22	21	21	21	21	21	22	22	21	22	22	21	21	21	21	21	21	21	21	21	21	22	21
8	21	21	21	21	21	22	22	21	21	21	21	21	21	20	21	21	21	21	21	21	21	22	22	23
9	22	22	22	22	22	22	22	23	23	22	22	23	22	21	21	NA	20	20	19	19	19	20	20	20
10	20	20	20	21	23	22	21	22	23	24	24	22	21	21	21	22	22	21	21	21	21	21	21	22
11	23	22	23	22	24	24	25	23	22	21	21	21	22	22	22	22	23	22	21	21	21	21	21	21
12	21	21	20	20	20	21	22	22	22	22	22	22	22	21	22	22	21	22	22	21	22	22	22	22
13	22	22	23	22	21	22	23	22	22	22	22	22	21	21	21	21	21	20	20	21	21	21	22	22
14	22	20	20	20	20	21	21	21	21	21	21	21	21	21	21	20	20	21	21	21	21	22	22	22
15	21	22	22	21	21	21	20	21	21	20	20	20	20	20	20	20	20	20	20	21	20	21	22	21
16	21	19	19	19	19	20	20	20	20	21	20	20	20	21	21	21	22	21	21	21	21	21	21	21
17	21	23	23	23	22	23	22	24	23	22	20	NA	19	18	18	18	19	19	19	18	18	18	18	18
18	18	18	17	17	18	20	21	21	20	21	21	21	21	21	21	21	21	20	20	20	20	21	21	21
19	21	21	22	21	21	21	21	21	21	21	21	20	21	20	20	21	21	20	20	20	21	21	21	21
20	21	21	21	22	21	22	22	22	21	22	21	21	21	21	21	21	21	21	21	21	21	21	21	21
21	21	21	20	20	20	20	19	20	20	20	20	20	21	22	24	25	27	28	29	29	31	31	31	29
22	29	28	28	27	27	20	20	19	19	18	18	18	18	18	18	18	18	18	18	18	18	18	18	17
23	18	18	18	17	17	21	21	20	20	20	20	20	19	19	20	21	21	20	19	19	19	19	19	19
24	19	19	19	19	19	20	21	21	21	21	21	21	21	20	21	21	21	20	20	20	20	21	22	22
25	22	21	21	20	20	20	21	22	22	21	21	22	NA											
26	NA	NA	NA	NA	NA	22	23	23	22	21	22	22	22	22	22	23	23	22	22	22	22	21	21	22
27	22	23	23	22	22	23	23	22	20	20	20	20	19	19	18	18	18	NA						
28	NA	NA	NA	NA	NA	20	20	21	20	20	20	19	19	19	19	19	19	19	18	18	18	19	19	19
29	18	18	18	18	18	21	20	21	20	20	20	20	21	20	20	20	21	21	20	20	20	20	20	20
30	20	20	19	19	19	20	20	21	20	20	21	21	20	20	21	21	21	20	20	20	20	20	20	20

Table AIII.4 Daily mean volatile organic compounds data (ppb) for Calgary Central for June and December, 1997.

VOC			June					Decembe	r	
VOCs	03	09	15	21	27	06	12	18	24	30
Propane	6	4	4	2	3	29	5	7	4	16
Butane	3	3	2	1	2	20	6	6	5	25
Isopentane	3	2	1	1	2	11	3	3	2	12
Ethane	5	4	5	4	4	26	5	8	5	14
Toluene	2	1	1	1	1	6	1	2	1	7
Ethylene	4	3	2	2	3	21	5	6	5	24
Acetylene	5	5	3	3	3	31	6	8	7	31
m & p- Xylene	1	1	0	0	0	6	1	1	1	6
2-Methlpentane	1	1	0	0	1	4	1	1	1	4
Pentane	1	1	1	0	1	5	1	1	1	4
Isobutane	1	1	0	0	1	7	2	2	2	7
Benzene	0	0	0	0	0	2	1	1	1	3
Propylene	1	1	1	1	1	6	1	2	1	7
2,2,4-Trimethylpentane	0	0	0	0	0	2	0	0	0	3
3-Methylpentane	0	0	0	0	0	2	1	1	0	2
1,2,4-Trimethylbenzene	0	0	0	0	0	2	0	0	0	2
o-Xylene	0	0	0	0	0	2	0	1	0	2
Hexane	0	0	0	0	0	2	0	0	0	2
2,3-Dimethylpentane	0	0	0	0	0	1	0	0	0	1
1-Butene/Isobutene	0	0	0	0	0	3	1	1	1	3

Table AIII.5 Hourly mean ozone data (ppb) for Calgary Central for December 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	11	9	13	20	20	13	5	1	1	1	1	3	15	24	21	9	2	1	1	3	4	3	1	1
2	1	2	6	6	6	6	4	2	2	3	3	4	6	4	8	3	1	2	3	2	1	2	6	11
3	14	16	16	14	16	15	8	4	3	5	8	7	5	4	3	2	2	3	4	2	0	0	0	1
4	1	1	0	1	1	1	1	2	3	3	3	3	3	3	2	2	1	1	1	2	3	3	3	4
5	3	4	4	3	3	2	2	1	1	2	3	3	4	3	3	2	1	1	1	1	1	1	1	1
6	2	2	1	2	3	2	3	3	4	5	5	5	6	6	5	4	2	3	4	4	4	3	4	4
7	4	4	4	5	5	6	6	5	5	4	5	5	6	5	5	4	4	4	4	4	4	4	4	3
8	4	3	3	2	2	2	2	2	3	3	3	4	4	4	3	2	3	2	2	3	3	2	2	2
9	3	6	9	8	13	17	11	4	2	3	3	4	7	8	8	5	2	2	1	2	4	5	7	5
10	9	10	9	12	13	13	9	4	2	6	8	7	10	8	7	7	4	2	4	6	7	3	3	5
11	2	8	9	23	22	26	12	13	10	18	23	16	15	21	21	20	13	15	22	19	25	23	25	30
12	28	25	19	22	9	5	2	5	7	17	21	18	14	12	12	7	4	12	11	4	9	17	5	12
13	11	12	13	18	21	18	20	21	22	11	5	4	5	4	4	3	2	2	4	3	4	4	3	2
14	3	1	1	3	5	24	13	7	14	14	23	23	33	38	37	38	33	32	34	35	35	35	36	36
15	36	36	35	29	31	24	18	10	3	5	8	15	21	19	9	3	3	14	8	10	11	3	2	1
16	2	2	2	2	2	1	2	2	2	2	2	3	3	3	3	3	2	3	3	4	3	4	3	2
17	6	11	23	28	23	18	15	10	18	24	26	21	20	19	15	12	4	2	2	3	10	5	6	9
18	11	9	6	0	0	1	2	9	7	10	11	12	15	15	20	10	3	1	2	3	6	9	1	2
19	1	1	0	0	1	1	1	2	2	2	3	4	5	5	14	10	8	3	8	10	3	2	2	1
20	2	2	1	3	5	13	6	2	1	1	3	4	5	3	7	16	4	3	13	13	22	9	9	10
21	17	23	22	23	24	21	25	24	21	25	22	19	21	16	16	17	16	13	8	10	8	13	3	1
22	1	5	5	7	3	1	1	1	2	2	3	4	6	6	3	3	5	5	7	6	13	14	22	27
23	32	35	32	34	32	30	22	7	9	10	16	17	18	18	0	0	0	7	12	13	17	18	20	18
24	18	18	17	17	20	16	12	7	3	5	7	6	6	10	7	2	1	1	9	19	19	22	21	18
25	19	20	23	21	20	21	20	19	16	17	17	16	16	14	11	10	11	6	3	2	1	1	2	11
26	16	16	20	24	26	24	19	17	15	17	15	14	11	8	26	16	21	23	16	25	30	29	31	27
27	31	28	26	31	30	27	22	23	22	19	19	24	27	26	24	20	13	9	6	5	3	3	14	12
28	10	23	19	21	28	34	32	31	30	27	25	23	24	20	21	21	17	14	6	5	5	16	11	13
29	6	1	8	21	11	6	2	1	2	1	3	1	2	4	6	9	11	13	16	16	12	11	16	22
30	15	3	6	1	0	0	0	1	1	1	2	2	3	2	1	1	2	3	3	1	1	5	15	22
31	19	22	27	28	20	18	2	1	2	2	2	5	5	2	2	2	7	9	9	11	9	5	5	5

Table AIII.6 Hourly mean nitric oxide data (ppb) for Calgary Central for December 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	2	2	1	1	1	3	22	67	79	86	100	112	24	5	8	23	72	94	70	26	15	110	68	28
2	20	13	6	6	6	8	18	51	53	59	65	70	50	60	33	78	99	65	296	306	65	26	13	4
3	3	2	2	1	2	3	13	35	41	34	29	40	64	65	120	147	204	283	490	423	123	87	84	31
4	24	20	26	25	24	27	53	101	178	131	140	106	104	78	89	85	82	64	46	30	17	16	17	13
5	18	11	11	11	15	13	23	41	61	60	58	57	51	65	62	66	80	67	54	45	28	44	68	81
6	112	154	141	84	78	92	95	146	220	282	295	353	441	509	435	234	138	139	188	194	231	177	230	203
7	222	245	280	267	321	307	283	201	168	89	85	100	111	87	93	77	74	63	57	32	22	21	20	24
8	26	19	23	15	20	33	36	81	120	99	75	74	93	108	111	82	105	123	125	136	214	140	104	86
9	17	10	5	7	2	2	8	28	44	46	61	63	32	24	27	43	59	83	85	38	19	18	12	13
10	7	5	5	4	3	4	12	40	49	29	28	41	30	32	49	37	81	79	36	19	26	38	46	24
11	44	13	19	1	7	1	7	13	15	6	6	9	14	6	7	8	14	16	5	4	3	3	2	1
12	1	1	3	0	8	34	82	54	28	8	5	6	10	17	12	28	45	16	21	35	18	8	31	15
13	8	8	6	4	2	3	4	2	3	22	71	51	47	71	62	141	145	111	31	243	346	381	248	129
14	99	68	87	97	48	1	16	44	7	17	6	6	5	0	1	1	1	0	1	1	0	1	0	0
15	0	0	0	0	0	3	6	18	51	45	28	26	8	11	25	60	43	14	17	10	7	24	69	112
16	116	150	78	40	63	44	129	244	197	264	254	285	176	209	282	403	337	355	368	494	452	565	626	446
17	116	7	1	0	1	2	7	21	5	3	3	7	10	10	12	15	48	77	56	31	11	16	13	7
18	4	4	7	16	27	27	32	14	13	11	13	18	14	17	10	21	73	105	39	30	17	12	60	32
19	35	27	36	61	30	57	92	160	183	204	213	169	170	170	18	20	31	59	25	26	178	178	271	119
20	116	214	121	29	14	4	22	35	62	151	69	85	47	95	39	8	88	96	8	10	3	16	20	24
21	10	3	3	3	2	2	2	2	2	2	4	6	6	11	9	8	7	7	13	8	8	7	52	89
22	39	11	12	9	16	39	74	133	157	194	182	169	86	56	122	182	33	39	23	16	10	7	4	3
23	2	1	1	1	1	2	4	21	16	17	12	12	0	0	0	14	23	25	10	8	5	6	3	4
24	3	3	3	5	2	3	7	18	29	28	36	58	67	30	47	72	81	145	19	4	4	3	2	3
25	2	2	2	2	2	2	2	2	3	4	5	7	7	8	10	9	6	11	21	24	45	50	23	6
26	2	2	1	1	1	1	2	3	3	4	8	11	18	32	3	8	4	3	9	3	1	2	1	2
27	1	1	1	0	1	0	1	2	2	4	5	3	3	4	3	4	7	11	14	16	27	49	6	7
28	12	1	2	2	0	0	0	0	1	1	2	3	4	4	4	4	4	5	11	10	15	2	5	2
29	9	21	8	2	4	16	26	59	41	67	31	56	39	29	18	22	21	11	6	5	6	7	5	2
30	12	17	8	19	28	45	94	142	135	83	106	146	99	138	140	94	286	457	470	302	223	74	5	4
31	4	2	1	1	2	2	62	186	135	163	244	76	89	138	226	147	35	18	15	10	25	25	11	10

Table AIII.7 Hourly mean nitrogen dioxide data (ppb) for Calgary Central for December 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	25	25	23	19	16	23	36	42	42	40	41	45	37	25	28	40	48	49	46	43	42	47	42	36
2	35	33	29	29	29	30	34	38	39	39	40	41	41	46	43	50	47	41	57	56	42	38	34	28
3	25	22	22	24	23	25	35	42	43	43	40	42	44	46	51	55	64	66	72	64	47	44	42	39
4	38	36	37	35	36	35	37	39	47	33	34	32	29	25	26	25	22	20	20	20	18	17	18	17
5	18	16	16	17	16	17	19	23	23	24	24	23	23	25	24	24	25	24	24	23	22	23	24	24
6	26	31	26	22	23	24	26	32	45	57	60	72	90	108	115	64	33	31	35	34	37	35	39	38
7	39	42	42	44	55	53	53	41	40	27	26	31	35	29	31	28	26	25	25	21	20	21	20	20
8	20	20	20	19	19	20	21	24	27	25	25	25	27	30	29	25	27	27	26	28	31	27	27	34
9	35	32	29	31	24	21	30	39	41	41	42	42	40	39	39	42	44	45	44	41	38	37	34	35
10	31	29	30	28	25	26	33	42	42	39	38	41	40	42	44	46	51	51	45	41	40	44	44	41
11	45	37	37	22	24	19	36	38	42	33	27	36	38	30	29	31	39	37	28	30	22	26	24	17
12	17	20	28	19	38	48	54	51	47	35	30	30	36	40	38	43	48	40	41	47	40	29	44	37
13	38	36	32	30	24	27	26	22	23	39	50	48	46	50	49	52	54	51	45	56	61	64	54	48
14	47	43	43	42	41	20	34	44	34	37	27	25	18	11	11	11	15	17	12	10	10	9	8	8
15	8	7	8	11	10	21	30	41	49	47	44	38	30	33	43	49	48	37	41	37	35	43	48	48
16	49	58	55	49	52	49	55	65	57	62	61	68	62	62	65	74	71	68	68	76	68	77	81	68
17	37	23	10	9	16	21	30	41	28	19	17	24	28	28	33	36	44	46	43	42	32	34	32	28
18	26	25	31	37	37	36	39	31	35	39	39	39	36	37	31	45	56	59	49	47	44	39	46	39
19	38	36	37	39	38	41	44	50	53	56	64	66	71	67	39	41	44	49	41	38	57	58	66	53
20	51	63	52	43	37	26	36	42	46	51	43	45	43	48	44	33	49	52	34	35	23	40	41	39
21	28	19	22	19	15	18	14	16	20	17	20	25	24	31	31	30	31	33	37	34	35	31	42	44
22	40	33	34	32	37	40	44	46	48	53	58	61	59	51	55	59	46	44	41	40	32	31	23	18
23	11	8	10	8	9	11	22	40	38	37	32	31	0	0	0	34	40	40	34	32	26	26	22	25
24	23	23	23	27	21	24	29	36	39	37	37	41	44	40	43	46	46	49	35	24	24	20	20	22
25	21	20	17	18	19	18	19	20	23	23	25	27	27	30	33	34	32	36	39	40	42	40	38	29
26	23	23	18	15	15	16	22	25	28	26	29	34	38	44	24	35	32	28	36	24	17	17	14	16
27	10	11	12	7	7	11	16	16	17	21	23	20	18	19	20	25	32	36	38	40	42	43	32	33
28	36	20	27	23	12	7	9	10	11	15	18	21	21	24	23	22	24	27	35	35	35	22	29	28
29	36	41	30	15	25	30	34	38	35	40	37	38	38	36	34	35	39	36	31	30	34	32	29	22
30	30	43	39	42	41	39	42	43	41	39	42	49	43	54	54	46	55	64	67	60	55	42	26	21
31	23	18	11	8	20	22	45	55	49	51	61	49	53	63	69	60	45	40	38	33	35	33	21	16

Table AIII.8 Hourly mean total hydrocarbon data (ppb x10²) for Calgary Central for December 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	24	24	24	22	22	23	24	25	25	25	26	27	24	23	22	23	25	26	25	24	23	26	25	24
2	23	23	22	21	21	21	21	22	22	23	23	23	23	23	22	24	25	24	31	30	24	22	21	21
3	21	21	21	22	21	21	22	23	23	23	23	24	24	25	27	28	30	33	40	38	28	27	26	25
4	25	24	25	22	22	22	23	24	27	33	37	36	35	31	0	30	28	26	25	24	23	22	22	22
5	22	22	22	24	24	24	24	26	26	27	28	27	27	26	26	25	25	25	24	23	23	23	24	25
6	26	27	27	26	27	27	27	29	32	37	39	40	43	47	52	42	32	29	31	31	33	31	33	33
7	34	35	35	34	37	39	42	42	35	30	29	29	30	28	27	26	27	26	26	25	24	23	24	25
8	25	24	24	24	24	25	25	26	28	28	27	28	28	29	28	28	29	30	30	31	32	30	28	26
9	23	23	22	22	21	21	22	23	24	24	25	24	24	23	23	24	24	25	25	24	23	23	23	23
10	23	23	23	21	21	21	21	22	23	22	23	23	23	23	24	24	24	25	23	23	23	23	24	23
11	24	22	22	21	21	20	21	21	21	21	21	21	22	21	20	21	21	21	20	20	20	20	20	20
12	20	20	21	21	22	24	26	24	22	21	22	22	22	22	22	22	23	22	22	23	22	21	22	21
13	21	21	21	21	22	22	22	22	22	23	25	24	24	25	25	27	27	26	23	28	34	36	30	26
14	25	24	24	25	23	20	22	23	21	21	20	20	19	19	19	19	19	19	19	19	19	19	19	19
15	18	18	18	19	19	20	20	21	22	23	22	22	21	NA	21	22	21	20	21	20	20	21	23	24
16	25	27	25	24	25	26	28	31	29	30	30	32	28	28	30	35	34	36	36	40	38	43	45	40
17	27	22	21	21	21	21	22	22	21	21	21	21	23	22	22	22	23	24	23	23	22	23	24	23
18	24	23	24	24	24	23	23	23	24	23	23	23	23	23	22	24	26	27	25	24	24	23	24	23
19	24	23	24	27	27	33	35	38	40	37	36	32	30	29	22	22	22	23	22	22	26	27	32	26
20	25	30	28	23	21	21	21	22	22	24	22	22	21	23	22	20	24	24	20	20	19	20	20	21
21	20	19	20	20	20	20	20	20	21	20	21	21	21	21	21	21	21	22	23	22	23	22	24	25
22	24	23	23	22	21	21	22	23	25	26	26	26	24	22	24	27	21	21	20	20	19	19	19	19
23	18	18	18	19	19	20	20	21	21	21	21	21	21	21	21	21	22	22	22	22	21	22	22	22
24	22	22	22	21	21	21	21	21	22	22	23	24	24	23	23	25	25	26	22	21	21	21	21	20
25	20	20	20	21	21	21	21	21	21	21	21	21	21	21	22	22	22	22	22	22	23	23	22	21
26	21	21	21	20	20	20	21	21	20	20	21	21	21	22	20	20	20	20	19	19	19	19	18	19
27	18	19	19	20	20	21	21	21	21	22	22	22	22	22	22	22	23	23	23	23	24	24	23	23
28	23	22	22	21	21	20	20	20	20	20	21	21	21	21	21	21	21	21	21	22	22	21	21	21
29	22	23	21	20	21	22	22	22	22	24	23	24	24	23	23	22	22	22	22	22	23	23	23	22
30	23	24	24	24	24	24	25	25	25	24	25	27	39	27	27	25	31	38	39	34	31	25	21	20
31	20	20	19	20	20	20	23	28	25	26	30	24	25	27	30	28	22	20	20	20	20	22	21	21

Table AIII.9 Hourly mean nitric oxide data (ppb) for Edmonton Central for June 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	4	5	5	3	1	1	2	8	5	3	3	4	3	4	4	2	3	4	4	3	5	4	12	9
2	1	1	2	1	4	13	34	50	17	24	13	18	10	14	10	14	11	11	7	3	4	3	5	3
3	2	1	1	7	14	21	39	48	14	10	8	7	10	8	8	11	14	6	3	1	2	1	2	1
4	1	1	1	1	5	14	16	35	32	25	21	23	44	46	51	52	41	38	15	5	1	0	0	0
5	1	1	2	0	6	6	24	55	41	23	14	17	16	15	21	25	20	11	9	5	9	16	27	31
6	34	20	2	0	4	16	37	45	24	17	20	29	18	18	15	14	8	9	2	1	3	3	4	15
7	11	3	2	1	1	2	3	6	7	5	7	7	9	3	20	166	81	41	30	3	2	1	9	0
8	0	0	0	0	20	0	18	2	3	6	16	14	6	4	3	3	4	4	4	2	4	3	10	1
9	3	29	10	12	12	27	47	38	28	12	9	6	6	7	11	15	9	14	2	3	4	5	26	26
10	1	0	0	1	5	13	32	26	12	14	7	8	8	5	9	11	12	13	7	6	6	14	27	21
11	2	1	1	3	12	11	46	37	21	9	8	6	20	8	36	23	17	24	21	9	4	5	25	5
12	0	0	0	1	8	19	23	27	16	16	21	25	21	9	9	11	12	5	12	8	13	21	15	1
13	1	2	1	1	1	7	14	16	12	9	10	14	13	10	13	16	13	6	7	5	4	5	5	5
14	3	5	3	1	3	2	4	9	5	5	5	6	6	5	5	5	5	3	4	4	3	4	9	5
15	7	6	4	3	5	2	7	4	2	4	4	4	4	3	4	5	4	4	1	2	1	1	2	5
16	2	1	1	0	2	4	15	28	17	13	10	13	10	10	9	12	11	7	3	2	1	2	2	3
17	3	11	3	16	31	30	73	51	16	13	17	14	7	8	14	16	10	4	10	6	5	4	1	1
18	1	1	1	1	1	2	10	20	12	13	10	10	9	8	8	13	13	10	7	4	6	3	3	1
19	1	1	1	1	1	4	10	13	8	9	10	10	11	15	9	13	12	7	5	5	4	4	3	3
20	2	1	1	2	2	4	11	22	19	21	23	20	24	19	25	28	41	18	22	9	11	18	18	16
21	9	5	6	2	3	6	5	9	6	29	12	14	23	17	17	13	15	23	10	6	15	12	18	24
22	6	6	4	3	6	5	6	6	5	7	10	13	16	6	7	12	15	24	4	5	5	3	18	1
23	2	2	2	8	4	23	52	38	12	11	10	10	12	15	17	15	14	10	8	3	2	4	3	6
24	2	1	0	0	2	8	19	24	15	14	15	12	15	10	11	20	20	14	10	7	6	4	5	3
25	2	1	4	2	2	12	29	49	38	29	24	11	8	9	8	13	11	6	6	3	8	6	5	2
26	2	2	2	2	2	9	19	19	18	16	10	8	5	7	15	14	10	6	4	1	4	6	7	2
27	NA	NA	NA	NA	3	7	17	23	16	14	15	15	15	17	16	18	13	9	7	7	7	17	25	12
28	13	NA	NA	NA	4	5	6	7	16	24	12	13	10	7	8	2	NA	NA	NA	NA	NA	14	27	36
29	NA	NA	NA	NA	NA	NA	NA	NA	NA															
30	NA	NA	NA	NA	NA	NA	NA	NA	NA															

Table AIII.10 Hourly mean nitrogen dioxide data (ppb) for Edmonton Central for June 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	16	15	18	8	5	8	9	18	12	8	7	7	5	6	7	5	6	8	10	11	20	28	33	20
2	7	5	10	8	16	22	29	32	21	14	14	14	13	13	13	18	14	17	13	9	16	15	24	22
3	13	10	13	20	25	28	31	30	24	18	16	15	17	16	15	21	23	13	24	11	30	11	11	9
4	5	5	4	6	13	26	28	34	32	29	28	27	35	37	38	34	32	29	22	18	11	10	8	5
5	4	5	11	6	17	19	19	24	24	20	21	20	16	17	17	18	19	13	13	15	21	26	24	25
6	24	21	15	9	17	19	20	23	19	15	19	24	23	21	24	25	22	20	13	13	24	22	24	30
7	24	18	12	8	11	13	14	16	18	14	17	13	13	32	11	108	98	43	52	9	15	6	6	0
8	NA	NA	NA	NA	8	7	29	11	11	13	18	14	10	7	6	6	6	7	9	8	10	18	22	21
9	23	33	23	22	21	22	23	24	27	15	12	10	11	12	13	19	13	30	46	15	22	26	35	20
10	7	6	10	9	15	24	36	29	22	21	14	18	19	14	23	25	26	26	19	21	22	37	32	30
11	25	23	15	23	24	21	32	33	29	19	18	16	34	22	42	36	31	31	33	24	20	25	30	15
12	9	8	8	12	16	18	23	23	18	22	26	29	25	20	21	24	28	19	31	34	37	36	24	10
13	10	12	8	10	6	16	13	15	17	15	14	20	19	18	18	21	17	14	16	15	16	16	10	11
14	7	11	9	6	6	7	9	13	9	8	9	8	7	8	8	9	9	8	8	12	15	22	25	21
15	22	20	15	11	17	8	13	7	4	4	4	5	5	4	5	5	5	5	5	10	14	14	10	11
16	12	6	5	3	7	8	13	16	14	13	11	14	12	11	11	16	13	12	9	11	13	20	20	18
17	20	28	25	25	23	21	26	29	21	18	20	22	15	16	18	22	20	12	14	14	19	19	10	7
18	8	6	5	7	6	10	21	24	18	15	12	11	9	9	10	13	20	17	12	10	12	15	13	8
19	6	6	7	5	6	6	11	10	8	7	8	6	6	12	7	10	8	7	6	6	5	5	5	4
20	4	3	3	3	4	6	10	10	12	12	10	10	13	11	15	17	20	12	15	12	12	16	15	14
21	9	8	9	6	6	10	10	9	8	17	10	13	17	13	14	11	16	19	13	13	19	18	15	15
22	11	10	10	10	9	9	9	7	8	9	12	13	12	10	20	24	23	31	21	21	22	17	30	12
23	13	15	10	21	16	22	29	23	12	11	12	11	17	20	18	19	21	19	14	12	10	13	10	12
24	9	6	6	5	6	9	11	12	10	11	11	12	11	12	14	16	20	22	23	15	15	17	19	13
25	9	6	8	6	10	13	17	20	24	20	15	16	12	14	13	15	18	12	14	13	24	20	11	8
26	7	8	9	14	11	20	24	25	27	24	19	13	15	17	21	19	14	10	13	11	18	25	28	18
27	13	9	7	4	9	13	18	21	16	15	15	16	14	11	14	13	11	9	6	7	9	13	18	16
28	17	NA	NA	NA	7	16	8	11	15	18	14	11	5	4	5	2	NA	NA	NA	NA	NA	11	31	19
29	NA	NA	NA	NA	NA	NA	NA	NA	NA															
30	NA	NA	NA	NA	NA	NA	NA	NA	NA															

Table AIII.11 Hourly mean total hydrocarbon data (ppb x10²) for Edmonton Central for June 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	19	19	20	19	19	19	19	20	19	19	19	19	19	19	19	19	19	19	19	19	21	22	24	22
2	20	21	21	21	21	20	22	24	21	20	20	21	21	20	20	21	20	19	20	20	21	21	21	21
3	21	21	21	22	24	24	24	24	23	21	21	21	20	20	20	20	20	19	20	20	20	20	20	20
4	21	20	20	19	21	21	21	22	23	22	22	21	22	24	23	23	22	22	20	19	19	19	19	19
5	19	19	19	19	20	21	22	24	24	24	22	22	21	20	20	21	21	19	19	19	20	21	23	23
6	25	23	22	21	22	23	24	24	23	22	22	22	21	21	21	21	21	20	20	21	22	22	22	24
7	23	21	20	20	20	21	21	21	21	20	20	20	20	20	20	20	20	19	20	21	21	22	21	21
8	21	21	21	21	21	21	21	21	21	21	22	21	19	19	19	19	19	18	19	19	20	20	21	21
9	22	26	24	24	25	25	26	24	23	21	21	21	NA	15	15	16	15	14	15	15	NA	20	21	20
10	19	18	19	18	20	21	25	22	21	20	19	20	20	19	20	20	20	19	19	20	21	22	21	22
11	23	24	23	25	25	23	26	24	22	20	20	19	20	20	22	21	20	20	20	20	20	20	22	21
12	19	19	19	21	20	20	21	22	21	21	24	21	20	20	20	20	20	20	20	20	22	22	21	20
13	20	20	20	21	19	20	21	21	21	21	21	20	20	19	19	19	19	18	19	19	19	19	18	18
14	18	18	18	18	18	18	18	19	18	18	18	18	18	18	18	18	18	17	18	19	19	20	21	21
15	21	21	20	20	19	19	19	18	18	18	18	18	18	18	17	17	17	17	18	18	19	19	19	18
16	17	17	17	17	18	18	19	20	19	19	19	19	19	19	19	19	19	18	18	19	19	19	20	20
17	21	24	25	25	24	25	27	27	24	22	21	20	19	19	19	20	19	18	19	19	19	20	19	19
18	19	18	17	17	18	18	19	19	19	19	19	19	18	18	18	19	19	18	18	18	19	19	19	18
19	18	18	18	19	18	18	18	18	18	18	18	18	19	19	18	19	19	18	18	18	18	18	18	18
20	17	17	17	17	18	18	18	19	19	19	19	19	20	19	19	20	21	19	19	18	19	19	19	20
21	19	19	19	18	18	18	18	18	19	19	19	19	19	19	19	19	19	19	19	19	20	21	21	21
22	20	20	19	20	20	20	20	19	19	20	20	20	19	19	19	21	20	21	19	19	20	20	21	19
23	19	19	20	20	20	21	23	22	20	19	19	19	19	20	20	20	20	19	18	18	18	19	19	18
24	18	19	19	19	18	19	19	20	19	19	19	19	19	19	19	19	19	21	21	21	18	23	20	20
25	20	19	21	22	20	20	22	23	23	22	20	20	20	20	19	20	19	18	19	19	20	19	18	17
26	17	18	22	22	22	21	21	20	20	21	19	19	19	20	18	19	18	17	19	19	21	21	24	21
27	21	21	22	20	21	21	22	21	21	21	21	20	19	19	19	19	19	17	18	19	19	19	19	20
28	22	24	23	22	21	21	21	20	22	19	18	18	18	18	18	18	18	17	18	18	18	19	20	20
29	25	25	29	25	34	24	22	21	19	18	19	19	19	19	18	19	19	19	19	19	19	19	21	22
30	21	21	27	26	23	24	23	22	20	20	20	19	19	19	19	19	19	18	19	18	18	18	19	19

Table AIII.12 Daily mean volatile organic compounds data (ppb) for Edmonton Central for June and December, 1997.

VOCs			June					Decembe	r	
	03	09	15	21	27	06	12	18	24	30
Propane	4	7	2	4	3	7	12	5	5	11
Butane	2	4	2	2	2	5	10	5	5	7
Isopentane	2	4	1	2	2	3	5	3	2	3
Ethane	7	9	3	2	5	8	15	6	7	13
Toluene	1	1	0	1	1	1	2	2	1	1
Ethylene	3	6	2	5	3	4	8	6	3	6
Acetylene	4	7	3	4	4	0	0	0	0	0
m & p- Xylene	1	1	0	1	1	1	2	2	1	1
2-Methlpentane	1	1	1	1	1	1	1	1	1	1
Pentane	1	2	1	1	1	1	3	1	1	2
Isobutane	1	1	1	1	1	2	3	1	2	2
Benzene	0	1	0	0	0	1	1	1	0	1
Propylene	1	1	0	1	1	1	2	2	1	2
2,2,4-Trimethylpentane	0	0	0	0	0	0	0	0	0	0
3-Methylpentane	0	1	0	0	0	0	1	1	0	1
1,2,4-Trimethylbenzene	0	0	0	0	0	0	1	1	0	0
o-Xylene	0	0	0	0	0	0	1	1	0	0
Hexane	0	1	0	0	0	0	1	1	0	1
2,3-Dimethylpentane	0	0	0	0	0	0	0	0	0	0
1-Butene/Isobutene	0	1	0	0	0	0	1	1	0	1

A26

Table AIII.13 Hourly mean ozone data (ppb) for Edmonton Central for December 1997.

Hour Date	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
1	11	16	18	18	24	22	15	6	4	5	6	12	16	16	17	13	6	5	4	3	11	4	1	2
2	5	6	7	7	10	9	6	4	4	4	5	6	7	5	5	4	4	4	3	2	2	3	3	2
3	3	3	3	3	3	3	3	4	4	4	4	5	5	4	4	5	6	5	3	4	2	2	3	4
4	3	2	5	7	8	10	8	7	5	7	9	9	11	10	8	5	4	3	4	5	5	6	7	6
5	5	6	7	5	8	9	9	5	4	5	6	7	8	8	6	6	5	3	2	2	4	5	6	6
6	6	9	10	10	9	11	9	7	4	3	4	4	5	6	5	3	3	2	3	3	3	3	3	4
7	4	3	3	3	8	10	11	12	13	13	13	14	13	12	12	11	10	8	5	7	13	14	15	13
8	14	15	14	17	17	12	12	6	6	7	7	8	9	10	8	5	3	3	2	2	2	2	1	1
9	1	1	1	1	3	3	3	4	4	4	4	5	6	6	8	5	5	4	4	5	5	5	5	7
10	9	11	12	14	15	17	17	6	4	4	7	8	12	13	15	10	5	8	8	8	7	6	12	13
11	20	21	24	22	19	14	12	7	4	4	5	4	6	8	6	4	4	4	10	10	5	7	13	17
12	20	18	20	23	23	22	14	6	6	12	8	9	6	8	9	4	4	3	3	2	3	4	6	6
13	6	11	18	19	25	30	30	26	23	13	13	10	10	7	9	10	11	9	11	4	4	7	12	10
14	9	10	6	5	6	4	4	6	20	22	17	15	13	11	16	31	35	35	35	28	25	21	14	17
15	25	28	27	19	17	29	21	19	8	13	20	21	23	25	16	13	8	5	3	2	4	12	15	18
16	16	13	8	5	5	4	4	3	3	4	5	6	6	5	3	3	3	2	2	2	2	2	4	6
17	2	3	5	15	19	13	9	4	3	3	6	6	4	14	19	12	6	11	22	11	9	12	9	8
18	11	16	23	24	20	17	11	6	6	8	11	13	17	19	19	15	4	4	3	3	4	6	11	8
19	4	6	6	2	4	6	5	4	3	4	5	5	5	4	3	3	4	3	3	2	3	3	3	3
20	3	3	3	3	2	2	3	3	3	3	4	8	4	4	4	3	3	3	3	2	2	3	3	3
21	6	10	13	11	15	20	19	23	22	27	31	31	29	28	26	28	27	26	25	23	21	18	22	23
22	17	27	25	27	25	23	20	12	4	4	10	12	9	7	7	5	4	4	2	2	2	4	4	5
23	7	9	12	11	20	19	18	10	9	13	15	16	17	22	23	17	8	12	20	24	32	25	20	13
24	24	24	24	22	22	20	14	8	3	8	13	14	15	17	17	18	18	21	22	19	20	20	24	26
25	30	29	22	16	13	19	20	28	32	31	34	35	36	37	33	30	25	19	19	17	18	21	19	14
26	18	24	28	25	28	24	22	20	19	16	13	10	8	9	4	2	2	2	1	2	2	2	3	2
27	7	21	25	24	35	34	12	32	26	17	27	31	21	24	26	22	17	17	16	12	9	15	16	17
28	20	15	20	19	23	29	30	28	27	27	25	24	29	32	25	21	23	22	18	17	17	17	20	20
29	20	19	18	21	25	33	31	22	13	24	21	23	34	33	32	29	19	16	5	8	17	19	21	25
30	21	23	21	18	21	20	12	7	3	2	3	3	3	3	8	3	2	2	1	1	1	4	7	11
31	11	8	5	5	14	12	11	3	4	3	2	3	4	4	5	11	9	10	13	16	17	21	22	23

	APPENDIX IV
Summary and comparison of peroxya and rural measurements from other l	acetyl nitrate measurements for Alberta with urban locations.

A28

Table AIV.1 Summary of measurements of peroxyacetyl nitrate and peroxypropionyl nitrate in urban areas.\*

Site	Month/Year	Number of Days Sampled	PAN Concentration (ppb) Average/Mean	Max	PPN Concentration (ppb) Average/Mean	Max	Reference
Anaheim, CA	6-12/1987	14	NA	19	NA	NA	Williams and Grosjean (1990)
Athens, Greece	2-11/1985	113	NA	3.7	NA	NA	Tsani-Bazaca et al. (1988)
Atlanta, GA	7, 8/1992	36	0.71	2.9	0.14	0.37	Williams et al. (1993)
Azusa, Ca	6-9/1987	11	NA	13	NA	NA	Williams and Grosjean (1990)
Boulder, CO	5, 6 and 8, 9/1987	12 45	0.63 0.59	2.0 3.8	0.08 0.07	0.3 0.6	Ridley et al. (1990)
Burbank, CA	6-12/1987	16	NA	19	NA	NA	Williams and Grosjean (1990)
Calgary, Alberta, Canada	7/1981 to 2/1982	213	0.14	6.6	NA	NA	Peake and Sandhu (1983)
Claremont, CA	6-9/1987	10	NA	30	NA	NA	Williams and Grosjean (1990)
Denver, CO	3/1984	9	0.64	2.0	0.02	0.09	Singh and Salas (1989)
Downey, CA	2/1984	10	1.2	6.7	0.06	0.40	Singh and Salas (1989)
Edmonton, Alberta, Canada	12/1983 to 4/1984	66		7.5	NA	NA	Peake et al. (1988)
Houston, TX	3/1984	9	0.75	7.9	0.045	0.54	Singh and Salas (1989)
Long Beach, CA	6-12/1987	16	NA	16	NA	NA	Williams and Grosjean (1990)
Los Angeles, CA	6-12/1987	16	NA	13	NA	NA	Williams and Grosjean (1990)
Palm Springs, CA	6/1989 to 6/1990	NA	1.6	7.6	NA	0.42	Grosjean and Williams (1992)
Paris, France	11/1985 to 11/1986	NA	1.1	20.5	NA	NA	Tsalkani et al. (1991)
Perrin, CA	6/1989 to 6/1990	NA	1.6	9.1	NA	0.73	Grosjean and Williams (1992)
Philadelphia, PA	4/1983	19	1.1	3.7	0.14	0.50	Singh and Salas (1989)
Rio de Janeiro Vila Isabel PUC/RJ	7/1985 7/1985	8 4	NA NA	5.4 3.3	NA NA	1.0 0.6	Tanner et al. (1988) Tanner et al. (1988)
Simcoe, Ontario, Canada	6/1980 to 3/1981	191	1.3	5.6	NA	NA	Corkum et al. (1986)
Staten Island, NY	4/1983	7	1.6	5.5	0.21	0.90	Singh and Salas (1989)
University of Calgary, Alberta, Canada	10/1980 to 8/1981	175	0.22	2.4	NA	NA	Peake and Sandhu (1983)

<sup>\*</sup> Taken from Reference USEPA, 1996 NA Not Available

**Table AIV.2** Summary of measurements of peroxyacetyl nitrate and peroxypropionyl nitrate in rural areas.\*

Site	Month/Year	Number of Days Sampled	PAN Concentration (ppb) Average/Mean	Max	PPN Concentration (ppb) Average/Mean	Max	Reference
Franklin Canyon, CA	9/1991	9	1.6	7.0	0.18	1.15	Grosjean et al. (1993)
Frijoles Mesa, NM	10/1987 to 1/1989	NA	0.26	1.9	NA	NA	Gaffney et al. (1993)
Kananaskis Valley, Alberta, Canada	9/1979, 4/1982, 6-8/1982	NA	≈0.5	2.3	NA	NA	Peake et al. (1983)
Niwot Ridge, CO	7/1984 6, 7/1984 8, 9/1984 6, 7/1987	16 23 21 46	0.28 ≈0.25 ≈0.25 0.81 <sup>a</sup> 0.12 <sup>b</sup>	2.3 NA NA 3.2	0.016 NA NA 0.08 <sup>a</sup> 0.01 <sup>b</sup>	0.17 NA NA 0.45	Singh and Salas (1989) Fahey et al. (1986) Fahey et al. (1986) Ridley et al. (1990)
Point Arena, CA	1/1984 Spring 1985	14 NA	0.12 0.05	1.1 NA	0.005 NA	0.07 NA	Singh and Salas (1989) Ridley (1991)
Scotia, PA	Summer 1986 6-8/1988	NA 47	≈0.6 1.0	NA NA	NA NA	NA NA	Ridley (1991) Buhr et al. (1990)
Tanbark Flat, CA	8-10/1989 8, 9/1990 8/1991	69 34 22	2.9 4.8 2.8	>16.1 22.0 12.8	0.75 0.76 0.43	5.1 4.3 2.66	Williams and Grosjean (1991) Grosjean et al. (1993) Grosjean et al. (1993)

<sup>\*</sup> Taken from reference USEPA, 1996. NA Not Available

a Flow from Boulder – Denver area
b Flow across the Rockies