University of Alberta

Analysis of Ambient Air Quality Trends in West Central Airshed

by

Nabila Haque ©

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements for the degree of

Master of Science
in
Environmental Science

Department of Civil and Environmental Engineering

Edmonton, Alberta
Fall 2006

Library and
Archives Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

Your file Votre référence
ISBN: 978-0-494-22281-2
Our file Notre référence
ISBN: 978-0-494-22281-2

NOTICE:
The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:
L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ABSTRACT

This research presents an evaluation of ambient air trends from Tomahawk and Carrot Creek, in rural western Alberta. Pollutants - O_3, NO_2, SO_2, and $PM_{2.5}$ - were examined to assess trends over time using, (a) various percentiles of hourly concentration distributions from each year, and (b) frequencies in which various benchmark concentrations were exceeded each year. Hypothesis tests were conducted (at $\alpha = 0.05$) to identify statistically significant deviations. Results from the two methods were found to be consistent with each other. At Tomahawk, no statistically significant change was detected in air quality with respect to O_3 and $PM_{2.5}$, while SO_2 and NO_2 showed decreasing trends. At Carrot Creek, SO_2 exhibited statistically significant decreasing trends, while O_3 and NO_2 showed no change. The decreasing trends observed with SO_2 appeared consistent with reduced natural gas flaring and venting data over the same time period. Only O_3 showed considerable diurnal and seasonal variations at both stations.

ACKNOWLEDGEMENT

I begin by thanking God Almighty for His mercy and kindness. I am grateful to Him for making my parents the biggest blessing in my life.

I express my deepest gratitude to my supervisors, Dr. Mohamed Gamal El-Din and Dr. Warren B. Kindzierski, for their support, encouragement, and extraordinary patience in explaining things throughout this research. It was a pleasure to build on their outstanding knowledge in the field of air quality.

I would like to take this opportunity to thank Dr. Stephen A. Craik, as his course allowed me to learn a lot about statistical analysis.

I would also like to thank West Central Airshed Society for providing funding and air quality data for this research.

I appreciate my student-colleagues in the environmental engineering group for providing a warm-hearted environment at the university.

Finally, I wish to thank my husband, Amar Bin Halim, for his continuous support through the whole period of this research.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATION

AAQG	Ambient Air Quality Guideline
AMD	Air Quality Monitoring Directive
AQM	Air Quality Monitoring
AQQG	Air Quality Objectives And Guidelines
CASA	Clean Air Strategic Alliance
CCME	Canadian Council of Ministers of Environment
CO	Carbon Monoxide
CWS	Canada-Wide Standards
EPA	Environmental Protection Agency
EUB	Energy and Utility Board
GIS	Geographic Information System
MK	Mann-Kendall
MSE	Mean of Squares of Error
MSR	Mean Squares of Regression
NAAQO	National Ambient Air Quality Objectives
NASTRO	North American Research Strategy for Tropospheric Ozone Synthesis Team
NO_2	Nitrogen Dioxide
NO_x	Oxides of Nitrogen
O_3	Ozone
Pb	Lead
PM	Particulate Matter
QA/QC	Quality assurance and control
QAP	Quality Assurance Program
SK	Seasonal Kendall
SO_2	Sulphur Dioxide
SO_x	Oxides of Sulfur
SPRC	Spearman partial rank correlation
SSE	Sum of Squares of Error
SSR	Sum of Squares of Regression
SST	Sum of Squares Total
TAS	t-test adjusted for seasonality
TECO	Thermo Environmental Instrument Company
TEOM	Tapered Element Oscillating Microbalance
US ATSDR	United States Agency for Toxic Substances & Disease Registry, Research Triangle Institute and Science International Inc
USEPA	US Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile Organic Compounds
WCAS	West Central Airshed Society
WHO	World Health Organization

SYMBOLS

α	Level of Significance
β	Slope

CHAPTER 1 : INTRODUCTION

1.1 INTRODUCTION

Air quality issues are among the most difficult environmental problems currently faced by societies as more and more studies have shown significant impacts of atmospheric pollution on human health and on the environment as a whole (Desauziers, 2004). Air pollution comes from many different sources; stationary sources such as factories, power plants, and smelters, smaller sources such as dry cleaners and degreasing operations; mobile sources such as cars, buses, planes, trucks, and trains; and naturally occurring sources such as windblown dust, and volcanic eruptions. All of these contribute to air pollution.

Air quality can be affected in many ways by the pollution emitted from these sources. These pollution sources can also emit a wide variety of pollutants. The gases ozone (O_3), nitrogen dioxide (NO_2), sulphur dioxide (SO_2) are known respiratory irritants and are associated with various health effects including pulmonary function decrements, increased hospitalization for respiratory causes, and mortality (Gold et al., 2000; Mustafa, 1994; Pope et al., 2002; Suh et al., 2000; USEPA, 1999).

Epidemiological studies, which rely on data from stationary ambient monitoring sites, have shown consistent associations between particulate matter (PM) and adverse health outcomes including cardiovascular effects (USEPA, 1999; Wichmann et al., 2000); therefore, responding effectively to concerns about degraded air quality is a challenge for many cities and regions and requires sound assessments and innovative strategic and tactical advice. Accordingly, it is of great interest in research studies to determine whether a significant change in air quality has occurred over the years.

Change in air quality in urban or rural environment is often assessed through the system of air quality monitoring (AQM) on the basis of the collected real-time measurements of ambient level pollutants at different strategic sites. It is essential to keep the record of development of an area to assess its impact on general trends of air quality and its change and more importantly to check compliance or non-compliance with air quality standards. Merely evaluating and reporting of monitoring data overlooks the important aspect of detecting changes in air with respect to time (i.e., trends) and hence may lack in providing a sound scientific basis required for managing and improving the environment (Bower, 1997; WCAS, 2005).

Trend analysis is an aspect of technical analysis that tries to identify underlying longer-term trends and often helps in the prediction of the future based on past data (Blanchard, 1999). Trend analysis of air quality data is of practical importance because of the effects of global climate change (Önöz et al., 2003). Its importance is ever increasing due to the impact of increasing human intervention in a changing environment (Weatherhead, et al., 1998). Various statistical procedures are used for the detection of gradual trends over time.

In Alberta, air quality issues are mostly local in nature, both in their causes and the solutions required. The present study focuses on the air quality at two of the West Central Airshed Society (WCAS) monitoring stations, Tomahawk and Carrot Creek. Both areas largely represent rural west-central Alberta. In general, rural air quality is affected by agricultural practices such as the use of fertilizers, the burning of wastes, and the raising of cattle, as well as the transport of pollutants from other areas (Barrie and Hoff, 1985; Kelly et al., 1984). The input of anthropogenic emissions in recent years (e.g., oil and gas plants, coal fired power generating plants) in these relatively remote areas greatly affects the concentrations of the air pollutants (Seinfeld, 1989) and thereby raised the concern for an evaluation of the change in air quality.

1.2 OBJECTIVE OF STUDY

The characteristics of O_3, SO_2, NO_2 and $PM_{2.5}$ were investigated over the time period, focusing on the change in the "mid-to-upper-range" of a cumulative frequency distribution of hourly concentrations of the pollutants. This study was performed with the following objectives:

- To illustrate procedures for statistical post-processing of air quality data that are straightforward and easy to implement for detecting trends. This was accomplished by using simple linear regression for analyzing trends in historical ambient air quality data collected at WCAS air monitoring stations.

- To identify whether and to what extent the concentrations of ambient air quality parameters have changed between the period 1997 and 2004 (i.e. trends), at the selected WCAS air monitoring stations.

1.3 STUDY AREA

The West Central Airshed Society (WCAS) zone now encompasses approximately 46,000 square kilometres in west central Alberta (Figure 1.1), delineated by the Alberta/British Columbia border on the west (heavily forested and characterized by foothills and mountainous area), the top of Township 54 on the north, the top of Township 42 on the south and Highways 20 and 759 on the east. Beyond the boundaries on the east of the airshed, is the Capital Region of Alberta (Edmonton and surrounding area) which is characterized by gently rolling terrain with greater anthropogenic activities (e.g. gas plants and coal-fired power plants) and residential acreage developments.

Some of the major communities within the WCAS boundary are Jasper, Hinton, Edson, and Drayton Valley. WCAS operates a network of ten continuous on-line air quality monitoring stations, located throughout the zone in a manner that ensures representation of areas with industrial activity as well as remote from man-made emission sources. The stations are Tomahawk, Carrot Creek, Violet Grove, Hinton, Genesee, Meadows, Power, Wagner, Edson, and Drayton Valley. Two station have been previously decomissioned, Hightower Ridge (as of August 31, 2004) and Steepr (as of August 31, 2003). The locations of the two stations selected, to carry out a trend analysis of the air quality (Tomahawk and Carrot Creek) are indicated in the figure (Figure 1.1).

The Tomahawk station (Station no. 901) is located 25 km northeast of Drayton Valley near the community of Tomahawk at the latitude 53° 22’ 12” N and longitude 115° 11’ 26” W. The area is about 793 m above sea level. The land use surrounding the station is predominantly pastured. The roadway influences for the station includes the paved highway of Hwy 624, about 700m from the station, which has a traffic volume of about 200 vehicles per hour. The major point sources identified are four coal-fired power plants about 30 to 40 km away from the station. Air quality monitoring was considered at this station due to its close proximity to power plant activities.

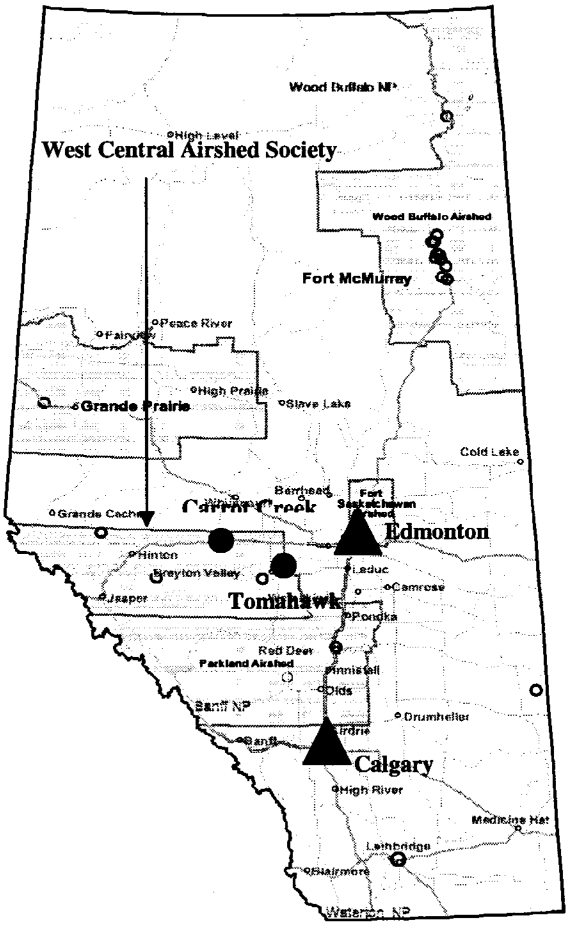

Figure 1.1 Province of Alberta Showing West Central Airshed Society Zone and Location of Tomahawk and Carrot Creek Air Monitoring Stations

The Carrot Creek station (Station No: 903) is located north of Highway 16, approximately 40 km east of Edson near the community Niton Junction at latitude 53° 36' 26" and longitude 115° 52' 37". This area is a little higher in elevation than Tomahawk, being about 860 m above sea level. The land use is also characterized by pasture. Apart from Highway 16, the nearest roadway influence includes a gravel municipal road, about 200m from the station, with a traffic volume of only 10 vehicles per hour. It has three gas plants as major point sources within a distance of 5 to 15 km from the station.

1.4 STRUCTURE OF THE THESIS

This thesis consists of six chapters. The second chapter reviews some background information on air quality monitoring, the properties of the criteria pollutants evaluated in this study, and some of the statistical tests applicable to ambient air quality trend analysis. In chapter three, the methodology is presented. Chapter four describes the application of the developed trend analysis methods for the study case, and discussion on the outcome follows in Chapter five. Chapter six contains the findings and reveals some future research directions.

CHAPTER 2 : LITERATURE REVIEW

2.1 AIR QUALITY

Air quality refers to the degree of pollution of the clean air (Zhang, 2005), where pollution signifies the presence of undesirable materials in air in quantities large enough to produce harmful effects (de Nevers, 2000). Air quality changes from hour to hour, day to day, even a longer time scale, depending on the concentrations of these undesirable materials or pollutants, which in turn depend on the magnitude of emissions from individual sources, density of emission, topography, and state of the atmosphere.

Godish (2004) provides a qualitative definition of air quality as where air is labeled "poor" when pollutants cause a reduction in visibility, damage materials, crops and other plants or cause adverse health effects, and labeled "good" when the sky is clear and none of the above adverse effects are observed. The USEPA (2003) defines air pollution as the introduction by man, directly or indirectly, of substances into the air resulting in harmful effects of such a nature as to endanger human health, impair living resources and ecosystems and damage material property and interfere with amenities and other legitimate uses of the environment. Although such qualitative assessment relates substantial information of the condition of the atmosphere relative to the pollutants, it cannot provide the basis required for formulating regulatory programs designed to protect the environment. For this later requirement, air quality must be defined in a quantitative term as in the context of concentrations of specific target pollutants, and observed impacts on environment and human health.

The USEPA (2003) uses six "criteria pollutants" as indicators of air quality — ozone (O_3), carbon monoxide (CO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), particulate matter (PM) and lead (Pb). For each of these, the USEPA has established "primary" standards to protect public health, and "secondary" standards to protect materials, crops and vegetation from damage, or to assure visibility. In Canada, air quality is defined, on a local basis, in terms of the presence of five common pollutants — sulphur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide (CO), suspended particulates, and ground-level ozone (O_3) (Environment Canada, 2005).

These days, the main source of atmospheric pollution is from the combustion of fossil fuel (energy production and heating processes) used by vehicles, homes, power stations as well as factories, industrial and incineration processes, and waste treatment and disposal (Colvile et al., 2001; Environment Canada, 2005; Tomás-Alonso, 2005). Evidently and understandably, there is an increasing interest worldwide on the adverse health effects that may result from exposure to atmospheric pollutants (Gold et al. 2000; McConnell et al., 2002; Mustafa, 1994; Neuberger et al., 2002; Pope et al., 2002; Suh et al., 2000; USEPA, 1999).

Impacts of these pollutants on animal health, vegetation, materials and climate have also been reported (Smith et al., 2003; WHO, 2000). When some of these pollutants combine, they produce smog or acid rainfall. Once formed, directly or indirectly, these constituents of pollution have the potential to affect the majority of Canadians (Environment Canada, 2005). Protection from such adverse effects on human health and environment is the primary goal of any air pollution control program.

2.1.1 Air Quality Objectives

Air quality criteria are defined as scientifically sound statements about effects observed or inferred to have been produced by various exposures to specific pollutants (Stern, 1973). Monitoring data are compared to a set of objectives which have been established to protect public health and the environment. The federal Canadian Environmental Protection Act provides for three levels of air quality objectives: Desirable, Acceptable and Tolerable (Environment Canada, 2004).

The objectives are based on the following definitions:

> **Maximum Desirable**: It defines the long-term goal for air quality and provides a basis for an antidegradation policy for the country and for the continuing development of control technology.
>
> **Maximum Acceptable**: It is intended to provide adequate protection against effects on soil, water, vegetation, material, animals, visibility, and personal comfort and well-being.

Maximum Tolerable: It denotes time-based concentrations of air contaminants beyond which, due to a diminishing margin of safety, appropriate action is required without delay to protect the health of the general population.

The Canadian Council of Ministers of the Environment (CCME) endorsed new national air quality standards for particulate matter (PM) and ozone (O_3) in June 2000 (CCME, 2000). These new standards, termed Canada-Wide Standards (CWS) are in addition to those detailed above.

2.2 AMBIENT AIR QUALITY MONITORING

Air Pollution concentrations vary greatly from place to place at any one time, and with time of day and from year to year at any one place (de Nevers, 2000; Stern, 1973). Before it is understood where and when the concentrations of hazardous air pollutants rise to unacceptable levels, it is necessary to have an extended period of data available from a network of pollution monitors (Colls, 1997). The identification and measurement of critical air parameters provides the backbone for defining and understanding the state of air and its changes with time (Demerjian, 2000).

2.2.1 Role of Monitoring In Air Quality Management (AQM)

Air quality monitoring is often used to determine the air pollution levels in urban or rural environments. Chow et al. (2002) highlighted the importance of monitoring networks and suggested installation and operation of monitoring networks containing an effective sampling set-up that represents the exposure of large populations to outdoor air. Monitoring data can be very useful in estimating the following (Bower, 1997):

- The level and distribution of exposure in the population
- The population groups with high exposure
- The risks of potential health effects.

The purpose of monitoring is not however limited to data collection. On the contrary, it provides important information required by scientists, policy-makers, and planners for making informed decisions on managing and improving the environment. Monitoring, in this regard, fulfils a controlling role in this process, providing the necessary sound scientific basis for developing policies and strategies, setting objectives, assessing compliance with targets and planning enforcement action (Bower, 1997; WCAS, 2005; WHO, 1997). It should also be recognized that in many circumstances measurements alone might prove insufficient for the purpose of AQM; therefore, monitoring often needs to be used in combination with other objective assessment techniques, including modeling, emission measurement and inventories, interpolation, mapping and interpretation (Bower, 1997).

These two activities strongly complement each other. Monitoring provides a useful but incomplete picture of the environment as it cannot quantify patterns of air pollution comprehensively in both time and space, however well funded and designed (Bower, 1997). Although models can provide a powerful tool for interpolation, prediction, and optimization of control strategies, they are effectively useless unless properly validated by real-world monitoring data. Accordingly, any integrated approach to exposure assessment should include both ambient monitoring and modeling as interrelated components (Bower, 1997; WHO, 1997).

2.2.2 Monitoring Objectives

Air quality monitoring consists of measuring individual pollutants over time at a number of locations in an organized, systematic program (Godish, 2004). The underlying principle of monitoring takes into account an array of issues including statutory requirements, policy and strategy development, local or national planning, measurement against standards, identification/quantification of risk, and public awareness (Bower, 1997). Bower (1997) summarized the typical monitoring functions as follows:

- Identifying threats to natural ecosystems or population health
- Informing the public about air quality and raising awareness
- Determining compliance with national or international standards
- Providing objective inputs to AQM, traffic and land-use planning
- Development/validation of management actions

- Development/validation of management tools (models, GIS, etc.)
- Assessing point or area source impacts
- Trend qualification/quantification, to identify future problems or progress towards management/control targets.

Influence of local/national issues and objectives renders each monitoring survey or network unique in arrangement which in turn helps in establishing a targeted and cost-effective quality assurance program (QAP), optimally designing networks, selecting priority pollutants as well as methods to measure them, and identifying requirements for data management/reporting (Bower, 1997; WHO, 1997).

2.2.3 Quality Assurance and Control

Quality assurance (QA) and quality control (QC) are essential parts of any air monitoring system. For air pollution, the USEPA (1993) defined quality assurance as a set of activities that are designed in such a way that ensures that the development and/or maintenance process is adequate for a system to meet its objectives. Quality Control has been defined as a set of activities designed to evaluate a developed work product (USEPA, 1993). Bower (1997) defines QA/QC as a program of activities that guarantee that the measurements meet defined and appropriate standards of quality with a stated level of confidence. Bower (1997) further relates that the function of QA/QC is not to achieve the highest possible data quality which would be an unrealistic objective under practical resource constraints. It only makes certain that the data are fit for an intended purpose. Major QA/QC objectives are to ensure the following (Bower, 1997):

- Accurate, precise and credible measurements
- Data are representative of ambient conditions
- Results are comparable and traceable
- Measurements are consistent over time
- High data capture that is evenly distributed
- Optimal use of resources

The functional components of a QA/QC program are identified by the World Health Organization as (WHO, 1997):

- Quality Assurance:
  - Definition of monitoring objectives
  - Network design, management, and training systems
  - Site selection and establishment
  - Equipment evaluation and selection
- Quality Control:
  - Routine site operations
  - Establishment of calibration/traceability chain
  - System maintenance and support
  - Data review and management
  - System review and development

2.3 PROPERTIES, SOURCES AND EFFECTS OF POLLUTANTS MEASURED BY MONITORS

2.3.1 Ground-Level Ozone

The increase in UV-B radiation reaching the earth as a result of the thinning of the stratospheric ozone shield is expected to have a negative impact on the environment and public health when present in sufficient quantities in the lower atmosphere. In establishing ambient air quality standards, regulations have been introduced to set limits on the emissions of pollutants in such a way that they cannot exceed prescribed maximum values (USEPA, 1999). To achieve these limits, predictive models were required and consideration was given to mathematical and computer modeling. Ozone, however, is unique among pollutants. It is not emitted directly into the air; rather it results from complex chemical reactions in the atmosphere (secondary pollutant). To track and predict ozone, one must create an understanding not only of ozone itself but also the conditions that contribute to its formation.

2.3.1.1 Formation of Ground Level Ozone

Ozone is a gas that occurs both in the Earth's upper atmosphere and at ground level. Ozone can be good or bad, depending on where it is found. Unlike many air pollutants, ground-level ozone is not emitted directly into the air; it is formed by gases called oxides of nitrogen (NO_x) and volatile organic compounds (VOC), which in the presence of heat and sunlight, react to form ozone. The following equation expresses the process (de Nevers, 2000):

$$VOC + NO_x + Heat + Sunlight = Ozone \qquad (1.1)$$

Tropospheric ozone (often termed "bad" ozone) is man-made, largely a result of air pollution from internal combustion engines and power plants. Automobile exhaust and industrial emissions release a family of nitrogen oxide gases (NO_x) and volatile organic compounds (VOC), which are by-products of burning gasoline and coal. NO_x and VOC combine chemically with oxygen to form ozone during sunny, high-temperature conditions of late spring, summer and early fall. High levels of ozone are usually formed in the heat of the afternoon and early evening, dissipating during the cooler nights. The following illustrations (Figure 2.1 and Figure 2.2) present the production of ozone from NO_x and VOC respectively.

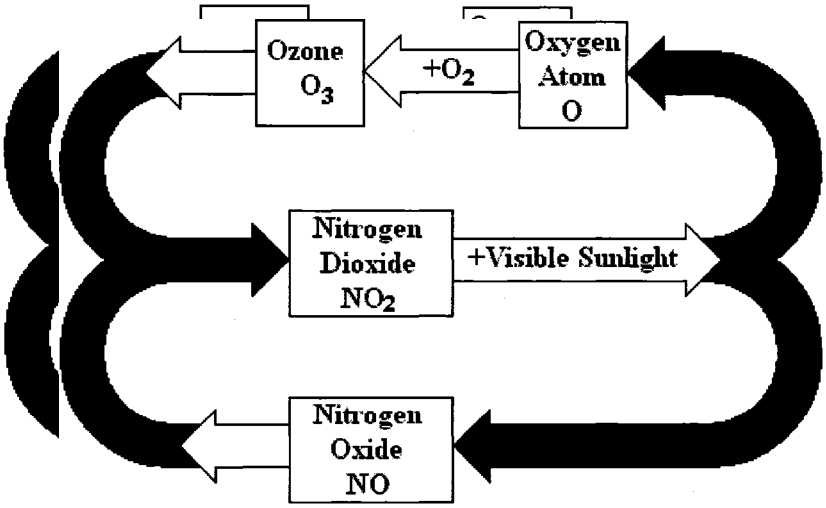

Figure 2.1 Ozone Production from NO_x (Adapted from Freudenrich, 2002)

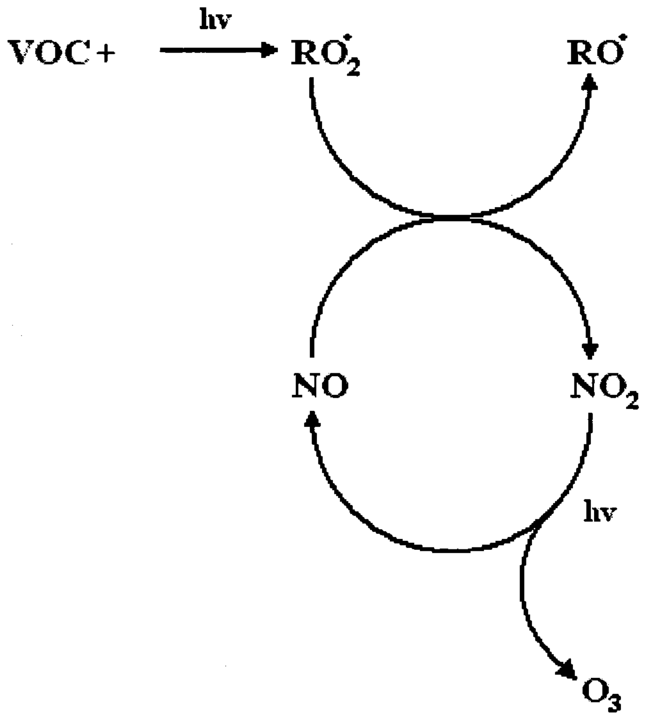

Figure 2.2 Ozone Production from VOC (Adapted from USEPA, 1996)

Ground-level ozone (the primary constituent of smog) has remained a pervasive pollution problem through out many areas of the world. Various meteorological parameters affect the atmospheric ozone balance. Changing weather patterns contribute to yearly differences in ozone concentrations from area to area (USEPA, 2001). Ultraviolet radiation, wind speed, and temperature influence the chemical reactions that occur in the atmosphere. In addition, surface scavenging and atmospheric mixing, and transport processes can alter the ozone balance (USEPA, 1996).

Regional terrain can also influence the dispersion of atmospheric pollutants. This transport of ozone precursors, as well as ozone itself, causes air pollution over wide regions. The problem is more acute near the polar regions of the world. Since solar radiation is strongest over the tropics, most of the global ozone is formed there. The sun in the tropics not only drives ozone formation, but also raises the tropospheric air to high altitudes; thus, ozone is transported away from the equator towards the poles, where it accumulates in the cold subpolar regions. At the equator itself, ozone formation as well as photochemical depletion is high. Ozone cannot accumulate. In the subpolar regions however, photochemical depletion is low and the transport from equator is an important source.

2.3.1.2 Factors Affecting Formation of Ground-Level Ozone

Sources of NO_x and VOC ozone precursor compounds have been found to be both anthropogenic and natural. Table 1 presents some of the examples of such sources. NO_x are largely formed in combustion processes from nitrogen present in the fuel source. Consequently, emissions from transportations, stationary source fuel combustion, industrial processes, and solid waste disposal are some of the main human activities that are responsible for NO_x (USEPA, 1996). Natural sources include lightning strikes, soils, wildfires, stratospheric intrusion, and evaporation over large bodies of water (USEPA, 1996). VOCs are equally emitted in large quantities from deciduous vegetation and conifers. Evaporative and combustion processes are anthropogenic sources of VOCs. Ozone formation is expected to increase with the ratio of VOCs to NO_x.

Table 2.1 Major Anthropogenic Activities that Contribute Urban Levels of Ozone Precursor Compounds (Adapted from USEPA, 1996)

Category	NOx Sources	VOC Sources
Transportation	Gasoline/diesel powered vehicle Aircraft Railcars Vessels Off-highway vehicles	Vehicles
Stationary sources	Electric utilities Industrial and Commercial/institutional boilers Industrial furnaces Space heaters	Electric utilities Industrial boilers and furnaces
Industrial sources	Petroleum refining Paper production Glass production Steel production Cement production Chemical production	Solvent use Petroleum product storage and transfer (fugitive emissions) Chemical manufacturing
Solid waste disposal	Incineration Open waste burning	Waste Disposal and recycling
Miscellaneous	Forest slash burning Agricultural burning Coal refuse burning Structure fires	

Meteorological Factors

In the atmosphere, several meteorological parameters affect the balance of ozone. Ultraviolet radiation, wind speed, and temperature influence the chemical reactions that occur in the atmosphere (USEPA, 1996). In addition, surface scavenging and atmospheric mixing and transport processes can alter the ozone balance as well (USEPA, 1996). The prime meteorological conditions for ozone formation and accumulation are high pressure, temperature and solar radiation, and light surface winds (Jacobson, 1999; Sandhu, 1999). UV radiation is required as an energy source to power the photochemical reaction in ozone formation. The amount of UV in any given location is a function of the season, cloud cover and atmospheric conditions.

Ozone and its precursor pollutants can also be transported into an area hundreds of miles upwind, which makes it hard to treat the source of the problem (Jacobson, 1999). Regional terrain also influences the dispersion of atmospheric pollutants. Temperature affects reaction kinetics and influences atmospheric mixing through convection currents. Wind speed also affects atmospheric mixing through pressure gradients (Sandhu, 1999).

Ozone Sinks in Nature

Chemical reactions in the gaseous or aqueous phase and deposition are known as the major sinks of ozone in nature (CEPA/FPAC WGAQOG, 1999). The chemical reactions of oxides of hydrogen, HO_x (=OH+HO_2), destroy ozone in the atmosphere and are known as ozone scavengers (CEPA/FPAC WGAQOG, 1999). NO_x conducts catalytic ozone destruction cycles. Reactions with unsaturated hydrocarbons consume ozone as well (CEPA/FPAC WGAQOG, 1999).

2.3.1.3 Effect Of Ozone

Stratospheric ozone depletion is a concern because the ozone layer in the stratosphere keeps 95-99% of the suns ultraviolet radiation from striking the earth. A number of consequences can result from increased levels of UV (ultraviolet radiation) at the earth's surface including genetic damage, eye damage, and damage to marine life. Increased UV radiation in the lower atmosphere, called the troposphere, can result in increased amounts of photochemical smog. Photochemical smog is already a health hazard in many of the world's largest cities (USEPA, 2005a).

Effect on Human Health

While beneficial in the upper atmosphere, ozone in the lower atmosphere can cause a variety of lung and respiratory disorders because it damages lung tissue, reduces lung function, and adversely sensitizes the lungs to other irritants. Delfino et al. (1997) found positive association between ambient ozone concentration and hospital emergency room visits in Montreal, Quebec based on respiratory illness. Lipfert and Hammerstorm (1992) observed a small but statistically significant association between ozone concentrations and respiratory admission for the high summer months, July and August. The USEPA (1999) reports that ozone can impair people's ability to breath and induce shortness of breath, chest pain, wheezing, and coughing.

People with respiratory problems are most vulnerable, but even some healthy people can be affected while engaged in moderate physical activity when ozone levels are high enough. Animal studies suggest that repeated exposure to high levels of ozone over several months may permanently damage the lungs and cause chronic respiratory illness (USEPA, 1999). Burnett et al. (1998) carried out a study about the association between ambient levels of gaseous air pollutant and daily deaths for non-accidental causes in 11 Canadian cities over a period of 11 years. This study revealed that risk from ozone was low for Calgary, Edmonton and Winnipeg.

Effect on Environment

Ozone is identified as one of the most damaging air pollutants to vegetation (Sandhu, 1999). Bates (1991) revealed links between ambient ozone concentrations and vegetation and crop injury. Short term, high level exposure may cause damage to leaves or needles, while exposure to frequent, low, hourly ozone concentrations with periodic, intermittent peaks may cause chronic effects like changes in plant growth and productivity (Sandhu 1999). Ozone has also been shown to cause material damage and affect animal health in addition to causing adverse effects on human health (Sandhu, 1999; USEPA, 1996).

The recently completed review by the US Environmental Protection Agency (USEPA) of the ozone standard highlighted concerns associated with ozone effects on vegetation for which the 1-hour ozone standard did not provide adequate protection. These effects include reduction in agricultural and commercial forest yields, reduced growth and decreased survivability of tree seedlings, increased tree and plant susceptibility to disease, pests, and other environmental stresses, and potential long-term effects on forests and ecosystems (USEPA, 1999).

2.3.1.4 Control Of Ozone

Control strategies are aimed at limiting emissions of ozone precursor compounds while management strategies tend to focus on minimizing exposure. The US. Environmental Protection Agency (USEPA) has established National Ambient Air Quality Standards (NAAQS) for six air pollutants which are ozone, lead, carbon monoxide, sulfur dioxide, nitrogen dioxide, and inhalable particulate matter. The standards were established to protect the public from exposure to harmful amounts of pollutants (Qin, et al., 2004). When the pollutant levels in an area have caused a violation of a particular standard, the area is classified as "non-attainment" for the pollutant (USEPA, 1997).

In July 1997, the USEPA revised the national ambient air quality standards for ozone (USEPA, 1997). After a lengthy scientific review processes the USEPA issued a rule that replaced the 1-hour ozone 12 ppb standard with a new 8-hour 80 ppb (160 $\mu g/m^3$) standard to better protect public health and the environment against longer exposures. Under the one-hour standard, ozone concentrations of 125 ppb (250 $\mu g/m^3$) or higher are considered to exceed the standard. The standard is not to be exceeded in an area more than three times in three consecutive years at the same monitoring site. If the standard is exceeded four times in three years at one site, then the area is in violation of the standard and no longer in "attainment." In the U.S., the USEPA can penalize non-attainment areas with sanctions and restrictions that impede industrial and commercial development, greater vehicle inspection requirements, and result in the loss of federal funding (Prybutok et al., 2000).

The USEPA has recommended several ozone control strategies to reduce air pollution from a variety of sources that contribute to the ground-level ozone or smog problem. Strategies currently being implemented include the following (USEPA, 1997):

- Vapor recovery nozzles at the gasoline pumps to reduce refueling emissions
- Cleaner burning gasoline reformulated to reduce VOC, NO_x and other pollutants
- Strict NO_x emission limits for power plants and industrial combustion sources
- Enhanced vehicle inspection programs in states
- Strict limitations on the solvent usage in factories

In Canada, the federal government sets National Ambient Air Quality Objectives (NAAQO) and at present, the value is set at 82 ppb for a one-hour average concentration (Sandhu, 1999). The NAAQO for ozone was set in 1976 as part of the 1973 Clean Air Act and was upheld under the Canadian Environmental Protection Act in 1989 (NASTRO 2000). More recently, Canada Wide Standards (CWSs) were developed, setting a 2010 target ozone level of 65 ppb averaged over 8 hours. In Alberta, the current one hour average Ambient Air Quality Guideline (AAQG) for ozone is also set at 82 ppb (160 $\mu g/m^3$) (Alberta Environment, 2005a). Alberta Environment is the regulatory body responsible for monitoring ozone via a network for continuous air quality stations. For the final quarter of 2001, the average hourly concentration measured for ground level ozone was 10 ppb (20 $\mu g/m^3$) for Edmonton, and 11 ppb (22 $\mu g/m^3$) for Calgary (Alberta Environment 2001). These values were the averages of three monitors in each city.

2.3.1.5 Ozone Monitoring

Ozone is continuously measured using an ultraviolet (UV) light process. The sampled air is exposed to UV light which is absorbed by O_3. The amount of UV light absorbed is roughly proportional to the amount of O_3 in the sample, that is, the more UV light that is absorbed, the greater the amount of O_3 that is present in the sample (CASA, 2005).

2.3.2 Sulfur Dioxide (SO_2)

Sulfur dioxide, or SO_2, belongs to the family of sulfur oxide gases (SO_x). SO_2 dissolves in water vapor to form acid, and interacts with other gases and particles in the air to form sulfates and other products that can be harmful to people. Changes in the abundance of sulphur dioxide have an impact on atmospheric chemistry and hence on the environment. Consequently, global observations of sulphur dioxide are important for environmental research.

2.3.2.1 Physical and Chemical Characteristics

The physical and chemical properties of SO_2 are presented in Table 2.2. SO_2 is a colourless gas, having a pungent smell. It is detectable by taste or odour at concentration levels of 1000 to 3000 $\mu g/m^3$ (380 to 1140 ppb). It is liquid under pressure and is readily soluble in water forming sulfurous acid (H_2SO_3) (US ATSDR et al., 1998a; WHO, 1997). SO_2 has high vapour pressure and low boiling and melting points. In pure solutions, SO_2 is oxidized slowly to form sulfuric acid (H_2SO_4).

Table 2.2 Physical and Chemical Properties of SO_2 (Adapted from US ATSDR et al., 1998a)

Property	Sulfur dioxide
Molecular weight	64.06 g/mol
Colour	Colourless
Physical state	Gas at ambient conditions
Melting Point	-72.7 °C
Boiling Point	-10 °C
Density	2.927 g/l (gas) or 1.434 g/cm^3 (liquid)
Odour	Strong odor, suffocating
Solubility in water at 0°C	22.8 g/100 cc
Solubility in water at 20°C	11.3g/100 cc
Solubility in water at 90°C	0.58 g/100 cc
Vapor Pressure	330 kPa at 20°C
Flammability limits	Non-flammable

When exposed to the atmosphere, SO_2 can react with soil, water, and air. Soil can absorb SO_2 by diffusion. Surface water may receive SO_2 through dry and wet deposition from surface runoff and subsurface drainage (US ATSDR et al., 1998a). In the air, SO_2 may be oxidized to sulfur trioxide (SO_3), H_2SO_4 and other sulfates (e.g., sodium sulfate) either photochemically or catalytically (Elsom, 1987; US ATSDR et al., 1998a; WHO, 1997).

SO_2 has a residence time in the atmosphere of approximately 10 days (US ATSDR et al., 1998a).

2.3.2.2 Sources of Sulfur Dioxide (SO_2)

Atmospheric SO_2 is produced from both natural and anthropogenic sources. Natural sources of SO_2 are from volcanic eruptions. The sulfur compounds emitted by volcanoes are mostly SO_2 and H_2S along with smaller amounts of SO_3 and various sulfates (Kellogg et al., 1972; US ATSDR et al., 1998a). Anthropogenic sources of SO_2 can be divided into industrial, domestic, and vehicular sources (WHO, 1979). Industrial sources of SO_2 are produced from combustion of fossil fuel such as coal and oil burning electric power plants (Taylor et al., 2005; Tomás-Alonso, 2005).

According to the USEPA, power plants contribute 67 percent of soot forming SO_2 emissions. Although federal law caps SO_2 emissions from power plants, more than half (216 of 400, or 54 percent) of the nation's power plants increased their annual SO_2 emissions from 1995 to 2003, even while annual SO_2 emissions from power plants decreased by 10 percent nationwide. During oil sands operations, SO_2 is produced from the combustion of coke used to fuel the utility plants and from the flaring of waste gas.

Copper smelters, oil refineries and domestic and industrial heating systems contribute to local sources of SO_2 (CASA, 2005). Since SO_2 is heavier than air, it settles to the ground within a few miles of its source as it enters the sulfur cycle. On the ground SO_2 oxidizes to sulfates which are a vital component of plant nutrients (Meyer, 1983). Among the domestic sources of SO_2 are burning soft or hard coal, oil, kerosene, stove oil, and light fuel oil (WHO, 1997). SO_2 is also found in bleaching agents, pesticides and fungicides, preservatives, disinfectants and antioxidants such as rubber, paints, vegetable oil and prepared foods (Pease, 1999). The major vehicular emission of SO_2 is from the burning of diesel in vehicles (WHO, 1997).

The emission of SO_2 is related to the sulfur content of the fossil fuel and the total amount of fossil fuel that is consumed; thus, the emission of SO_2 is related to population density of an area (US ATSDR et al., 1998a). Stern et al. (1994) reported studies conducted from October 1985 to March 1986 in Saskatchewan and Ontario to compare the outdoor rural and urban SO_2 concentrations as a result of long-range transport of the air pollutants from industrial sites. It was observed that in five rural communities in Saskatchewan, the mean outdoors SO_2 concentrations was 1.1 $\mu g/m^3$, while the SO_2 concentrations in 5 urban communities located in southwestern Ontario averaged 5.5 $\mu g/m^3$. Thus the concentration of SO_2 was lower in rural communities (Stern et al., 1994).

In another study conducted by Kindzeriski and Sembaluk (2001), indoor and outdoor concentrations of SO_2 were measured in late fall for five weeks in the urban center of Sherwood Park and the rural community of Boyle, Alberta. It was found that the rural community of Boyle (indoor: 0.5 $\mu g/m^3$; outdoor: 4.3 $\mu g/m^3$) had consistently lower concentrations of SO_2 both indoors and outdoors compared to the urban centers of Sherwood Park (indoor: 1.4 $\mu g/m^3$; outdoor: 9.9 $\mu g/m^3$). This finding could be explained as a result of increased vehicular activities and industrial emissions in the urban area in Sherwood Park (Kindzeriski and Sembaluk, 2001). It was interesting to note that the mean outdoor concentrations of SO_2 in these urban centers were low in comparison to levels of SO_2 in a rural community in southern Ontario, where the average was 19 $\mu g/m^3$. This variation is due to the location of the community, which is downwind from industrial sources in Ontario. This variation could also be aggravated by strong winds leading to a more rapid transport of the pollutant to greater distances (Daum et al., 1989).

2.3.2.3 Effect on Health and Environment

Effects on Sulfur Dioxide on Human Health

Sulphur dioxide is an irritant gas, which stimulates nerves in the lining of the nose, throat, and lung airways. It produces a reflex cough, irritation, and a feeling of chest tightness. It may provoke an asthmatic attack in those pre-existing asthma or chronic lung disease. The primary means of exposure to SO_2 is through inhalation, although dermal exposure poses a secondary yet significant route to SO_2 (Maroni et al., 1995; US ATSDR et al., 1998a). Exposure to very high concentrations, over 10,000 ppb (26600 $\mu g/m^3$) over a 15 minute period, causes painful irritation of eyes, nose, mouth, and throat and produces short term chemical injury to the linings of the airways which causes severe breathing difficulties and even death (US ATSDR et al., 1998a; WHO, 1997).

Normal healthy volunteers exposed to sulphur dioxide in exposure chambers have been shown to have demonstrable narrowing of airways after exposures of 4,000 to 5,000 ppb for 5 minutes. Effects were not detectable at concentrations under 1,000 ppb. Individuals that are more susceptible to SO_2 exposure include exercising asthmatics, asthmatics adult and children, the elderly with pre-existing respiratory or vascular problems, workers and non-asthmatics sensitive to cold (US ATSDR et al., 1998; WHO, 1997). Long-term exposure to SO_2 may causes lung edema, lung tissue damage, and sloughing off the cells of the inside layer of the respiratory tract (Turalio Ğlu, 2005; US ATSDR et al., 1998a; WHO, 1997). Some of the symptoms of SO_2 exposure as a function of time and concentration of SO_2 are summarized in Table 2.3.

Table 2.3 Symptoms of SO_2 Exposure (Adapted from WHO, 1979)

Concentration (μg/m3)	**Length of Exposure (min)**	**Effects**
2900-2300	10	Increased pulse rate Decreased tidal volume Increased respiratory rate
2900	10-30	Increased pulmonary resistance
2500	15	Increased respiratory resistance
2000	60-180	Decreased cross-section of nasal mucous flow Decreases cross-section of nasal passage
1100	120	No effect on pulmonary function through exposure

It has been reported that changes as a result of the Clean Air Act of 1956 and subsequent developments have had the effect of limiting general population exposures to sulphur dioxide (Alberta Environment, 2005b). Exposures today tend to be for short periods rather than prolonged periods. In addition, according to a report by U.S. PIRG Education Fund (2005), exposures tend to occur at locations downwind from power stations rather than in urban areas.

Effects of Sulfur Dioxide on Vegetation

Excesses airborne SO_2 can have intense effects on vegetation. Exposure to SO_2 can cause bleached patches on broad-leaved plants or bleached streaking on either side of the mid-vein of leaves (Elsom, 1987). Long term SO_2 exposure interferes with the photosynthesis action of the plants as it bleaches the chlorophyll, leading to discolorations of the leaf; thus, SO_2 exposure may reduce growth and yield of the plants. Plants that are more susceptible to SO_2 exposure include alfalfa, barely, cotton, lettuce, Lucerne, rhubarb, spinach, and sweet pea. SO_2 exposure is not always damaging to plants. Vegetative exposure to SO_2 may be beneficial in areas with an SO_2 deficit. After some time, SO_2 may decrease the pH of the soil, developing the need for lime (Elsom, 1987).

2.3.2.4 Control of Sulfur Dioxide (SO_2)

SO_2 is among the criteria pollutants (Pease, 1999). In Albertan and Canadian air quality guidelines, the acceptable limits for 1 hour, 24 hour, and annual concentrations of SO_2 in the air is 450 $\mu g/m^3$, 150 $\mu g/m^3$, and 30 $\mu g/m^3$ respectively. These guidelines are intended to provide adequate protection against acute and chronic exposure to SO_2. According to the NAAQS, for averaging times of annual, 24 hours, and 1 hour, the Maximum Desirable Level for SO_2 has been set as 11 ppb (30 $\mu g/m^3$), 57 ppb (150 $\mu g/m^3$) and 172 ppb (450 $\mu g/m^3$) respectively. The Maximum Acceptable Level has been set as 23 ppb (61 $\mu g/m^3$), 115 ppb (306 $\mu g/m^3$) and 334 ppb (888 $\mu g/m^3$). The Maximum Tolerable Level has been set as 306 ppb (814 $\mu g/m^3$) (Health Canada, 2005).

For vegetations, Alberta Environment has adopted Environment Canada's most rigorous objectives for sulphur dioxide. The following have been decided for the prevention of effects on vegetation (CASA, 2005):

- 172 ppb (450 $\mu g/m^3$) as a 1-hour average concentration;
- 57 ppb (150 $\mu g/m^3$) as a 24-hour average concentration; and
- 11 ppb (30 $\mu g/m^3$) as an annual average concentration.

2.3.2.5 Monitoring of Sulfur Dioxide (SO_2)

SO_2 is monitored continuously by pulsed fluorescence. In this method, air is drawn through a sample chamber where it is irradiated with pulses of ultraviolet light. Any SO_2 in the sample is excited to a higher energy level and upon returning to its original state, light or fluorescence is released. The amount of fluorescence measured is proportional to the SO_2 concentration (CASA, 2005).

2.3.3 Nitrogen Oxides (NO_X)

Nitrogen oxides, or NO_x, is the generic term denoting a group of highly reactive gases, all of which contain nitrogen and oxygen in varying proportions. All fossil fuel burning processes produce NO_x. The principle oxides formed are nitric oxide (NO), which represents 90%-95% of the NO_x formed and nitrogen dioxide (NO_2), which represents most of the remaining nitrogen oxides.

2.3.3.1 Formation of Nitrogen Oxides (NO_X)

Nitrogen oxides are formed primarily in the high temperature zone of a furnace where sufficient concentrations of nitrogen and oxygen are present (US ATSDR et al., 1998b). Fuel nitrogen and nitrogen contained in the combustion air both play a role in the formation of NO_x. The largest percentage of NO_x formed is a result of the high temperature fixation reaction of atmospheric nitrogen and oxygen in the primary combustion zone. Nitric oxide is the primary oxide of nitrogen that is released into the atmosphere by the combustion processes as a result of the reaction of N_2 and O_2 at very high temperatures. Nitrogen dioxide (NO_2) is formed in ambient air though the oxidation of nitric oxide (NO).

Nitrogen dioxide is a brown paramagnetic gas. Nitrogen dioxide reacts with water in a disproportionation reaction to form nitric acid.

$$2NO + H_2O \rightarrow HNO_3 + HONO \qquad (2.2)$$

NO_2 is a strong oxidant and in one of the most photochemically active species in a polluted atmosphere. It is essential to the formation of smog through photochemical reactions with volatile organic compounds (VOCs). The equation below is an important first step in these processes:

$$NO_2 + hv \rightarrow NO + O \qquad (2.3)$$

Nitrogen dioxide and nitric oxide (NO) are commonly classified together as NO_x, because of their inter-conversion during smog formation reactions. The forward and backward reaction establishes a steady–state concentration between NO and NO_2. Of the two, NO_2 has a more adverse effect on human health (Jin et al., 2005):

$$NO_2 + O \rightarrow NO + O_2 \tag{2.4}$$

$$NO + O \rightarrow NO_2 + O_2 \tag{2.5}$$

2.3.3.2 Physical And Chemical Properties of Nitrogen Oxides (NO_X)

Many of the nitrogen oxides are colorless and odorless. However, one common pollutant, nitrogen dioxide (NO_2) along with particles in the air can often be seen as a reddish-brown layer over many urban areas (US ATSDR et al., 1998b; WHO, 2003).

Nitrogen dioxide, NO_2, is a highly reactive gas. It reacts with water in a disproportion reaction to form nitric acid, making the moist gas highly corrosive. NO_2 is a strong oxidant and is one of the most photochemically active species in a polluted atmosphere (US ATSDR et al, 1998b; WHO, 1997). It is essential to the formation of smog through photochemical reactions with volatile organic compounds (VOCs). NO_x concentration will increase with temperature, the availability of oxygen, and the time the oxygen and nitrogen simultaneously are exposed to peak flame temperatures.

Because of their inter-conversion during smog formation reactions, nitrogen dioxide (NO_2) and nitric oxide (NO) are commonly classified together as NO_x. Nitrogen oxides (NO_x) play a major role in the formation of ozone, particulate matter, and acid rain (Mauzerall et al., 2005; Sandhu, 1999; USEPA, 2001).

2.3.3.3 Sources of Nitrogen Oxides (NO_X)

Nitrogen oxides are released from both natural and anthropogenic sources. Major sources of man-made emissions are high-temperature combustion processes, such as those occurring in automobiles and power plants (Mauzerall et al., 2005; USEPA, 2001). Automobile exhaust acts as the major contributor among the anthropogenic sources of NO_x in the atmosphere. Stationary fuel combustion and various industrial processes also have significant contributions. Indoor combustion sources of NO_2 include gas and wood stoves and unvented propane, natural gas and kerosene heaters.

The production of NOx is considered more significant in natural sources than in anthropogenic sources, mainly as the result of the activity of nitrogen consuming microorganisms in soil (Jin et al., 2005). There has been an evident increase in natural NO_x generation due to the larger worldwide use of fertilizers over the present and recent past decades (Sawyer et al., 2003). Natural sources of NO_x are lightning, biological and biological processes in soil, and stratospheric intrusion (Cho and Peirce, 2005; Sawyer et al., 2003).

2.3.3.4 Environmental Problems from Nitrogen Oxides (NO_X) Pollution

NO_x causes a wide variety of health and environmental impacts because of various compounds and derivatives in the family of nitrogen oxides, including nitrogen dioxide, nitric acid, nitrous oxide, nitrates, and nitric oxide (Carslaw, 2005; Jin et al., 2005; Mauzerall et al., 2005; USEPA, 2001). NO_x, in the atmosphere, contributes to global warming and helps form acid rain. NO_x can react with other pollutants to form toxic chemicals. It further hampers the growth of plants.

Effects on Human Health

When inhaled, nitrogen dioxide can penetrate relatively deeply into the airways, where it can cause irritation and damage to tissue. Information about the effects of NO_2 inhalation has come from controlled animal and human studies as well as epidemiological studies. Mustafa (1994) presents an extensive review of the toxicology and health effects of nitrogen dioxide. NO_2 is an irritant gas and if breathed can cause severe damage at the lungs.

Toxicity experiments conducted on animals proved that even if a spot exposition to NO may rarely leave permanent effects, a continuous and prolonged exposition (for some week to some months) to NO_2 concentration (even lower than 1,880 $\mu g/m^3$) may have severe consequences. It mainly affects the lungs, but also other parts such as the liver and blood may be affected (Schlesinger, 2000). Due to its high solubility in fat, NO_2 can penetrate deeply into the lungs where it damages capillaries and generates the spread of inflammation of the tissues (Wang et al., 2004).

Continuous exposition at low concentration of NO_2 can cause cough, headache, loss of appetite, and stomach problems. Such exposure to NO_2 may result in development of emphysema-like pathogenic changes (Freeman and Haydon, 1964). Although the health effects associated with NO_2 are less clear, Touloumi et al. (1997) suggest that 'all-cause-mortality' is increased by 3.5% for approximately a 200 ppbv increase in levels, where those who already suffer from ailments such as asthma are affected most. Environmental studies had proven that children that sustained a continuous exposition to NO_2 end up with an increase in breathing diseases and reduced breathing efficiency (Wang et al., 2004).

NO_2 can also aggravate both asthma and allergic reactions. It impairs the defense mechanisms of the lungs against bacteria, viruses, and other air pollutants such as ozone and particulate carcinogens (Schlesinger, 2000). Nitrogen oxides have significant indirect effects on health through their contribution to the formation of ground-level ozone and the conversion in the air to very small particles (Jin et al., 2005).

NO is not irritant itself but reacts with hemoglobin giving meta-hemoglobin which can prove lethal in children (Socolow, 1999). The U.S. Environmental Protection Agency observed that when present in high concentrations (greater than 10 milligrams of nitrate per liter of water) it may cause a condition that occurs primarily in infants called methemoglobinemia, or "Blue Baby Syndrome" (Socolow, 1999) It is caused when oxygen in hemoglobin (the compound that carries oxygen from the lungs through the body) is replaced by nitrite (Schlesinger, 2000) which leads to mild to severe oxygen deprivation, which can result in brain damage and even death.

Effects on Environment

Oxides of nitrogen at certain concentrations can also seriously injure vegetation (Fenn et al., 2003). Effects include bleaching or killing of plant tissues, falling of leaves, reduction in growth rate, deterioration of fabrics, and fading of dyes. Increased nitrogen loading in water bodies, particularly coastal estuaries, upsets the chemical balance of nutrients used by aquatic plants and animals. Additional nitrogen accelerates "eutrophication," which leads to oxygen depletion and reduces fish and shellfish populations (Sawyer et al., 2003).

The effect of NO_x has a greater impact, as one member of the NO_x, nitrous oxide, is a greenhouse gas (Sawyer et al., 2003; USEPA, 2005b). It accumulates in the atmosphere with other greenhouse gasses causing a gradual rise in the earth's temperature. This rise will lead to increased risks to human health, a rise in the sea level, and other adverse changes to plant and animal habitat. Besides having adverse effects of its own, in the air, NO_x reacts readily with common organic chemicals and even ozone, to form a wide variety of toxic products, some of which may cause biological mutations. Examples of these chemicals include the nitrate radical, nitroarenes, and nitrosamines (Sawyer et al., 2003). The nitrate salts formed from nitrogen oxides can corrode metals (USEPA, 2005b). Airborne nitrate particles and nitrogen dioxide can block the transmission of light, reducing visibility in urban areas and on a regional scale in the national parks (USEPA, 2005b).

2.3.3.5 Control of Nitrogen Oxides (NO_X)

USEPA's Efforts to Reduce NOx

Since the 1970's, the USEPA has required motor vehicle manufacturers to reduce NO_X emissions from cars and trucks and achieved significant reduction in the last ten years, NO_x emissions from highway vehicles decreased by more than 5 percent, while vehicle miles traveled increased significantly (Envirotool, 2005). To help reduce acid rain, the USEPA devised a two-phased strategy to cut NO_x emissions from coal-fired power plants. The first phase, finalized in a rulemaking in 1995, aimed to reduce NO_x emissions by over 400,000 tons per year between 1996 and 1999. The second phase began in 2000 with the aim of reducing NO_x emissions by over 2 million tons per year (USEPA, 2006).

As NO_X and ozone can be transported long distance, the Clean Air Act requires "upwind" states to implement programs that will help "downwind" states meet the ozone standards. The USEPA issued a rule in 1998 that requires 22 states and the District of Columbia to revise their Implementation Plans to further reduce NO_x emissions by taking advantage of newer, cleaner control strategies. States are allowed flexibility in determining how to reduce emissions, maintaining the goal of reducing total emissions of NO_x by 1.2 million tons in the affected states by 2007 (USEPA, 2003).

Standards in Canada

In Canada, air quality objectives for NO_2 reduction have been based on prevention of human health effects (CASA, 2005). Alberta's Ambient Air Quality Guidelines for NO_2 are as follows:

- 212 ppb (400 $\mu g/m^3$) as a 1-hour average concentration;
- 106 ppb (200 $\mu g/m^3$) as a 24-hour average concentration; and
- 32 ppb (60 $\mu g/m^3$) as an annual average concentration.

2.3.3.6 Monitoring Methods for Nitrogen Oxides (NO_X)

NO_x are measured continuously based on the principle of chemiluminescence (CASA, 2005). 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 goes directly to the analysis chamber, gets mixed with O_3 and light is produced. The amount of this light indicates the concentration of NO as it is proportional to the NO concentration; thus, NO is measured in the sample air. In the second pathway, a catalytic converter is used to first convert the entire NO in the sample air to NO_2. The sample then goes to the analysis chamber. The measurement in this pathway is the sum of NO_2 and NO, expressed as NO_x. In the end, the difference between the readings of the two pathways is determined electronically and gives the NO_2 concentration (CASA, 2005).

2.3.4 Particulate Matter (PM)

Particulate Matter is the general term used for a mix of solid particles and liquid droplets found in the air. According to Seinfeld (1997), particulate matter is “any substance, except pure water, that exists as a liquid or solid in the atmosphere under normal conditions and is of microscopic or submicroscopic size but larger than molecular dimensions”

2.3.4.1 Physical and Chemical Characteristics of Particulate Matter (PM)

Particulate matter includes both fine and coarse particles. The former refers to particles less than or equal to 2.5 micrometers ($PM_{2.5}$) while the latter refers to particles that are greater than 2.5, but less than or equal to 10 micrometers in diameter (PM_{10}) (Cheng et al., 2000; Tucker, 2000; USEPA, 1997; Vassilaskos, et al., 2005).

An additional peculiarity of particulate matter is that it can be formed in the atmosphere from other gaseous pollutants (de Nevers, 1995; Vassilaskos, et al., 2005); therefore, particles are also characterized as either primary or secondary. Primary particles are those that are formed during combustion, but may also consist of dust, small soot flakes, pollen, etc. Secondary particles consist mainly of sulphate and nitrate salts that are formed in the air from sulphur dioxide and nitrogen oxides (de Nevers, 1995; USEPA, 1997). Any source that emits these substances therefore contributes to their formation.

Atmospheric PM is a complex mixture of nitrate, sulfate, ammonium, trace element, and elemental and organic carbon (Hueglin et al., 2005). Fine particles are typically acidic while those in the coarse range are basic (Sandhu, 1998). Airborne particulate matters are characterized by their light density and small size. They have a long residence time and can travel long distances in the atmosphere (CEPA/FPAC, 1999). The chemical composition of particles depends on location, time of year, and meteorological situation (Vassilaskos et al., 2005). The source of origin and the process of formation usually influence their shape. Kantrinak et al. (1993) found that urban particles and combustion particles tend to have an irregular shape. Their physical properties affect the formation, growth, transport, and removal of particles. For small particles (≤ 1 µm), dry deposition and precipitation scavenging are the predominant removal mechanism, while for larger particles sedimentation is more appropriate (CEPA/FPAC, 1999).

2.3.4.2 Sources of Particulate Matter (PM)

Particles may arise from a wide variety of sources, natural or man-made. Natural sources include sea spray, pollens, fungal spores, or soil particles (de Nevers, 1995; Sandhu, 1998). For the soil-type fine particles, anthropogenic sources include road dust, dust from construction, dust from ore processing and refining, and dust from agriculture

(Namdeo and Bell, 2004; Sandhu, 1998). For carbon-type particles, sources are diesel vehicles, prescribed or open burning, wood stove and fireplaces, and boilers (DeGaetano and Doherty, 2004; Sandhu, 1998; Vassilaskos et al., 2005).

Generally, any activity that involves burning of materials or any dust generating activities are sources of PM. Sulphate is an important contributor to the PM in ambient air levels (Putaud et al., 2004). Combustion of fossil fuels such as coal or fuel oil is still an important source of SO_2 emission in many countries. A number of investigations on the impact of plumes of power plants and on the formation of sulphate from gaseous precursors in emission plumes have been carried out since the 1970s (Eatough et al., 1981; Newman, 1981; Williams et al., 1981). Once in the air, SO_2 oxidation, results in the formation of new particles in the PM range <1 μm (Jaecker-Voirol and Mirabel, 1989; Korhonen et al., 1999). In poor NH_3 and rich mineral dust or sea-spray environments, H_2SO_4 may react with mineral dust or sea-salt particles resulting in the formation of $CaSO_4$ or Na_2SO_4, which is in the coarse PM range (Moreno et al., 2003; Pio and Lopes, 1998; Querol et al., 1998).

In Canada, industrial activities, forest fires, non-industrial fuel combustion, and transportation were reported as the main sources of PM, especially $PM_{2.5}$ (Deslauriers, 1996). Other activities like incineration only contribute a small amount. In a study conducted in two major cities of Alberta, Edmonton and Calgary, Cheng et al. (1998) summarized characteristics of particulate matter and demonstrated that $PM_{2.5}$ loadings are higher during the winter. It was further demonstrated that a higher reaction of soil was found in the coarse fraction (55% to 65%) than in the fine fraction (7% to 8%). For rural areas, Sandhu (1998) reported that the background concentration for $PM_{2.5}$ in Alberta was low (3 to 6 $\mu g/m^3$), whereas that for PM_{10} was within 10 to 24 $\mu g/m^3$. The ratio of $PM_{2.5}$ to PM_{10} was about 0.3. Measurements made near significant local sources indicated that local and regional sources have considerable impacts on $PM_{2.5}$ and PM_{10} concentrations and can cause a significant increase (Sandhu, 1998).

2.3.4.3 Environmental and Health Effects

Effect on Human Health

When inhaled, particulate matter can accumulate in the respiratory system and is associated with numerous health effects (Vedal, 1995). Exposure to coarse particles is associated with the aggravation of respiratory conditions. Fine particles, which penetrate more deeply into the lungs, are most closely associated with such health effects as increased heart and lung disease, increased respiratory symptoms and disease, decreased lung function, and especially significant, premature death (CEPA/FPAC, 1999).

A large number of studies made both in the US and in Europe have shown that when the concentration of small particles in air rises, even from low levels, there is a rise in mortalities from respiratory, cardiac, and circulatory diseases, and more people seek hospital care for bronchitis and asthma (Burnett et al. 1995, Vedal 1996). Calculations have shown that in Austria, Switzerland, and France (Künzli et al., 2000) small particles (PM_{10}) at current levels in air gave rise to 40,000 premature deaths a year in these countries, and the average life expectancy of people living in an urban environment is reduced by 18 months. Furthermore, they initiate half a million asthma attacks each year which leads to a total of 16 million person-days of activity lost.

Although scientific studies have linked breathing PM to various health problems, it is still uncertain as to how exactly these particles cause damage (Sioss and Smith, 2000). It is believed that the very smallest particles are the most harmful because when they are inhaled they can penetrate quite deeply into the lungs (WHO, 2003). Their shape and chemical composition as well as their size are thought to enhance their capacity. The actual chemistry and processes that leads to the formation of $PM_{2.5}$ are yet to be clearly understood (Jones, 1996).

Adverse Environmental Effects

Due to their long persistency in the air, airborne particulate matters have a significant effect on distant vegetation (Smith, 1990). Because of acidic and heavy metal components, particulate matter deposition can damage vegetation as well as lead to acidic conditions in water and soil (USEPA, 2000). Fine particles in the atmosphere can cause visibility impairment through scattering and absorption of light (CEPA/FPAC, 1999). $PM_{2.5}$ scatters and absorbs light more efficiently than larger particles (CEPA/FPAC, 1999). The elementary carbon (EC) component in $PM_{2.5}$ can stain materials after deposition. Surfaces of historical buildings, monuments, and statutes deteriorate not only from the depositions but also additionally from the cleaning work required to remove them (CEPA/FPAC, 1999).

2.3.4.4 Guidelines and Standards for Particulate Matter

US Environmental Protection Agency (USEPA) Standards

The USEPA standards are based upon protecting public health as well as public welfare, material and ecological systems. Since 1971, under the U.S. Clean Air Act, the USEPA has set National Ambient Air Quality Standards (NAAQS) for airborne particles (USEPA, 2003). At the time, standards for PM emphasized particles smaller than 10 microns in diameter. Studies indicate that even finer particles (smaller than 2.5 microns) contribute more to adverse effects on human and were more responsible for visibility impairment (USEPA, 1997).

As a result, with advice from the Clean Air Scientific Advisory Committee, USEPA introduced new standards that focused more on fine particles in the atmosphere. The USEPA annual $PM_{2.5}$ primary standard is 15 $\mu g/m^3$ (USEPA, 2003). To attain this standard, the 3-year average of the arithmetic mean of 24-hour concentrations the must not exceed 15 $\mu g/m^3$. This concentration is measured from single or multiple population oriented monitors. The 24-hour primary standard, the 98th percentile of the distribution of the 24-hour concentrations for a period of 1 year, averaged over 3 years, must not exceed 65 $\mu g/m^3$ at each monitor within an area. The 24-hour and annual secondary standards are set the same as the primary standards.

Canada-Wide Standards

Previously, the Canadian national air quality objectives (maximum acceptable levels) for total suspended particulates were 120 $\mu g/m^3$ for a 24-hour average concentration and 70 for an annual mean, while the Alberta ambient air quality guidelines maintained a value of 100 and 60 $\mu g/m^3$ respectively (Sandhu, 1998). In June 2000, Canada-Wide Standards

(CWS), a new standard for particulate matter (PM) and ozone, was passed at a meeting in Quebec City in June 2000 (CCME, 2000). Ozone and PM were considered together as they share common sources and contributions to smog formation. The ozone standard is the 3-year average of the 4th highest daily maximum 8-hour average concentration and is set at a level of 65 ppb. The compliance date is 2010.

With respect to PM, a Canadian $PM_{2.5}$ standard of 30 ug/m^3 for 24 hours at the 98th percentile averaged over 3 years with a compliance date of 2010 was set (CCME, 2000). This was considered a much needed effort to achieve a long-term goal of reducing the risks of these pollutants to human health and the environment as a whole. As PM and ozone have common sources, and as they both contribute to smog, they have been included in the same CWS (CCME, 2000).

In addition, CCME (2000) maintained that individual jurisdictions should continue to apply their air quality objectives and/or guidelines for the coarse fraction of PM to guide management actions. It is further stated that in jurisdictions highly impacted by transboundary air pollution from the United States, exceedences of the two standards may not be entirely due to activities related to environmentally derived Canadian air pollution sources. Under such circumstances, achieving the CWSs will be strongly dependent on reductions of this transboundary contribution. Also, high background levels of PM and ozone that may occur as a result of natural events, such as forest fires, natural formation and stratospheric intrusion, need to be considered (CCME, 2000).

2.3.4.5 Monitoring Methods for Particulate Matter (PM)

In Alberta, particulate matter is monitored on a continuous (hourly) and as well as an intermittent (every sixth day) basis. PM_{10} and $PM_{2.5}$ are monitored on a continuous basis using the Tapered Element Oscillating Microbalance (TEOM) (CASA, 2005). In the TEOM an air sample is drawn in through an inlet stream and aerodynamically separates particles according to specified diameters (e.g. 2.5 or 10 μm). The air sample then passes through a filter that is attached to a tapered element in the mass transducer and the tapered element vibrates at its natural frequency. As particles are deposited onto the filter the oscillating frequency adjusts according to the amount of mass deposited.

$PM_{2.5}$ and PM_{10} are also monitored on an intermittent basis using a dichotomous sampler (Brook et al., 1997; CASA, 2005). Like TEOM, the sampler aerodynamically separates the particles into two size fractions, fine (<2.5 μm) and coarse (2.5 to 10 μm). Fine and coarse particles are collected by drawing a known volume of air through two individual pre-weighed filters for a period of 24-hour and then the total particulate concentrations in the respective size ranges may be calculated for the 24-hour period.

2.4 DISPERSION OF POLLUTANTS IN THE ATMOSPHERE

Air pollutants, when released to the moving, fluctuating atmosphere, are carried in many complex ways (Stern et al., 1973). They are most concentrated at the source. If there were no vertical or horizontal mixing of the atmosphere, a slug concentrated with the pollutant would stay in one place. However, the atmosphere is turbulent so it mixes the air around the release, diluting the concentrated slug and spreads it out, in a downwind direction, away from the location where the pollutant is seeping into the atmosphere. Even during relatively stable atmospheric conditions, known as atmospheric inversions, there is some mixing that occurs, carrying the pollutant away from the source of the release. The combination of winds and the tendency of warm air to rise to higher elevations will do two things to the pollutant that is released to the atmosphere (Colls, 1997):

> *Dilution:* The spreading out of the pollutant mixes it with a larger volume of air and the concentration is decreased;
>
> *Transportation and spreading:* The plume of pollution is carried away from the source and spreads out to cover a larger geographic area downwind from the release (Godish, 2004).

These two phenomena together form the action known as dispersion (Colls, 1997).

2.4.1 Meteorological Conditions Affecting The Dispersion of A Chemical

There are 5 primary meteorological factors affecting the concentration of air pollutants that determine how a given pollutant will disperse in the atmosphere (Colls, 1997; Godish, 2004; USEPA, 2005c):

Temperature: The higher the temperature, the faster the substance will evaporate from the source of the release to the surrounding air.

Wind Speed: The higher the wind speed, the greater the rate of spread of the chemical plume downwind, away from the release. The extent of the geographic area covered by a plume of the chemical is directly related to wind speed. Wind speed or velocity is influenced by topography. Movement of air near the earth's surface is retarded by frictional effects proportional to the surface roughness; so, wind speed will be greater farther from the ground surface.

Wind Direction: The direction of the wind will determine which geographic areas are affected by the plume of the chemical released to the atmosphere. Wind direction at the scene of a release is fickle. Localized wind can vary considerably in direction at any given time.

Atmospheric Stability: Stability is the tendency of the atmosphere to resist vertical motion or to suppress existing turbulence. This tendency directly influences the ability of the atmosphere to disperse pollutants emitted into it. When the stability is low, vertical motion is not suppressed and pollutants will disperse higher from the ground's surface. When this is occurring, the atmosphere is said to be unstable. Stability is measured by the variation of ambient air temperature with respect to the height above the ground. A stable atmosphere is one in which the ambient air temperature is greater further from the ground surface and an unstable atmosphere is one in which the ambient air temperature is less further from the ground surface. Stability and wind speed are related in that when the air near the earth surface is pushed down because of greater stability the wind speed increases. There is an analogy to that of fluid flow in pipes, in that as the cross-sectional area is decreased, the velocity must increase for the flow to remain the same (the law of continuity). If there is no wind, as on a calm day, it is worse to have a greater stability condition because the pollutants when emitted will tend to stay concentrated closer to the ground.

Humidity: Some chemicals are soluble in water vapor; hence, the higher the humidity, the higher the concentration of the chemical in the atmosphere close to the ground.

2.4.2 Topographic Considerations Affecting Dispersion

The topography of the terrain downwind of the release affects the way that the pollutant is spread and distributed into the community (Godish, 2004). In models, this consideration is referred to as ground roughness. In general, there are two extreme categories that need to be considered with regard to ground roughness (USEPA, 2005c):

Obstructions: The presence of hills, buildings, or other structures in the path of a plume of a chemical dispersing from a release will tend to keep a higher concentration closer to the source (with pockets of high concentration accumulating on the windward side of valleys or building walls). This condition is sometimes referred to as the "urban" condition (Alberta Environment, 2005b; USEPA, 2005c).

Flat terrain: A flat open terrain will carry the slug of chemical in the plume further from the source (affecting a greater area) and dilute it more (resulting in less dangerous concentrations). This is sometimes referred to as the "rural" condition (Alberta Environment, 2005; Godish, 2004; USEPA, 2005c)

2.5 DETECTING TRENDS OF POLLUTANTS IN AIR

2.5.1 Trend Analysis

Trend analysis is understood as the process of analyzing data to identify underlying longer-term trends. In other words, it can be considered as an aspect of technical analysis that tries to predict the future, based on past data (Blanchard, 1999). Detection of temporal trends is one of the most important objectives of environmental monitoring. In the case of air, routine monitoring of pollutants is extremely useful as a comparison of the pollutant emission changes with changes in ambient concentrations of pollutants. It potentially can provide information on the source-receptor relationship and is also used to evaluate the effectiveness of emission control program. The principal research question of interest is often whether or not a trend over time exists, and if it does, then how to characterize and quantify this trend. Other research questions of interest include comparing trends across seasons and comparing sites.

An important decision in temporal trend analysis is associated with the length of the period over which the trend is to be analyzed. Weatherhead et al. (1998) stated that detectability of a trend can be expressed in two ways. One is through precision of a trend estimate, measured by its standard deviation, and the other is through the number of years of data required to detect a trend of given magnitude using the trend estimate. Weatherhead et al. (1998) concluded that it takes a considerable length of time, several decades perhaps, of high-quality data to detect long-term trends likely to take place in nature. Periods shorter than that may not be representative enough of the long-term trends.

The utility of trend analysis depends on the magnitude of pollutant emission and reduction, the quality and length or record of the monitoring data, and the meteorology driven variations in ambient pollutant concentration (Blanchard, 1999). Air quality data typically do not fit a normal distribution. The data tend to be more skewed and exhibits a few, high concentration events; thus, trends in extreme values in a data set may differ significantly from trends observed in a statistic that describes the bulk of the data. Researchers developed a variety of statistical procedures to distinguish between random fluctuations and more persistent temporal changes. The following section discusses some of the relevant procedures.

2.5.2 Test for Trend Detection

The purpose of a trend test is to determine whether the values of a series generally increase or decrease, in statistical terms, over some period of time (Önöz, et al., 2003).

To answer a statistical question, the usual approach is to translate the question into a hypothesis - a statement that can be subjected to test. Depending on the results of the test, the hypothesis is accepted or rejected. The hypothesis to be tested is known as the null hypothesis (H_0), and for every null hypothesis, there is an alternative hypothesis (H_a). In the case of analyzing a trend, the null hypothesis H_0 that there is no trend, is tested against the alternative hypothesis H_a that a true trend exists.

Two primary types of trends may be considered in hypothesis testing and in trend estimation: step-trend and monotonic trend hypothesis (Hirsch et al., 1991; Kundzewicz and Robson, 2004). Hirch et al. (1991) defines step trend hypothesis as that where the data collected before a specific time are assumed to belong to a distinctly different population than the data collected after that time. The difference between the two populations is assumed to be one of location (e.g. mean or median) but not necessarily of scale (e.g., variance). The monotonic trend hypothesis is defined by Hirch et al. (1991) as where the population shifts monotonically, i.e., no reversal of direction takes place over time; however, it does not specify if the shifts occur continuously, linearly, in one or more discrete steps, or in any other specific patterns.

Kundzewicz and Robson (2004) relate that to compare between the null and alternative hypotheses, it is required to select a test statistic and then evaluate its significance, based on the available evidence. The test statistic, a numerical value calculated from the data series that is being tested, is selected so that it highlights the difference between the two hypotheses (Kundzewicz and Robson, 2004). Both parametric and non-parametric statistical tests can be used to decide whether there is a statistically significant trend.

Environmental data have proven to have many characteristics that complicate statistical analyses including non-normality, unequal sampling intervals (which often can be viewed as equal sampling intervals with missing data), seasonality, serial correlation, covariate effects, and the presence of outliers (Libsiseller et al., 2005). Several studies have attempted to compare the power and efficiency between and within parametric and non-parametric methods, in order to establish the most suitable methods for various probability distributions and to try to overcome the factors that complicate the analysis.

Hess et al. (2001) presented an overview of six commonly used statistical procedures for detection and estimation of linear trends. The methods discussed include (1) the Spearman partial rank correlation (SPRC) test, (2) the Seasonal Kendall test (with and without serial dependence adjustment), (3) regression on yearly averages, (4) the Generalized least squares with autoregressive (AR) errors, (5) the Komogov-Zebenko method and (6) a t-test. Through comparison, Hess et al. (2001) concluded that the t-test adjusted for seasonality (TAS) and the (original) Seasonal Kendall test are more effective than the remaining methods discussed. The conclusion was based on the ability of these tests' high α level (false rejection rate) and also on maintaining high power with different trend functions. It was however, indicated that the TAS has higher power than SK test when there is a step change trend.

In another study, Önöz and Bayazit (2003) evaluate the power of the parametric t-test with that of the non-parametric Mann-Kendall test. It is expected that a powerful test will reject a false hypothesis with high probability. Here, they found that the t-test is a bit more powerful when the probability distribution is normal; but, for moderately skewed distributions, the power ratio of the two types of test is close to one, suggesting that the t-test and the Mann-Kendall test can be used interchangeably. It has also been pointed out that non-parametric trend detection methods are less sensitive to outliers (extremes) than are parametric statistics.

In addition, a nonparametric test can test for a trend in a time series without specifying whether the trend is linear or nonlinear (Önöz and Bayazit, 2003). The problem for analysis of air quality data with the non-parametric methods is that these have some of the same shortcomings, namely, they entail the assumption that the observations are independent, and ignore the effect of covariates. Researchers are developing techniques and options to overcome the stated problems.

The following sections describe some statistical tests considered relevant for analyzing trends in air quality, namely, the Linear Regression, t-test, F-test, Seasonal Kendall test, and Mann-Kendall test.

2.5.2.1 Linear Regression

Linear regression tries to model the relationship between two variables by fitting a linear equation to the data under study (Harnett, 1982). A simple linear regression line has an equation of the following form:

$$Y = a + bX \tag{2.6}$$

Where, X is the explanatory variable or independent variable and Y is the dependent variable. Here, b represents the slope of the line, while a is the intercept (the value of Y when X = 0).

The most common method for fitting a regression line is the method of least-squares (Hays and Winkler, 1971). This method calculates the best-fit line for the data by minimizing the sum of the squares of the vertical deviations from each data point to the line (Spiegel, 1961). As the deviations are first squared, then summed, there are no cancellations between positive and negative values.

There, however, remains a question as to how useful the knowledge of the independent variable is in predicting the values of the dependant, the very attribute that is termed as "statistically significant" (Harnett, 1982). Thus to determine whether or not the estimation of the y values is improved by using the regression line, the null hypothesis needs to be tested.

One simple example of a test statistic is the linear regression slope which can be used to test for a trend in the mean (Kundzewicz and Robson, 2004). It is one of the most common methods of testing trends, has been applied for decades, and is well known (Slini et al., 2006). In its basic form, this approach assumes that data are normally distributed (Kundzewicz and Robson, 2004; Slini et al., 2006). Kundzewicz and Robson (2004) relate that if there is no trend (the null hypothesis), then the regression slope should have a value near to zero. Otherwise, if there is a large trend in the mean (the alternative hypothesis), then the value of the slope would be other than zero (being positive for increasing trend and negative for decreasing trend).

The level of significance, often denoted by α, measures whether the test statistic is very different from the range of values that would typically occur under the null hypothesis (Kundzewicz and Robson, 2004; Spiegel, 1961). It is defined as the probability that a trend is erroneously detected when none is present (Kundzewicz and Robson, 2004). The error of rejecting the null hypothesis when it is true is termed as Type I error (Harnett, 1982; Kundzewicz and Robson, 2004; Spiegel, 1961). The level of significance expresses the maximum probability the experimenter is willing to risk a Type I error. Another type of error occurs when the null hypothesis is accepted (i.e. no trend is present) when it should be rejected (the alternative hypothesis is true, i.e., a trend exists). The second type of error is termed Type II error (Harnett, 1982; Kundzewicz and Robson, 2004; Spiegel, 1961). In testing a given hypothesis, low type II error probability (i.e. the risk of incorrectly accepting the null hypothesis is low) indicates a powerful test, and more powerful tests are to be preferred (Kundzewicz and Robson, 2004).

2.5.2.2 t-Test

The t-test, a parametric test, is used to test the null hypothesis $H_0 : \beta = 0$, i.e., whether a linear trend is statistically significant. Its application in testing the significance of the slope is a very similar test to that about a population mean. A t-test can aid in detecting trends by checking whether the mean of first half of the data is statistically significant from the mean of the second half of the data. It is a simple method and requires no extensive statistical training; however, this test is applicable in the case of normally distributed random variables and is not suitable for serially dependant data (Hess et al., 2001). As the t-test is based on linear regression, it checks only for linear trends (Önöze and Bayazit, 2003).

If μ_1 is the mean of the first half of the data and μ_2 is that of the second half of data, then the approximate 95% confidence interval for the difference μ_2-μ_1 is as follows (from Moore and McCabe as is cited in Hess et al., 2001):

$$(\mu_2 - \mu_1) \pm t_{0.975,f}\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}} \tag{2.7}$$

where,

$$f = \frac{(s_1^2/n_1 + s_2^2/n_2)^2}{(1/(n_1-1))*(s_1^2/n_1)^2 + (1/(n_2-1))*(s_2^2/n_2)^2} \quad (2.8)$$

The hypothesis that there is no trend is rejected when the interval contains 0. It may be noted here that if the data contains odd number of years, the middle year may be omitted for simplicity in calculations (Hess et al., 2001).

Harnet (1982) presented a little different approach with the t-test. In this approach, a mean (β) is also tested. The population is assumed to be normal and the population's standard deviation is unknown. Here the sample statistics is taken as b, the hypothesized population's value is β_0, and the sample standard error is s_b (standard error of the regression coefficient b) where s_b is defined as follows:

$$s_b = s_e \sqrt{\frac{1}{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \quad (2.9)$$

s_e is defined by the following formula

$$s_b = s_e \sqrt{\frac{1}{\sum_{i=1}^{n}(x_i - \bar{x})^2}} \quad (2.10)$$

The value s_b is a measure of the amount of sampling error in the regression coefficient b. Now the null hypothesis, $H_0 : \beta = 0$, is tested by subtracting the hypothesized value β from b and dividing by the standard error of the regression coefficient. i.e.,

$$t_{(n-2)} = \frac{b - \beta}{s_b} \quad (2.11)$$

This statistic follows a t-distribution with (n-2) degrees of freedom (Harnett, 1982). The calculated value of t is compared with the critical value (t_c) of t obtained from a table of critical values for that statistic at (n-2) degrees of freedom.

If, $t < t_c$, the null hypothesis is not rejected (indicating no trend)

If, $t > t_c$, the null hypothesis is rejected (indicating a trend)

2.5.2.3 F-Test

The F-test is another analytic tool for testing the null hypothesis, H_0: $\beta = 0$. This test utilizes the measures of unexplained and explained variation (Harnett, 1982). The F-statistic is the ratio of explained to unexplained variation in the dependent variable after they have been adjusted for degrees of freedom (Harnett, 1982; Hays and Winkler, 1971). It can be used as a statistical test to evaluate the statistical significance of a trend. The hypotheses for the F-test are the same ones for the t-test on the slope, namely, H_0: $\beta = 0$ vs. H_a: $\beta \neq 0$ (where, β represents slope).

In order to create an F-test, a ratio of variances is needed: the variance explained (SSR), the variance unexplained, and the sum of squares total (SST). First, the mean square is needed for the F which requires the degrees of freedom (df) for dividing the Sum of Squares values. The procedure leading to the F statistic is presented in the following table.

Table 2.4 Parameters for an F-test (after www.upa.pdv.edu)

Source of Variance	Sum of Squares Abbreviation	SS Formula	Interpretation	Mean Square	F-test
Regression	*SSR*	$\sum(\hat{y}-\bar{y})^2$	Variation in the y variable explained by the regression equation. Deviation of the predicted scores from the mean. Improvement in predicting y from just using the mean of y.	$MSR = \frac{SSR}{1}$	$F = \frac{MSR}{MSE}$
Residuals (or error)	*SSE*	$\sum(y-\hat{y})^2$	Variation in the y variable not explained by the regression equation. Deviation of y scores from the predicted y scores. Error variation.	$MSE = \frac{SSE}{n-2}$	
Total	*SST*	$\sum(y-\bar{y})^2$	Total variation in y. Deviation of y scores from the mean of y.	Not used	

Intuitively, one would expect that if the model explains something, then the numerator should be greater than the denominator (Massart et al., 1989). If the values of the MSR are high relative to the values of the MSE, then a larger portion of the total variability of Y is explained by the regression line, implying that the null hypothesis should be rejected. If, however, the MSR is small relative to the MSE, then the regression line does not explain much of the variability in the sample values of y, and the null hypothesis would not be rejected. Thus, the null hypothesis H_0: $\beta = 0$ can be tested by using the ratio of the mean squares, MSR/MSE. This ratio can be shown to have an F-distribution with 1 and (n-2) degrees of freedom (df) (Harnett, 1982). As with the t-statistic, the calculated value of F is compared with its critical value (F_C). F_C must be found in a table of the critical values of the test statistic, using the appropriate degrees of freedom (i.e., the numerator degrees of freedom are k, and the denominator degrees of freedom are (n-k-1).

If $F_0 \geqslant F_C$, H_0 is rejected.

If $F_0 < F_C$, H_0 is not rejected.

H_0 is rejected if the computed "test" value of F (F = MSR / MSE) exceeds the tabled value of F for k degrees of freedom in the numerator and n-k-1 degrees of freedom in the denominator. Rejection implies that the regression fit is significant (i.e., it is meaningful and provides a reasonable model for the regional trend of the data set). In order to decide whether to accept or reject the null hypothesis, the level of significance (α) of the result is used ($\alpha = 0.05$ or $\alpha = 0.01$). This allows the determination as to whether or not there is a "significant change" in the trends, i.e., whether any change is a matter of chance, e.g. due to experimental error, or so small as to be unimportant. It should be noted that a significance test never proves a null hypothesis, only fails to disprove it. The null hypothesis has the priority and is not rejected unless there is strong evidence against it, or in other words it only indicates that there is insufficient evidence against H_0 in favour of H_a.

The above discussion shows that the F-test is equivalent to the t-test for H_0: $\beta = 0$, as they are both measures of the strength of the relationship in linear regression (Harnett, 1982). Harnett, (1982) further relates that the F-test has the advantage over t-test in that it can be generalized to a test of significance when there is more than one independent variable. On the other hand, the t-test is more flexible since it can be used for one-sided alternatives, while the F-test lacks this flexibility.

2.5.2.4 Seasonal Kendall Test

In the seasonal Kendall analysis, data are first blocked for a time division so that values from different time divisions will not be compared. This blocking prevents the seasonality of the data from invoking a trend and reduces variability when there is a seasonal effect (Hess et al., 2001; Libiseller et al., 2005; Wang et al., 2005). Often months are used as blocks (Hirsch et al., 1982, as cited in Wang et al., 2005). Here, the information from all the seasons is then aggregated by summing the individual S_k statistics and their variances. A positive S indicates a positive trend, while a negative S indicates a negative trend. Another good quality of this test is that missing values do not invalidate the test as long as the pattern of missing values is random (Wang et al., 2005). In power studies with independent seasons, the seasonal Kendall analysis has been shown to be a powerful choice for a general procedure when the overall monotonic trend is of interest (Hirsch et al., 1982, as cited in Hess et al., 2001). When the seasons are not independent, this method does not maintain appropriate alpha levels.

Sen's Estimator of Slope

In order to estimate the magnitude of the trend, Hirsch et al., extended the slope estimator proposed by Sen (1968) and Theli (1950) (Hess et al., 2001; Gilbert, 1987). If a linear trend is present, the true slope (change per unit time) can be estimated by using a simple non-parametric procedure developed by Sen (1968), using a rank-based linear models approach which he called an aligned rank approach (Gilbert, 1987). His method is based on the residuals of the fit. The method does not allow serial correlation and assumes no ties. This last point is a no a large problem because ties can be given average scores; but, serial correlation is a more difficult problem. Seasonality and covariate effects need to be taken into account as well.

2.5.2.5 Mann-Kendall Test

Kendall (1938) proposed a measure, *tau,* to measure the strength of the monotonic relationship between two variables, say x and y. Mann (1945) suggested using the test for significance of Kendall's *tau*, with one of the variables being time, as a test for trend. The test is well known as Mann-Kendall's test (MK), which is powerful for uncovering deterministic trends. The basic principle of Mann-Kendall (MK) test for trend is to examine the sign of all pair-wise differences of observed values. During the past two decades, applications in environmental sciences have given rise to several new MK tests. In 1984, Hirsch and Slack published a test for detection of trends in serially dependent environmental data collected over several seasons. Several other articles have been devoted to multivariate tests for trends in data sets representing a number of sites or variables (Lettenmeier, 1988; Loftis et al., 1989; Loftis et al., 1991).

CHAPTER 3 : METHODS

3.1 DATA

Pollutants and measurement techniques varied between the two stations (Tomahawk and Carrot Creek) along with observation periods. Data for meteorological parameters were not available in this study, although this would not limit the underlying purpose of trend analysis (Sandhu, 1999). Table 3.1 gives parameters, measurement techniques, and observation periods for the two stations. A detailed statistical analysis of historical ambient air quality of data of both stations, Tomahawk and Carrot Creek, has been presented in Appendix A.

Table 3.1 Study Observation Sites, Measuring Instruments and Observation Period for trend Analysis (after www.wcas.ca)

Stations	Parameters	Instrumentation	Observation Period
Tomahawk	Ozone (O_3)	Bendix 8002	1997-2004
	Sulphur Dioxide (SO_2)	TECO 42-CTL	1997-2004
	Nitrogen Dioxide (NO_2)	TECO 42-CTL	1998-2004
	Particulate Matters (PM2.5 PM10)	TEOM (A/B) PM10 TEOM (A/B) PM2.5	2000-2004
Carrot Creek	Ozone (O_3)	TECO 49-CTL	1998-2004
	Sulphur Dioxide (SO_2)	TECO 43-CTL	1998-2004
	Nitrogen Dioxide (NO_2)	TECO 42-CTL	1998-2004

Hourly concentration data were obtained in electronic format from West Central Airshed Society (Johnson, B. 2005). These data were obtained in temporal order of year, month, day and hour. Initially 8 years of historical data (1997 to 2004) were considered for O_3, SO_2 and NO_2, and 5 years (2000 to 2004) were considered for $PM_{2.5}$ and PM_{10}. Carrot Creek commenced data collection from 1998 and this station does not monitor for $PM_{2.5}$ and PM_{10}. The AMD (1989) suggests a minimum of 90% time of operation (% completeness) is required for each instrument and accompanying data recording system on a monthly basis for continuous ambient monitoring. For this study, an arbitrary cut-off of 80% completeness was used to determine whether to include an annual dataset in the trend analysis. This criterion represents 7,008 hourly values for an annual dataset and was judged sufficient for the purposes of this study. Although this criterion does not comply with the AMD (1989), it is similar to that used by others (i.e. 85% as used by Jo et al., 1999).

The 1999 dataset for Tomahawk had to be eliminated for O_3 and SO_2. Similarly, datasets for the years 1998 and 1999 for Tomahawk had to be eliminated for NO_2, and 2000 for $PM_{2.5}$. PM_{10} had to be dropped altogether from the study due to insufficient datasets (only 3 years out of 5 had >80% completeness). Similarly for Carrot Creek, the years 1998 and 1999 were eliminated for all three pollutants (Appendix A).

A thorough examination of data was initially performed and erroneous data patterns were removed from each dataset. If an hourly value was missing from the dataset, that specific hour was not included in the subsequent trend analysis dataset.

The median concentration (50th percentile) was used for representing the central value for an annual dataset. As most environmental data are usually skewed to the right (i.e. most data values are low and only a few values are high), the arithmetic mean would be biased by high concentrations (Gilbert, 1997; USEPA, 2002). Selected percentiles of the hourly concentrations for each pollutant were calculated for each year and scatter plots were generated. In addition, changes in the one-hour maximum and median concentrations were observed through their increase or decrease to obtain a solid overview of the monitoring data and in turn to supplement understanding of the trend analysis.

3.2 METHODS FOR TREND ANALYSIS

3.2.1 Temporal Behaviour Analysis

Temporal behaviour was studied through daily, day of week and seasonal trends. Diurnal patterns were computed as the average of all observations recorded for one particular hour in each of the 24 hours after Su et al. (2004a,b). For instance, the average O_3 concentration at 15:00 was calculated as the average of all 15:00 readings for the whole study period, regardless of day of week or season of year. In addition, 24 hours rolling averages were calculated for $PM_{2.5}$ to examine conformity to the Canada-Wide Standard after Su et al. (2004b).

3.2.2 Short-Term Trend Analysis

A different approach was adopted in this study for trend analysis compared to the more conventional use of only average and maximum concentrations, and frequency of exceedence of maximum concentrations above air quality criteria (Angle and Sandhu, 1986; Carslaw, 2005; Fuentes and Dann, 1994; Gehrig and Buchmann, 2003; Günes, 2005; Jo et al., 2000; Qin et al., 2004; Wolff et al., 2001). In the case of air quality in the West Central Airshed Society zone, where air quality is good most of the time, the exceedence of maximum concentrations above air quality criteria is not a frequent occurrence. Here, assessing observed air quality against criteria will not prove sensitive enough to detect changes to air quality. This study did not examine changes in concentration maxima over time. It examined changes in the "mid-to-upper-range" (50th to 98th percentiles) of the cumulative frequency distribution for pollutant concentrations over time, which represents more frequent air quality conditions.

The two approaches were formulated for analyzing trends:

- benchmark approach
- frequency of exceedence approach

3.2.2.1 Benchmark Approach

This approach consisted of trend detection using various percentiles of the hourly concentration dataset from each year. After screening the data, cumulative distributions were derived from the dataset of each year. The cumulative frequency distribution was used to determine the number of observations that lie above (or below) a particular value in a dataset. Data were sorted in an ascending order and ranked. The cumulative frequency was calculated by adding each frequency (rank) to the sum of its predecessors. The last value would always be equal to the total for all observations, since all frequencies would already have been added to the previous total.

Cumulative frequencies were expressed in percentages to obtain the percentile cumulative distribution for each year. Initially for each year every 5th percentile from the 50th to the 95th, and the 96th and 98th percentiles were used for trend analysis. Observing the noticeable changes in the trend from percentile to percentile, 6 percentiles, 50th, 65th, 80th, 90th, 95th and 98th, were selected as benchmarks for all final calculations (after Klemm and Lange, 1999). These percentiles were plotted with other years and trend lines were superimposed over each plot.

3.2.2.2 Frequency of Exceedence Approach

This approach employed frequencies (number of hours) in which various benchmark concentrations were exceeded each year. Benchmark concentrations were determined from the initial or baseline dataset for each pollutant (concentrations corresponding to the 50th, 65th, 80th, 90th, 95th and 98th percentiles for that initial year). For Tomahawk, the year 1997 was used for O_3 and SO_2, the year 1998 was used for NO_2, and the year 2000 was used for $PM_{2.5}$ as benchmarks. For Carrot Creek, all benchmark concentrations were selected from the year 1998 for all three pollutants. The number of hours (frequency) of exceedence of a particular benchmark concentration was recorded for each subsequent year. These frequencies were then plotted and fitted with trend lines.

3.2.2.3 Statistical Significance Test of Trends

The expected summary statistics in both approaches were assumed to be linear in a year to facilitate their plotting as a straight line and to allow analysis using simple linear regression.

As a final step, a hypothesis test at a significance level of $\alpha = 0.05$ was conducted for the best-fit lines to decide whether there was a statistically significant trend. The null hypothesis, H_0: $\beta=0$ (no trend), was tested against the alternative hypothesis, H_a: $\beta\neq0$ (trend) (Harnett, 1982). The parametric t-test was used to test H_0.

Another way of testing the null hypothesis was also examined – the F-test (i.e. using the measure of unexplained and explained variation) (Harnett, 1982). The F-test is comparable to the t-test for testing H_0: $\beta=0$ as they are both procedures of the strength of a relationship in linear regression (Harnett, 1982).

CHAPTER 4 : RESULTS

4.1 TEMPORAL VARIATION

Temporal variations were observed for the pollutants at the stations, Tomahawk and Carrot Creek. Only O_3 and $PM_{2.5}$ showed considerable variation and NO_2 to some extent. Results are presented in the following sections.

4.1.1 Tomahawk Station

At the Tomahawk station, O_3 and $PM_{2.5}$ showed significant diurnal and seasonal patterns. Some variation was observed in seasonal trends for NO_2. The results are discussed below.

4.1.1.1 Ozone (O_3)

Hourly Variation

Figure 4.1 shows the variation of concentrations of O_3 with hour of the day. Concentrations were averaged throughout the year, since the pattern is generally the same for summer and winter, long and short, high and low concentration months (Angle and Sandhu, 1986). Tomahawk station has a 16 ppb (32 $\mu g/m^3$) difference between the minimum average which occurs after sunrise, and the maximum average which occurs in the late afternoon. The distinct relationship with the hour of the day signifies the effect of the photochemical reactions of its formation (Su et al., 2004a). The daily peak appeared to occur between 15:00 and 16:00 and the daily minimum occurs at 7:00. The overall ground-level ozone concentrations in Tomahawk were found to be well below the AAQG value of 82 ppb/hour (164 $\mu g/m^3$) within the study period, with an average hourly concentration close to 30 ppb (60 $\mu g/m^3$).

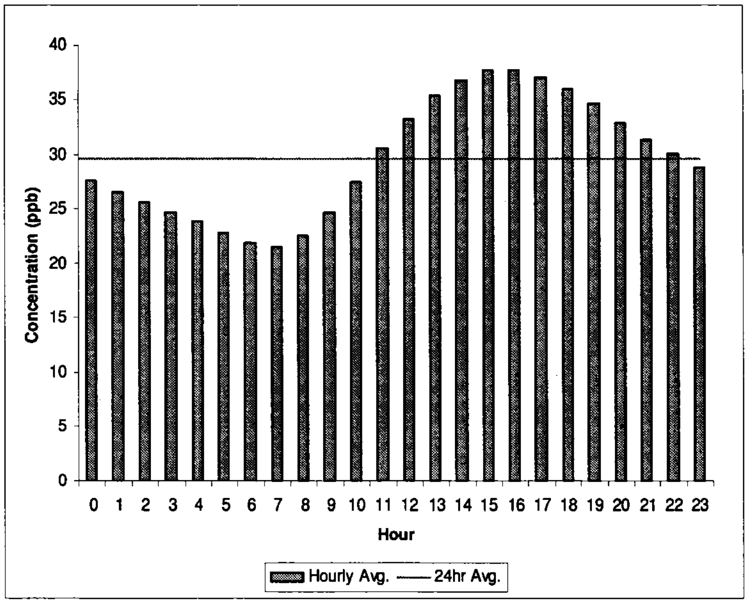

Figure 4.1 Tomahawk 1997-2004 Diurnal Hourly Average Concentration Trends for O_3

Weekly Variation

Very little variation was observed in the weekly average concentration pattern for ozone for all the years analyzed (Appendix D). Maximum hourly ozone values on the weekend did not show a discernible a pattern either, with only 2002 data showing marginally higher values as the week progressed (Saturday being the highest).

Monthly Variation

There was a well-defined seasonal variation in both composite mean and maximum O_3 concentrations at Tomahawk. The monthly trend of average hourly ozone concentrations increased during late winter, attaining their peak in April, then, the concentrations diminished steadily as the summer season progressed (Figure 4.2), reaching minimum O_3 concentrations between September and December. The monthly patterns for the maximum hourly ozone concentrations showed a different trend. Here the concentrations gradually increased from January and reached a peak in July, then decreased back as winter approached once again (Figure 4.3). Two exceedences of the AAQG occurred in July and one exceedence in June.

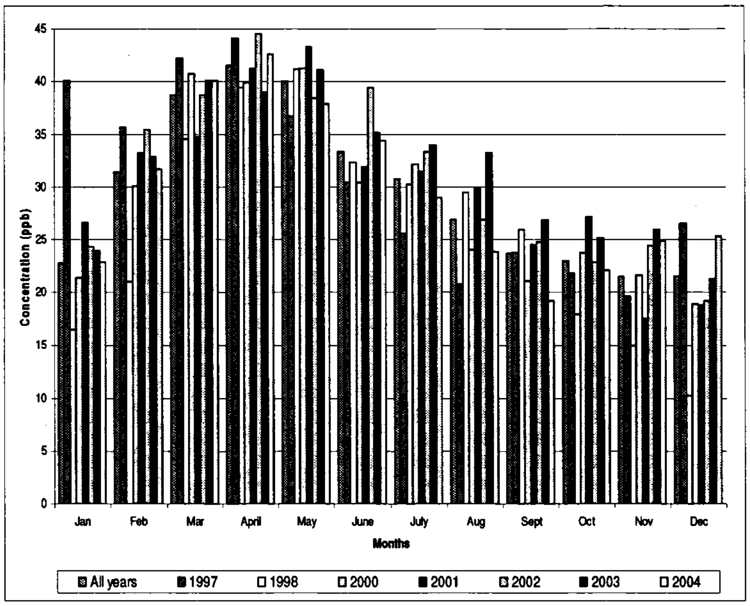

Figure 4.2 Tomahawk 1997-2004 Seasonal Trends for O_3 Based on Average Hourly Concentration

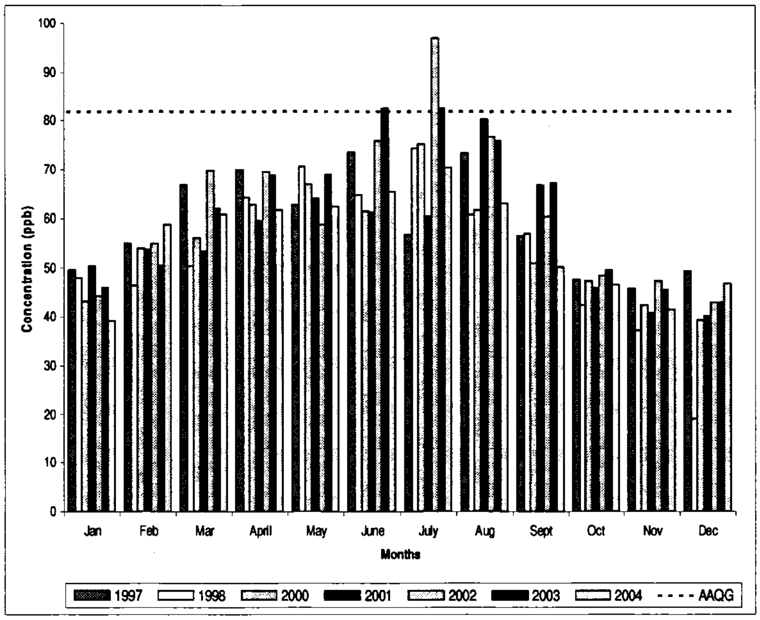

Figure 4.3 Tomahawk 1997-2004 Seasonal Trends for O_3 Based on Maximum Hourly Concentration

4.1.1.2 Particulate Matter ($PM_{2.5}$)

Hourly Variation

The daily values of $PM_{2.5}$ concentrations have been computed from the average values of each hour across the whole study period. The 24-hour rolling average remained close to 4 μg/m^3, which is considerably lower than the 2010 target value of 30 μg/m^3 of the CWSs. It is also well below the United States Environmental Protection Agency (USEPA) daily $PM_{2.5}$ standard, which is 65 μg/m^3 (established in 1997) (Vassilakos et al., 2005). Starting at a concentration of around 4 μg/m^3 at the zero hour, $PM_{2.5}$ concentrations showed a small daily peak at 9:00 am (Figure 4.4). The concentration then steadily decreased and remained below the 24 hr-average until it started rising again around 5:00 pm. A second and slightly higher peak was observed at 8:00 pm and although the concentrations decreased, they were observed to stay above the average in the last 3 hours of the day.

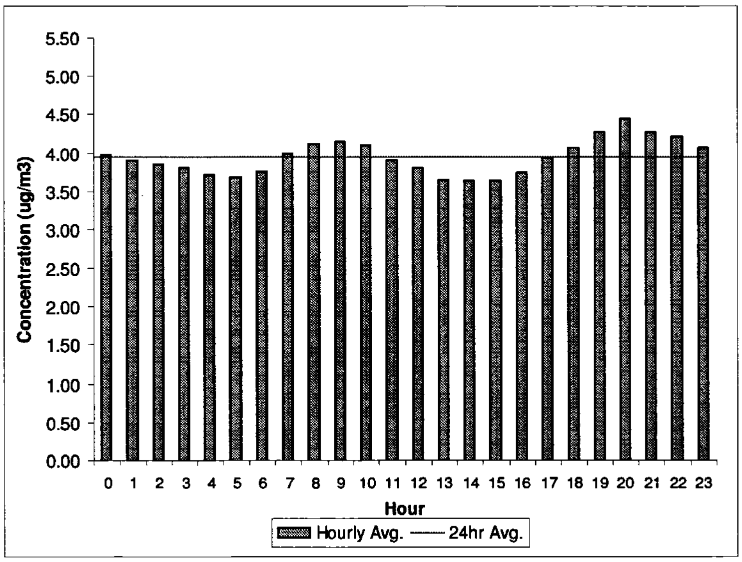

Figure 4.4 Tomahawk 2001-2004 Diurnal Hourly Average Concentration Trends for $PM_{2.5}$

Weekly Variation

In general, average hourly $PM_{2.5}$ concentrations are expected to be slightly lower on the weekends and uniformly high during the weekdays, regardless of season (DeGaetano and Doherty, 2004). The data for Tomahawk did not seem to relate to the day of the week

(Appendix D). The year 2002 might comply mildly to this pattern, while the rest of the years showed no such trend, in some cases even going opposite.

Seasonal Variation

No clear seasonal trend was apparent in the data of Tomahawk, despite the fact that on a number of occasions $PM_{2.5}$ has exhibited strong seasonal trends in previous studies (Hien et al., 2002; Laakso et al., 2003) (Figure 4.5). Sandhu reported (1998) that the typical behaviour of $PM_{2.5}$ levels in Alberta shows high values in winter, characterized by lowest mixing heights. At Tomahawk, relatively high values were observed during late summer (August) and then again in early winter (December).

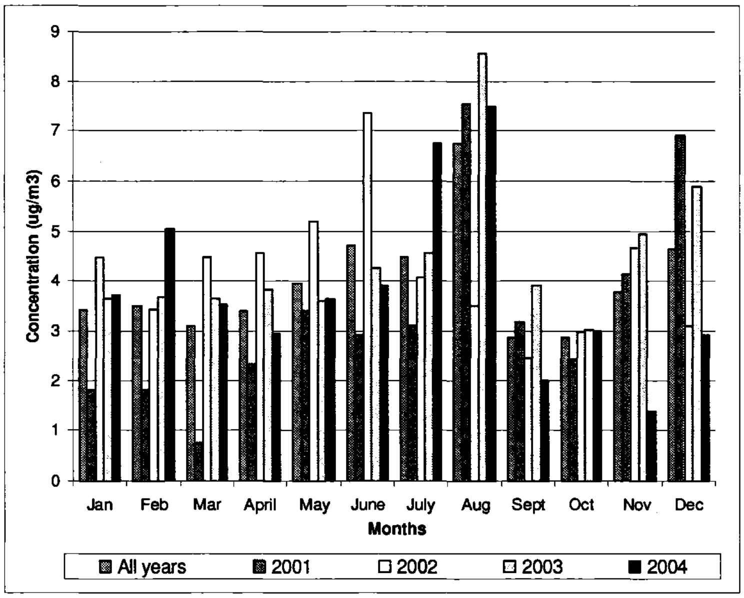

Figure 4.5 Tomahawk 2001-2004 Seasonal Trends for $PM_{2.5}$ Based on Average Hourly Concentration

The maximum hourly concentrations did not show a seasonal trend (Figure 4.6a). No trend was visible when the maximum of the 24-hour rolling average was examined (Figure 4.6b). However, one exceedence of the AAQG was observed in December, 2003.

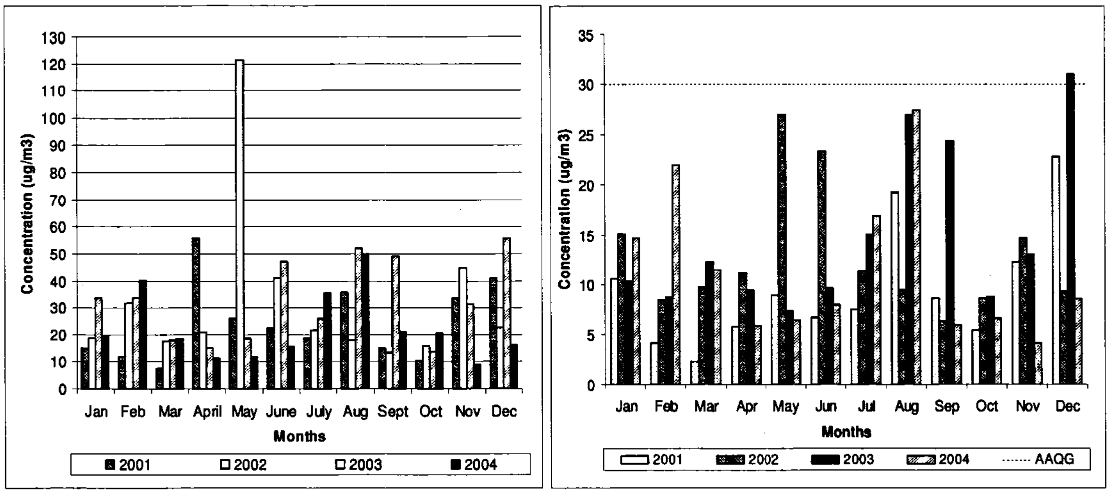

Figure 4.6 Tomahawk 2001-2004 Seasonal Trends for $PM_{2.5}$ based on (a) Maximum Hourly Concentration and (b) Maximum 24-hr Average Pattern

4.1.1.3 Nitrogen Dioxide (NO_2)

Average hourly concentration for NO_2 did not show a distinct diurnal pattern (Appendix D). Concentrations range from 3 to 6 ppb (6 to 11 $\mu g/m^3$). A dip was observed after noon with minimum concentrations at 2:00 pm. Otherwise, concentration remained almost constant during the 24 hours. No weekday/weekend effect was observed for the NO_2 concentration (Appendix D); however, the data reflected a clear seasonal variation (Figure 4.7). Monthly, NO_2 average hourly values were highest during the winter, and then gradually decreasing, reaching a minimum during the summer. The maximum hourly average has been recorded in December 2001 as 13 ppb (25 $\mu g/m^3$) and the minimum was around 1 ppb (2 $\mu g/m^3$) during June 2000. The monthly distribution for maximum hourly concentration did not show a discernible pattern (Appendix D).

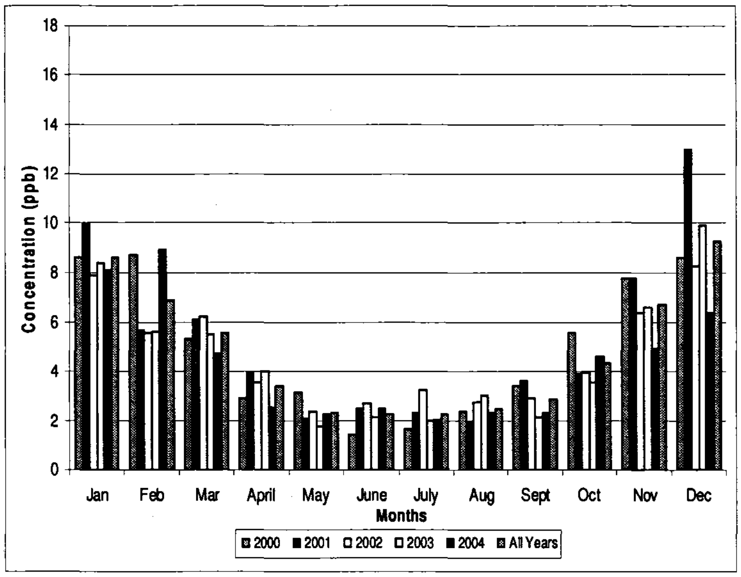

Figure 4.7 Tomahawk 2000-2004 Monthly Average Concentration Trends for NO_2

4.1.2 Carrot Creek

At Carrot Creek, variation was noticed in the diurnal and monthly trends of O_3 and in the monthly trend of NO_2 only. $PM_{2.5}$ was not measured in the station.

4.1.2.1 Ozone (O_3)

Hourly Variation

The hourly average ground-level ozone concentrations at Carrot Creek were largely below the AAQG value (82 ppb/hour) in the study period, with an average hourly concentration of 28 ppb (56 $\mu g/m^3$) and the 95th percentile value of 39 ppb (78 $\mu g/m^3$) (Figure 4.8). The association of the data with the hour of the day appeared to be very similar to the Tomahawk station. The ozone peak occurred between 15:00 and 16:00 and again at 4:00. The daily ozone minimum occurred at 7:00. During the early morning hours, concentration values remained quite low compared to Tomahawk and with no variation as opposed to the gradual decrease with increasing hours observed at Tomahawk. Also, the crest during the daytime was higher (and with more variability) than at Tomahawk.

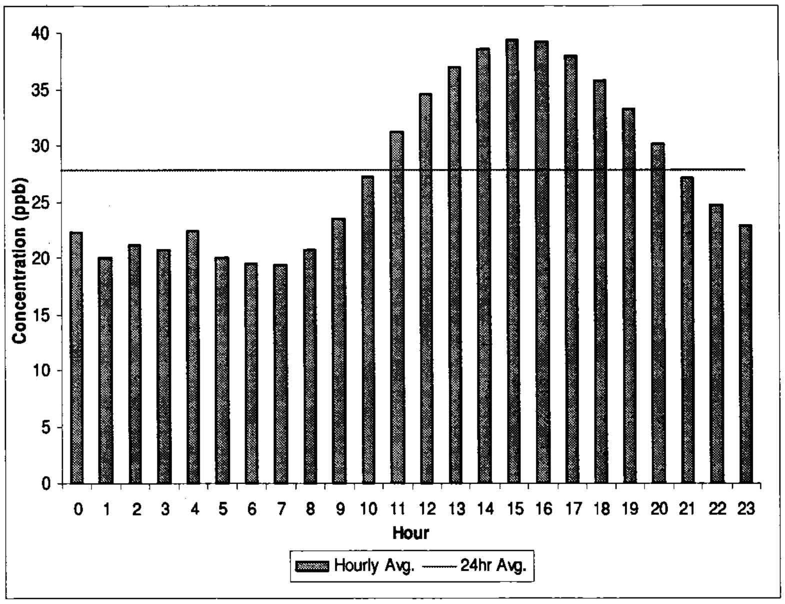

Figure 4.8 Carrot Creek 2000-2004 Diurnal Hourly Average Concentration Trends for O_3

Weekly Variation

The Carrot Creek station appeared to exhibit a weekly trend unlike Tomahawk, although not a very strong one (Appendix E). For all the years analyzed, low ozone values occurred during the beginning of the week, on either Monday or Tuesday. As the week progressed, average hourly ozone values rose slightly, reaching the highest values on Saturdays and Sundays. In the period 2000–2001, the weekend effect on O_3 became somewhat intensive at this station (Appendix E). Maximum hourly ozone values on the weekend show no definite pattern.

Monthly Variation

Once again, O_3 exhibited a similar seasonal variation to Tomahawk. The monthly trend of average hourly concentrations slowly increased during the late winter, with their peak attained between April and May (Figure 4.9). For most of the year, the maximum was in April, except in 2001 whose maximum was on May. A small, but visible second peak was attained in October. The values then diminished gradually with the minimum concentrations being recorded in December. Very much like Tomahawk, the monthly patterns for the maximum hourly ozone concentrations showed a different trend than the above (Figure 4.10). Though the trend was not as sharp as in Tomahawk, it was quite clear that the concentrations gradually increased from January and reached a peak in July, and then decreased back as winter was approached again. Here the increase from January to July was not as distinct as it was for Tomahawk. During this period, the maximum concentrations are somewhat closely distributed. Only one exceedence of the AAQG occurred and it was in July, 2002. The highest seasonal O_3 concentrations were lower at Carrot Creek than at Tomahawk for most of the study years.

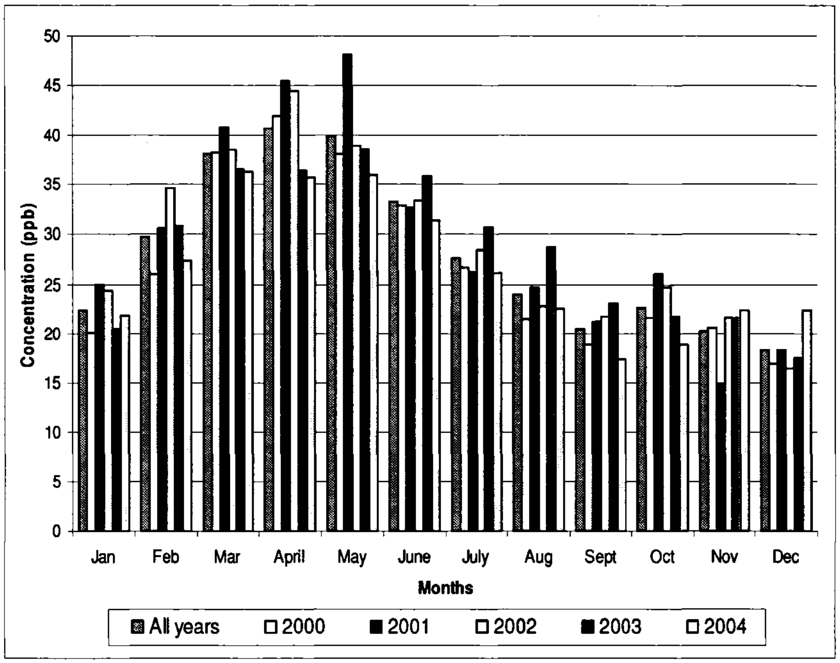

Figure 4.9 Carrot Creek 2000-2004 Seasonal Trend for O_3 Based on Average Hourly Concentration

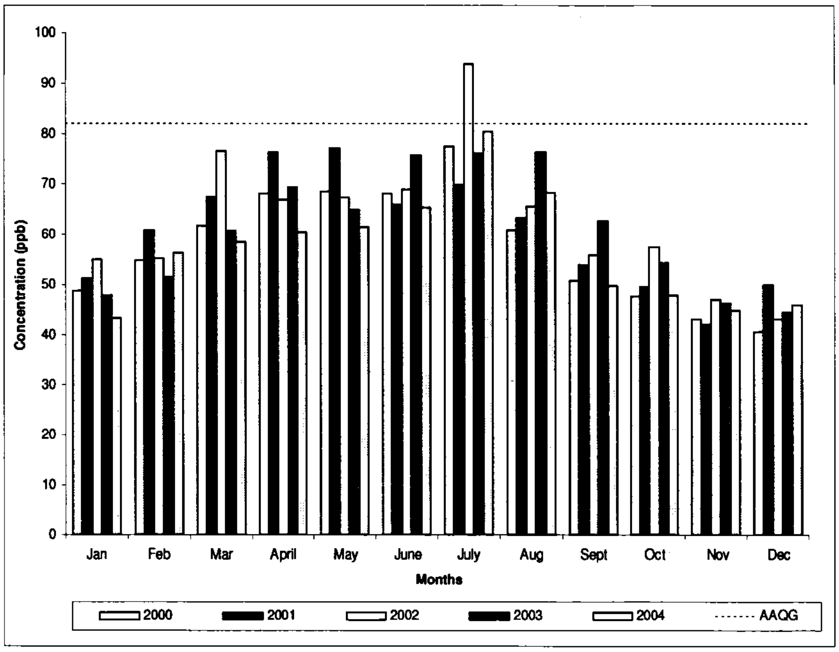

Figure 4.10: Carrot Creek 2000-2004 Seasonal trends for O_3 Based on Maximum Hourly Concentration

4.1.2.2 Nitrogen Dioxide (NO_2)

Average hourly concentration for NO_2 at Carrot Creek reflected a more defined diurnal trend than Tomahawk (Figure 4.11). Two peaks were observed. The first one occurred at around 9:00 and was immediately followed by a dip. The minimum was reached around 15:00 to 16:00. A sharp rise followed, reaching the second and higher peak at midnight (10 ppb ≈ 20 $\mu g/m^3$). No weekday/weekend effect was observed at Carrot Creek, which was expected for a rural area. As in the case of Tomahawk, the data reflected a clear seasonal variation (Figure 4.12). Monthly NO_2 average hourly values were highest during late winter or spring, followed by a gradual decrease towards a minimum summer concentration. The maximum hourly average was around 16 ppb (31 $\mu g/m^3$), recorded in February 2003, and the minimum was around 2 ppb (4 $\mu g/m^3$) during August 2003. The monthly distribution for maximum hourly concentration did not show any trend. Though concentrations at Carrot Creek were always well bellow the air quality guideline, they were observed to be higher than Tomahawk at most accounts.

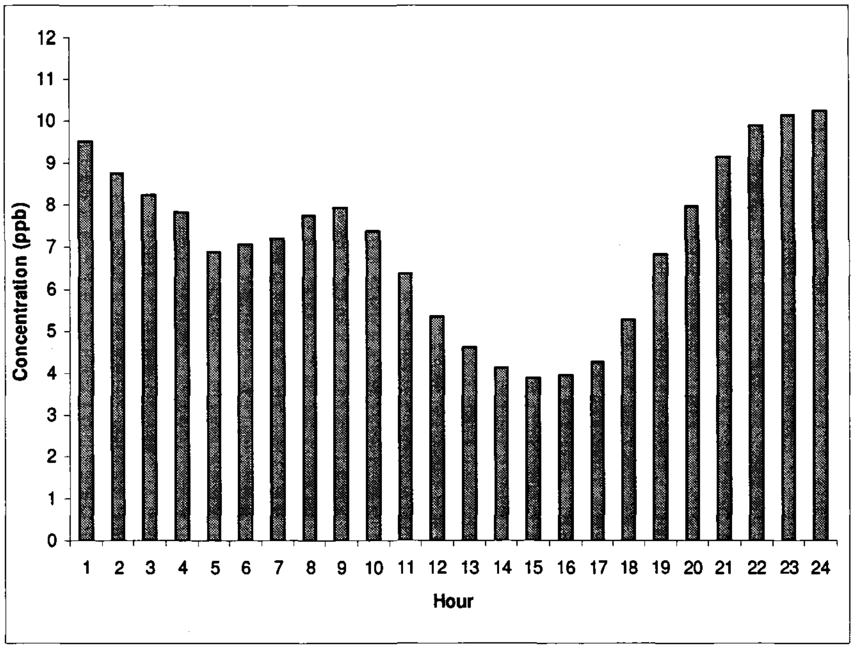

Figure 4.11 Carrot Creek 1998-2004 Diurnal Hourly Average Concentration Trends for NO_2

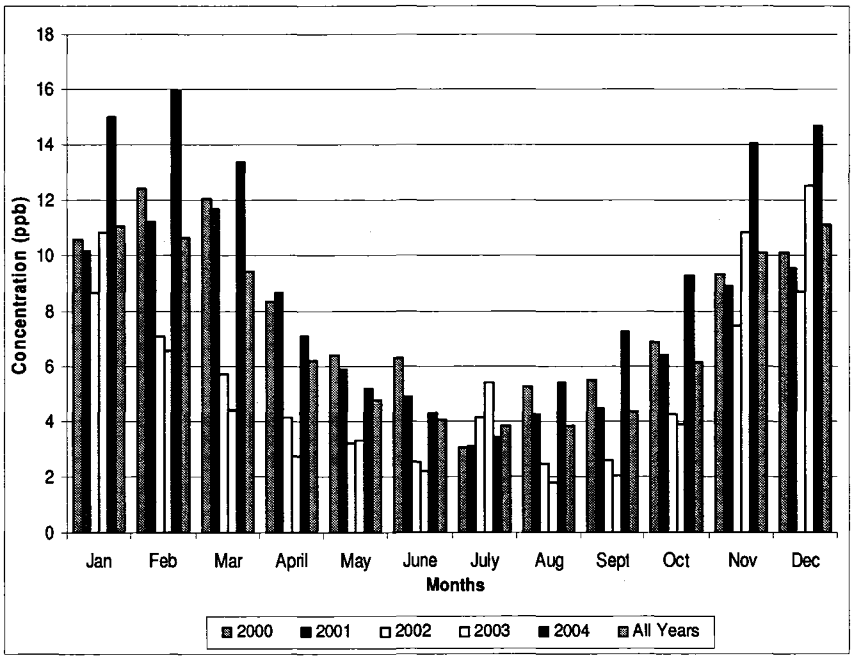

Figure 4.12 Carrot Creek 2000-2004 Monthly Average Concentration Trends for NO_2

4.2 SHORT-TERM TREND ANALYSIS

Trends were observed over a period of 7 to 8 years (varying with pollutants) at the stations Tomahawk and Carrot Creek for all pollutants. The results observed are presented in the following sections.

4.2.1 Tomahawk Station

Trends for ozone, sulphur dioxide, nitrogen dioxide, and particulate matter were analyzed at Tomahawk. The following sections discuss the results.

4.2.1.1 Ozone (O_3)

Cumulative Frequency Distribution

The hourly concentrations for O_3 were sorted in an ascending order to obtain a cumulative frequency distribution. This was carried out separately for each individual valid year. From the cumulative frequency distributions for 1997, 1998, 2000, 2001, 2002, 2003 and 2004, a general pattern was distinct. A typical distribution has been presented in Figure 4.13. (For all distributions, please refer to Appendix B). It appeared there was a sharp increase in the concentration only up to the 10th percentile, after which a gradual and steady increase followed up to almost 90th percentile. The charts indicated that almost in all cases 90% of the data fell within 50 ppb (100 $\mu g/m^3$) of the hourly concentration (Figure 4.13). Then again a relatively steep rise was observed in the distribution for the last 10%, reaching 70 ppb (140 $\mu g/m^3$) and more (varying from year to year). In general, 5% or less of the time the concentration reached a very high concentration (>70ppb). Aside from the common pattern, only the year 2002 showed the concentration going extremely high. For final analysis the 50th, 65th, 80th, 90th, 95th and 98th percentile values of the distribution (i.e., an emission rate that is expected to be exceeded only 50%, 35%, 20%, 5% and 2% of the time respectively) were selected to represent the benchmark concentrations reasonably expected to recur.

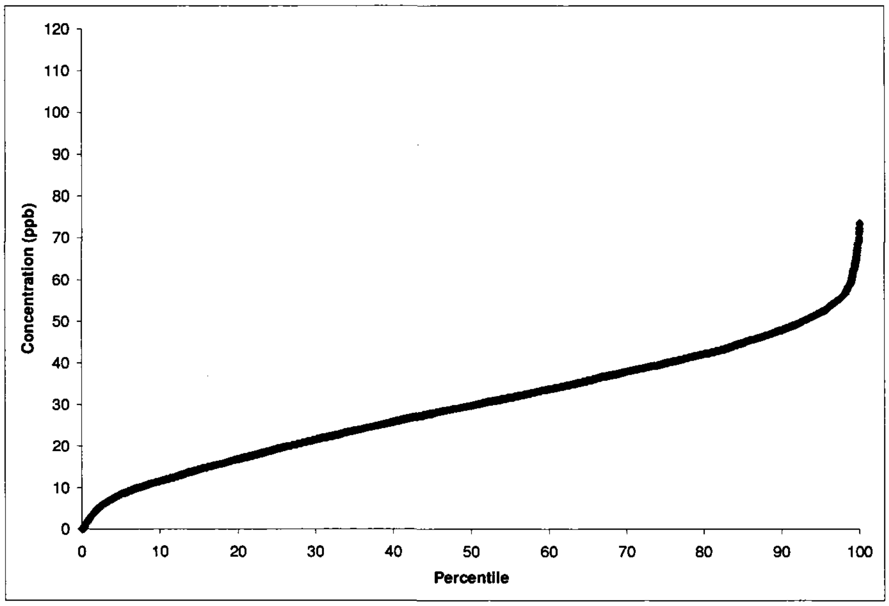

Figure 4.13: Carrot Creek 2000-2004 Monthly Average Concentration Trends for NO_2

Trend Detection Using Hourly Concentration

At Tomahawk, the maximum one-hour average O_3 concentration (97 ppb $\approx$ 194 $\mu g/m^3$) was recorded at 1:00 p.m. on July 13th, 2002. This maximum value exceeded the one-hour guideline of 82 ppb/hour (164 $\mu g/m^3$ per hour) average concentration of O_3. The second maximum was observed in 2003 marginally exceeding the guideline. There were no other exceedences recorded in the rest of the years, though the values lay close within the range of 70 ppb (140 $\mu g/m^3$) to 80 ppb (160 $\mu g/m^3$) (86 to 98% of the one-hour guideline). The median O_3 concentration over the years ranged from 27 ppb (54 $\mu g/m^3$) to 32 ppb (64 $\mu g/m^3$). Lower median O_3 concentrations were mostly observed from midnight to the early morning hours and higher median levels were more in the afternoon.

Despite rather high maximum hourly concentrations, minimal variation was observed when concentrations trends (i.e. best-fit lines) for all years together were analyzed. For the period examined at Tomahawk, a minor increasing trend was visually apparent at all percentiles (Figure 4.14). However none of the six trend lines proved statistically significant at $\alpha = 0.05$; indicating that no significant change has taken place in ozone concentration during the study period.

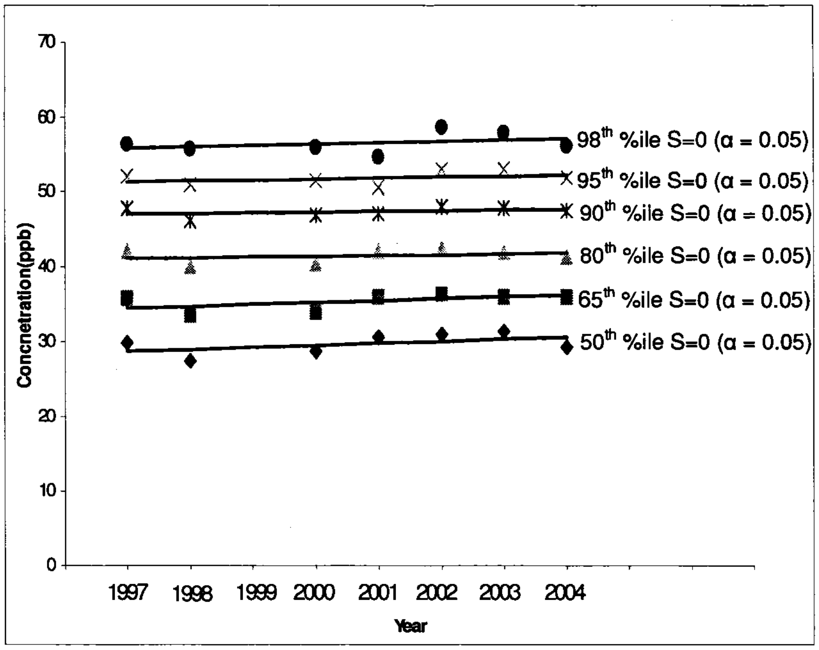

Figure 4.14: Concentration Trends for O_3 at Tomahawk at Different Percentiles

Trend Detection Using Frequency of Exceedence

Frequency of exceedences was understandably higher at the 50th percentile and gradually decreased as the percentile increased. At Tomahawk, the largest exceedence at the 50th percentile was observed in the year 2003 (55.15%). The second maximum was recorded for year 2002 with 53.14%. However, the peak shifted to year 2002 in the case for the rest of the percentiles. The years from 2001 to 2004 appeared to lie within close range of the maximum frequency of exceedence. This was most likely due to meteorological conditions that were favourable to O_3 formation during these years, especially the year 2002 (after Qin et al., 2004). It was noticeable that after the 80th percentile, year 2001 fell behind 2002 for the higher percentiles. The year 1998 evidently maintained the lowest number of hours of exceedence at all the percentiles, indicating a relatively clean year (after Qin et al., 2004).

Trends observed using the frequency of exceedences approach is presented in figure 4.15. From the analysis it was evident that the application of the second approach provided identical results as none of the trends proved to be statistically significant. Thus, the frequency of exceedence approach supported the findings of the previous approach that no significant change had taken place in O_3 concentration during the study period. A summary of the findings of the later approach is also presented in table 4.1.

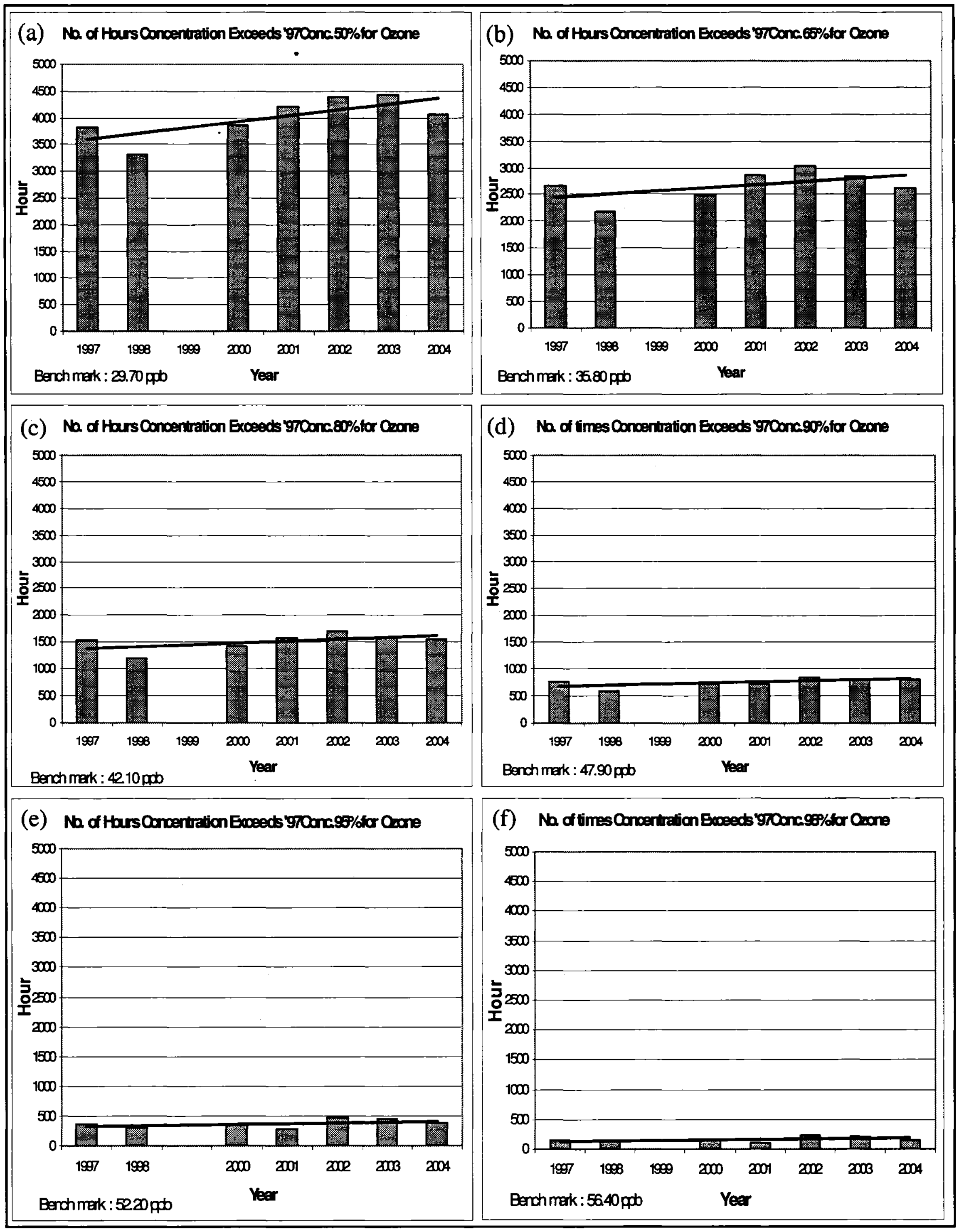

Figure 4.15 Trend Detection for O_3 at Tomahawk Using Frequencies of Exceedences of Various Benchmark Percentiles Each Year (a) 50%, (b) 65%, (c) 80%, (d) 90%, (e) 95%, (f) 98%

4.2.1.2 Sulphur Dioxide (SO_2)

Cumulative Frequency Distribution

A general pattern of distribution was clear from the cumulative frequency distributions for 1997, 1998, 2000, 2001, 2002, 2003, and 2004. The distributions lay very close to 0 ppb at least up to the 40th percentile for most of the years. For 2002, a rise was apparent only after the 70th percentile. For all years, a small, but gradual increase was apparent after the 40th percentile up to 90th percentile. It was apparent that in general, 90% of the data fell within the small concentration value of 2 ppb (5 $\mu g/m^3$) of hourly concentration (Figure 4.16). However, a very steep increase was observed for the last 10% for all years, reaching up to a maximum close to 7 ppb (19 $\mu g/m^3$) in 1997. All the distributions are presented in Appendix B.

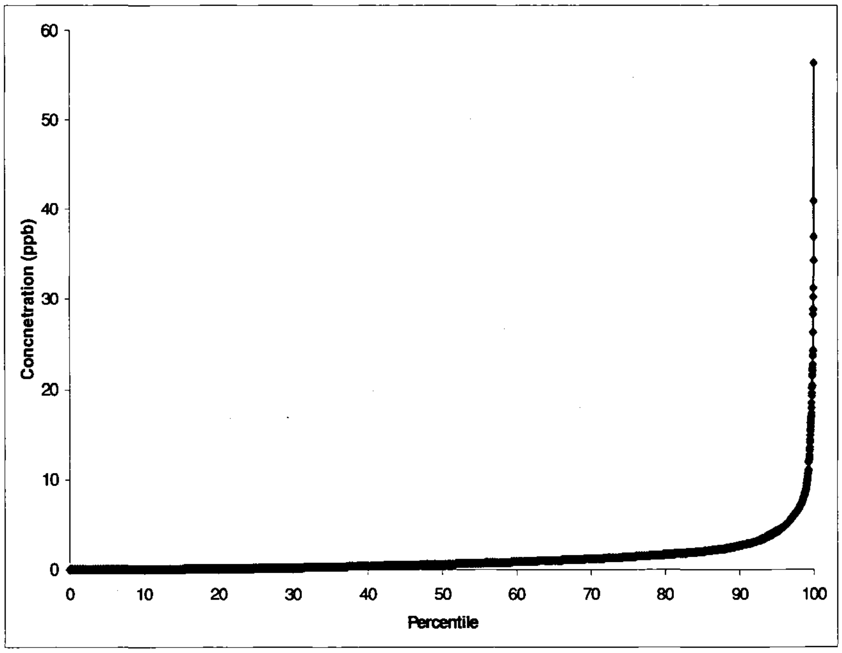

Figure 4.16 Percentile Cumulative Distribution of SO_2 at Tomahawk for 1997

Trend Detection Using Hourly Concentration

SO_2 concentrations at Tomahawk were found to be typically low, sometimes below the detection limit (21% at an average each year) and always below Alberta's one-hour guideline (1997-2004). The maximum one-hour concentration of 56 ppb (149 $\mu g/m^3$)

was measured at 4:00 p.m. on September 10th, 1997, which was 36% of the one-hour guideline for SO_2. Maximum concentrations in the other years ranged from 22 to 52 ppb (58 to 138 $\mu g/m^3$) or in other words, 14 to 33% of the one-hour guideline. Median SO_2 levels were quite low.

In trend analysis, it was observed that at Tomahawk, slopes were more and more steeply decreasing as the magnitude of the percentile increased (Figure 4.17). Within the changes in Tomahawk, trends at the 65th, 80th and 90th percentiles were found to be statistically significant at α=0.05.

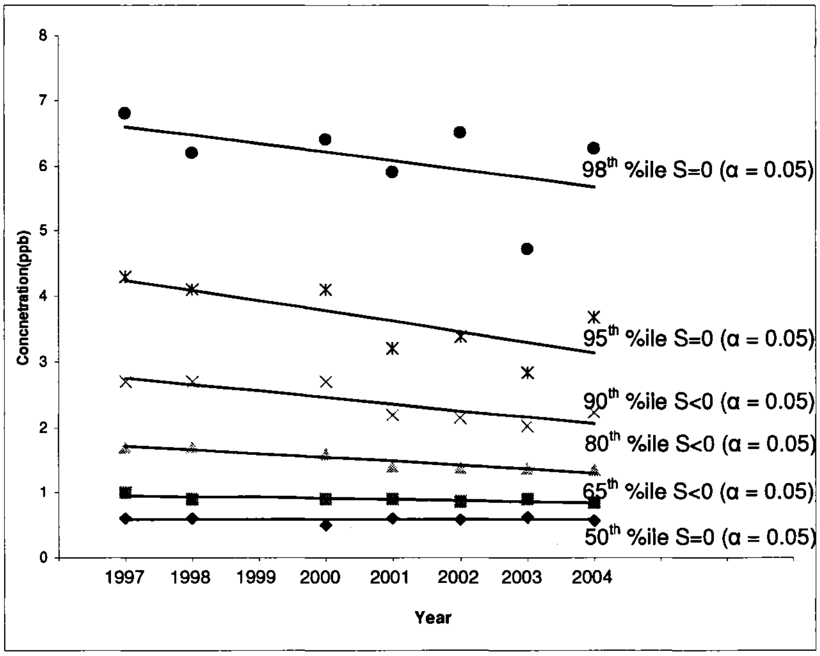

Figure 4.17 Concentration Trend for SO_2 at Tomahawk at Different Percentiles

Trend Detection Using Frequency of Exceedence

The distribution of the frequency of exceedences drastically changed from the 50th percentile to the 65th. At the 50th percentile, the year 2002 and 2003 exceeded the '97 benchmark concentration by 49.42% and 50.86%, respectively. Year 2004 remained close while the years 1998, 2000 and 2001 were lower than 1997. At the 6th percentile, all the years went below the year 1997 and almost similar patterns followed for the higher percentiles. Despite being among the higher ranges, the year 2003 showed quite low exceedences at the 80th, 90th, 95th and 98th percentiles. Although year 2000 started as with the minimum number of exceedences at the 50th percentile, it soon finished as one of the highest as the percentile increased and gradually decreased with the increase in percentiles.

From the 65th to the 98th percentiles, the trend of the number of hours of exceedences decreased rapidly. At the 98th it remained relatively flat (Figure 4.18). The results from the second approach presented almost the same outcome. SO_2 at Tomahawk showed observable decreasing trends at all percentiles except for the 50th percentile. Statistically significant decreasing trends ($\alpha = 0.05$) were observed at the 65th, 80th, and 90th percentiles, whereas a lack of statistically significant trends was observed at 50th, and then again at 95th and 98th. A summary is also available in table 4.1.

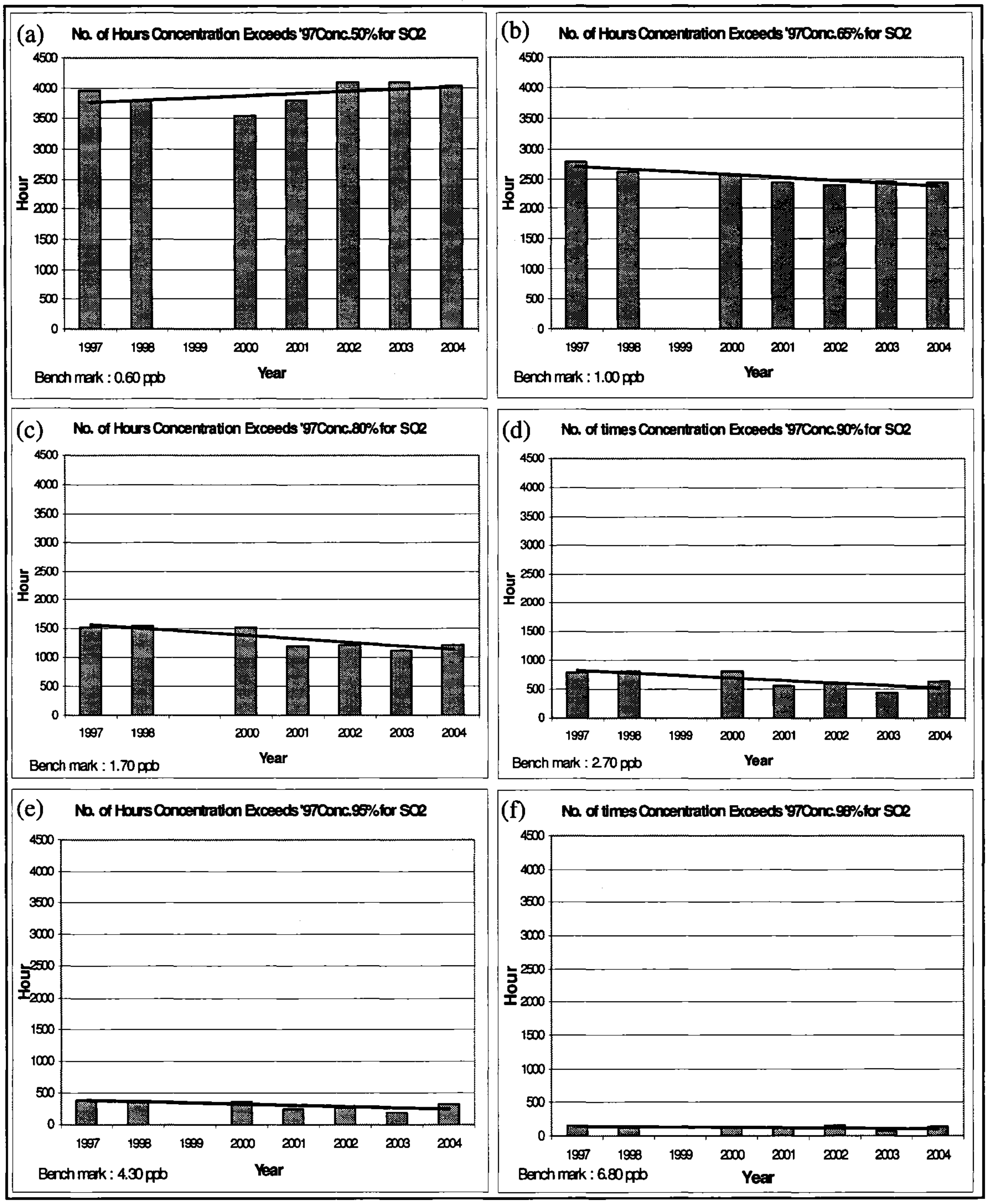

Figure 4.18 Trend Detection for SO_2 at Tomahawk Using Frequencies of Exceedence of Various Benchmark Concentrations Each Year, (a) 50%, (b) 65%, (c) 80%, (d) 90%, (e) 95%, (f) 98%

4.2.1.3 Nitrogen Dioxide (NO_2)

Cumulative Frequency Distribution

A typical percentile cumulative distribution for NO_2 has been presented in Figure 4.19 (All distributions are available in Appendix B). The distribution appeared a bit different from those of either O_3 or SO_2; in this case change was apparent from a very low percentile and also the change was gradual all the way to the higher percentiles. However, a general pattern of distribution was very conspicuous for NO_2 as well for all the valid years, i.e., 2000, 2001, 2002, 2003 and 2004. In most cases 60% of the data fell within the range of 5 ppb, and 90% fell within 10 ppb (19 $\mu g/m^3$). A sharp rise followed for the last 10%. About only 5% of the data were above 15 ppb (29 $\mu g/m^3$). Exceptionally high values were observed only in the year 2004. Once again, the 50th, 65th, 80th, 90th, 95th and 98th percentile values of this distribution were determined as the benchmark concentrations for final analysis.

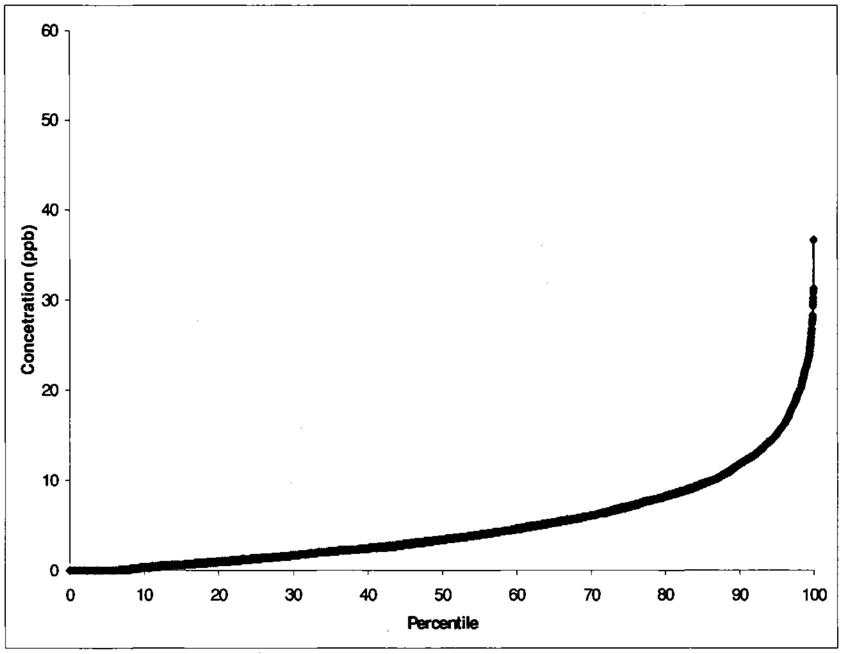

Figure 4.19 Percentile Cumulative Distribution of NO_2 at Tomahawk for 2000

Trend Detection Using Hourly Concentration

NO_2 levels were below Alberta's one-hour guideline during the study period. At Tomahawk the maximum NO_2 concentration was, 58 ppb (111 $\mu g/m^3$), recorded at 10:00

pm on February 24th, 2004, which is 27% of the one-hour guideline. However, the maximums of the other years were a bit low, ranging between 15 to 18% of the one-hour guideline. For this station, the median NO_2 concentration ranged from 2 to 4 ppb (4 to 8 $\mu g/m^3$).

At Tomahawk, decreasing trends were observed at all percentiles, among which the 65th, 80th and 90th percentiles were statistically significant (Figure 4.20).

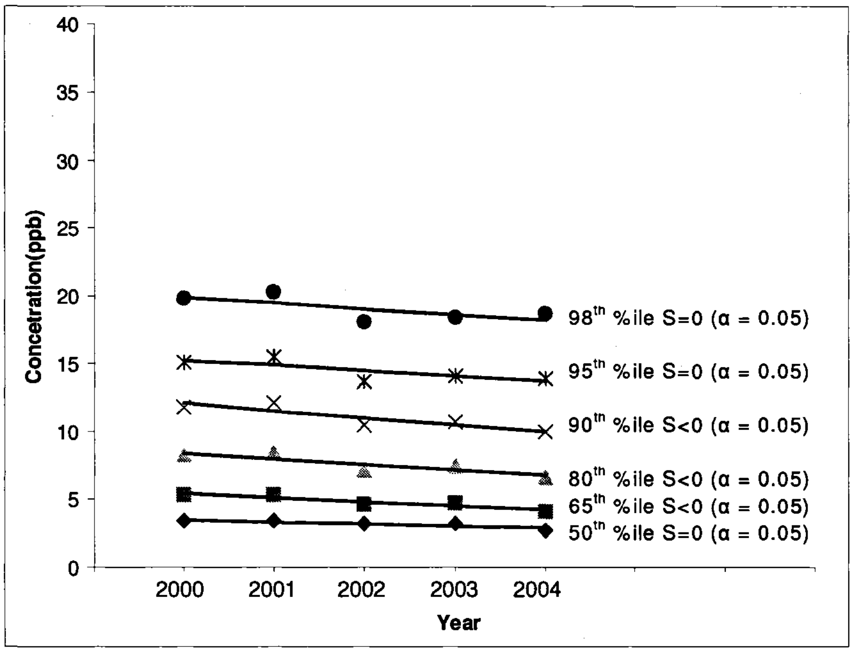

Figure 4.20 Concentration Trends for NO_2 at Tomahawk at Different Percentiles

Trend Detection Using Frequency Of Exceedence

The year 2004 showed an exceptionally low number of hours of exceedence of the benchmark concentration, while overall, the frequency decreased from 1997. The frequency in general appeared to decrease from the year 2000 onward at all percentiles, with 2000 being the highest with the frequency of exceedence at the 50th, 65th and 80th percentiles and 2001 leading from the 80th to 98th percentiles. At the 95th and 98th percentiles, the exceedences in 2002 became lower than even 2004. Hence, it could be observed that in case of NO_2, the state in 2002 was a little different than what has been previously observed for O_3 and SO_2.

Once again, the approach using the "frequency of exceedence" generated the exact same results as the first approach for NO_2 trend analysis at this station. A decreasing trend was observed at all percentiles (Figure 4.21), among which the 65th, 80th and 90th percentiles were statistically significant (Table 4.1).

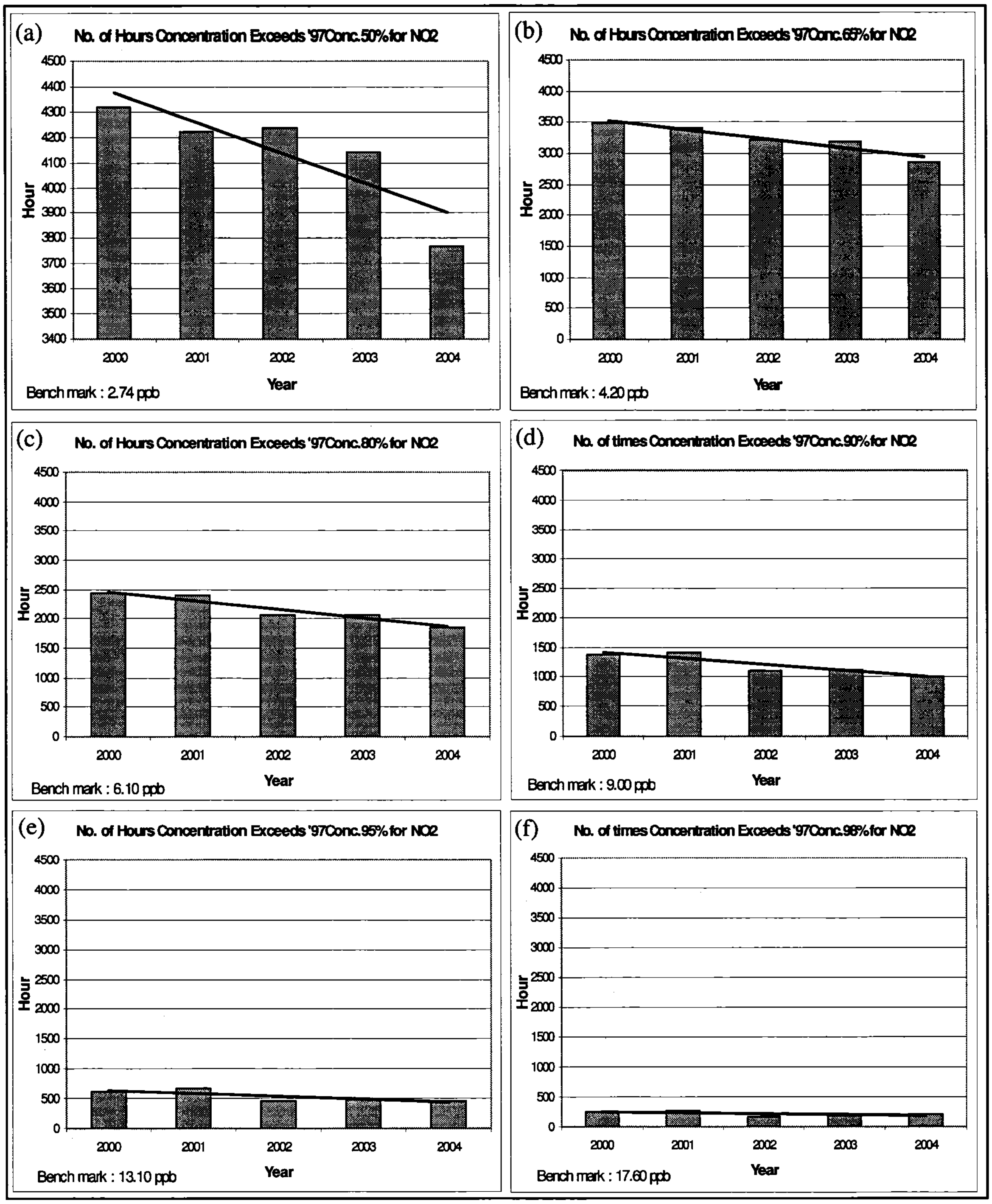

Figure 4.21 Trend Detection for NO_2 at Tomahawk Using Frequencies of Exceedence of Various Benchmark Concentrations Each Year, (a) 50%, (b) 65%, (c) 80%, (d) 90%, (e) 95%, (f) 98%

4.2.1.4 Particulate Matter ($PM_{2.5}$)

Cumulative Frequency Distribution

As mentioned earlier, of the two stations, Tomahawk alone measures particulate matter. The cumulative distributions for $PM_{2.5}$ showed less variation than O_3 and NO_2 but a bit more than SO_2. A general pattern of distribution was again followed through out the valid years, 2001, 2002, 2003 and 2004, an example of which has been presented in figure 4.22 (All distributions are available in Appendix B). In most cases, 90% of the data were below 10 $\mu g/m^3$, indicating low concentrations prevailing most of the time. The following sharp increase led to ±50 $\mu g/m^3$ for all years except 2002, which has an exceptional high value of 121$\mu g/m^3$.

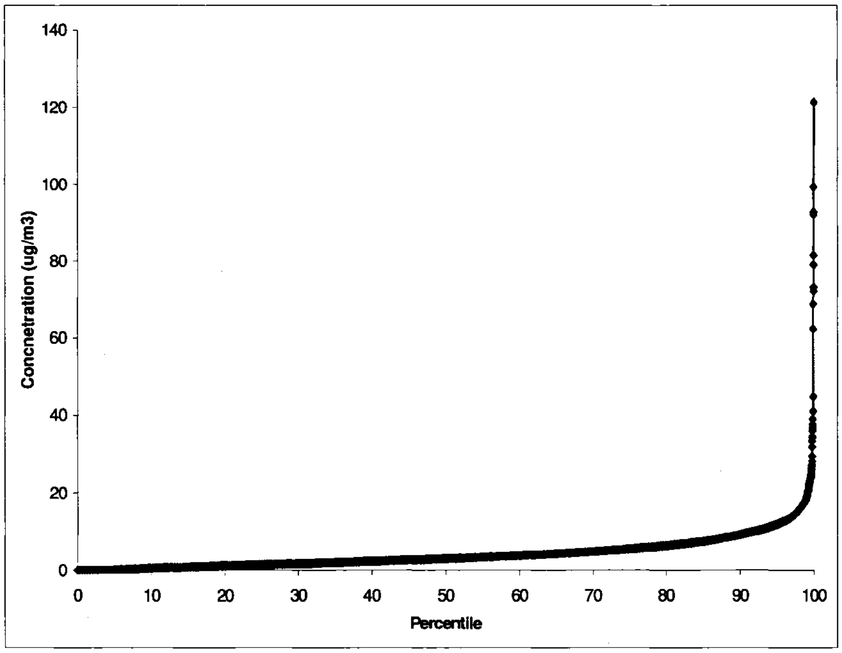

Figure 4.22: Percentile Cumulative Distribution for $PM_{2.5}$ at Tomahawk for 2002

Trend Detection Using Hourly Concentration

One very high particulate concentration was recorded at Tomahawk during the study period; 121 $\mu g/m^3$ at 10:00 pm on May 20th, 2002. No other maximum were this high. The maximum $PM_{2.5}$ concentrations recorded in other years were around 56 $\mu g/m^3$ or less.

Based on median concentrations, the highest particulate levels measured were 3 µg/m^3. The remaining median $PM_{2.5}$ levels were within 2 to 3 µg/m^3.

Increasing trends were apparent, especially at the higher percentiles (90th to 98th) (Figure 2.23). However, statistically none of the trends proved significant. Hence, despite the seemingly rising slopes, the current study approached the conclusion that at Tomahawk station, no significant change has occurred in the level of $PM_{2.5}$ throughout the study period.

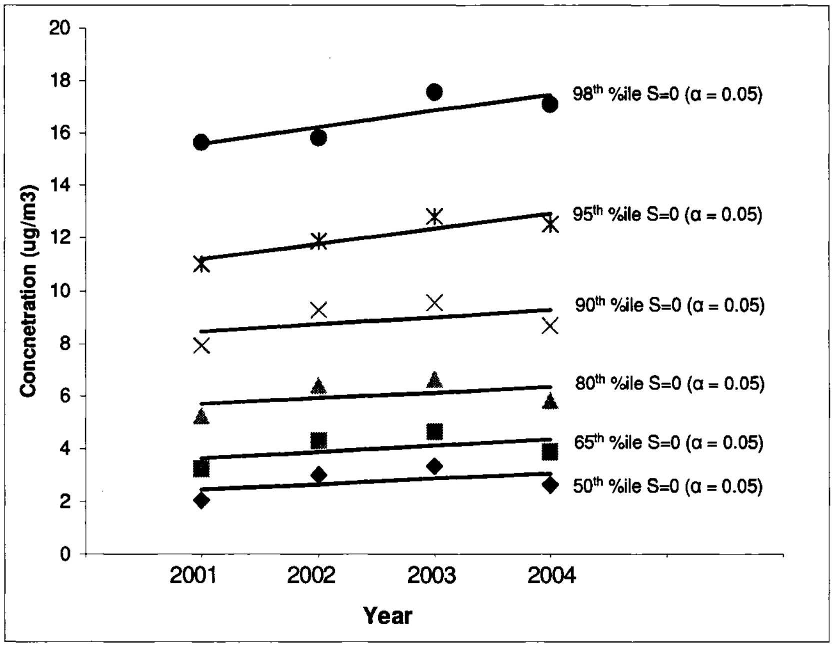

Figure 4.23 Concentration trend for $PM_{2.5}$ at Tomahawk at Different Percentiles

Trend Detection Using Frequency of Exceedence

The year 2002 and 2003 always had higher frequency of exceedence than 2001. That of 2004 was low though not lower than 2001. This pattern was observed at all percentiles except the 98th, where the year 2002 went below 2004. Year 2003 continued as the year with the highest frequency of exceedence through all six percentiles.

For trend analysis, the same results were obtained from the "frequency of exceedence" approach as the benchmark approach. All percentiles showed increasing trends, especially the higher percentiles (90th to 98th) (Figure 4.24). But then again, none of the trends proved to be statistically significant, leading to the conclusion that no significant change has occurred in the level of $PM_{2.5}$ throughout the study period.

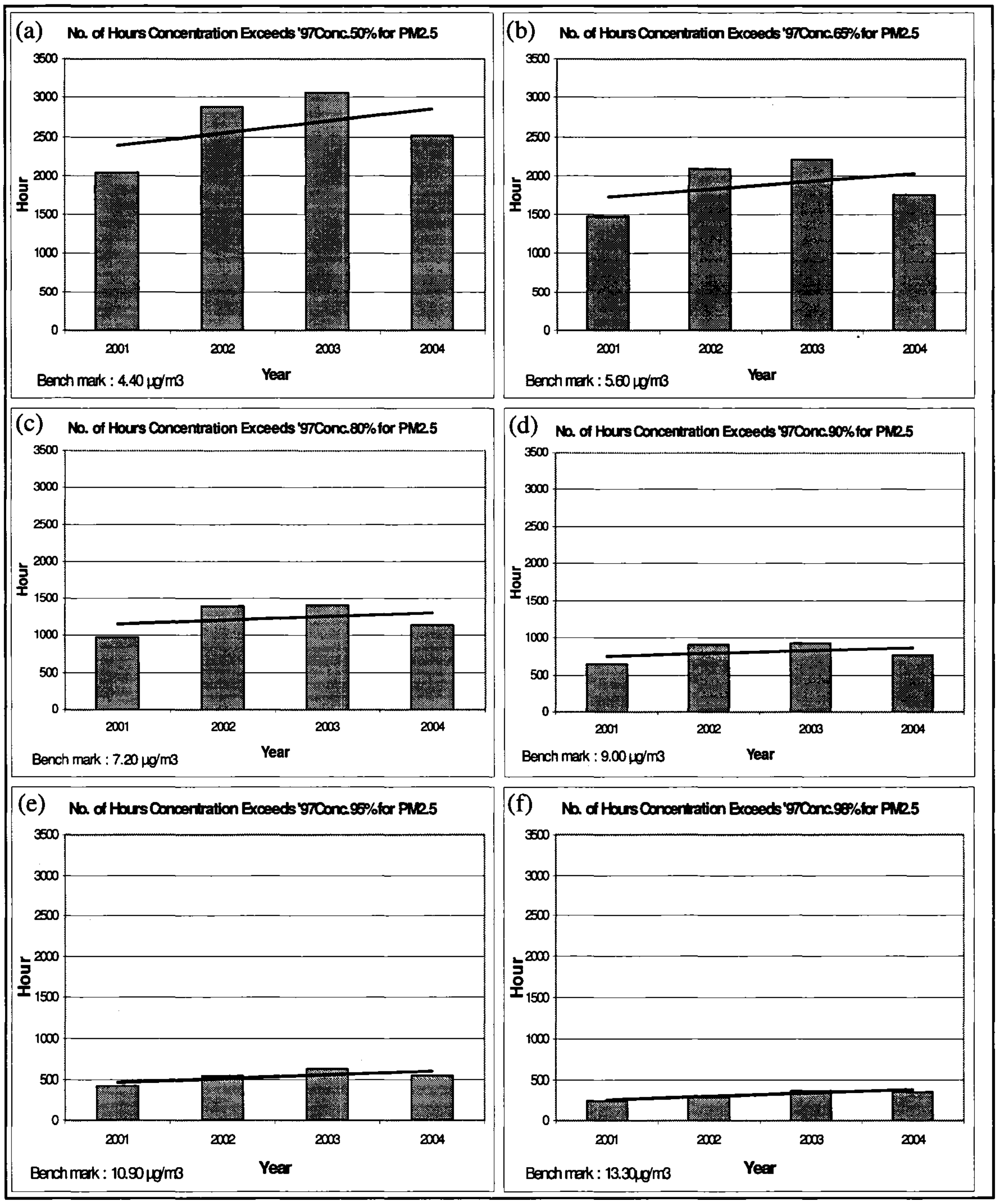

Figure 4.24 Trend Detection for $PM_{2.5}$ at Tomahawk Using Frequency of Exceedences Of Various Benchmark Concentrations Each Year, (a) 50%, (b) 65%, (c) 80%, (d) 90%, (e) 95%, (f) 98%.

4.2.2 Carrot Creek Station

The trend for ozone, sulphur dioxide, and nitrogen dioxide were analyzed at the Carrot Creek station. The observations have been discussed in the following sections.

4.2.2.1 Ozone (O_3)

Cumulative Frequency Distribution

From the cumulative frequency distributions of hourly ozone concentration for 2000, 2001, 2002, 2003, and 2004, a general pattern was distinct. The pattern was similar to what has been observed at the Tomahawk station, only that at Carrot Creek the rise appeared to be a bit steeper and the first 10% data changed very slowly compared to the sharp increase in the concentration up to the 10th percentile at Tomahawk. After that there was a gradual and steady rise up to almost 98th percentile. The charts indicate that almost in all cases 90% of the data lay close to 50 ppb (100 $\mu g/m^3$) of hourly concentration (Figure 4.25). In general, 5% of the time concentrations went higher than 52 ppb and only 2% of the times they went beyond 55 ppb (110 $\mu g/m^3$). Therefore, most of the time, reasonable concentrations were maintained at this station. As was done for Tomahawk station, the 50th, 65th, 80th, 90th, 95th and 98th percentile values of this distribution (i.e., an emission rate that is expected to be exceeded only 50%, 35%, 20%, 5% and 2% of the time respectively) were chosen to represent the benchmark concentrations.

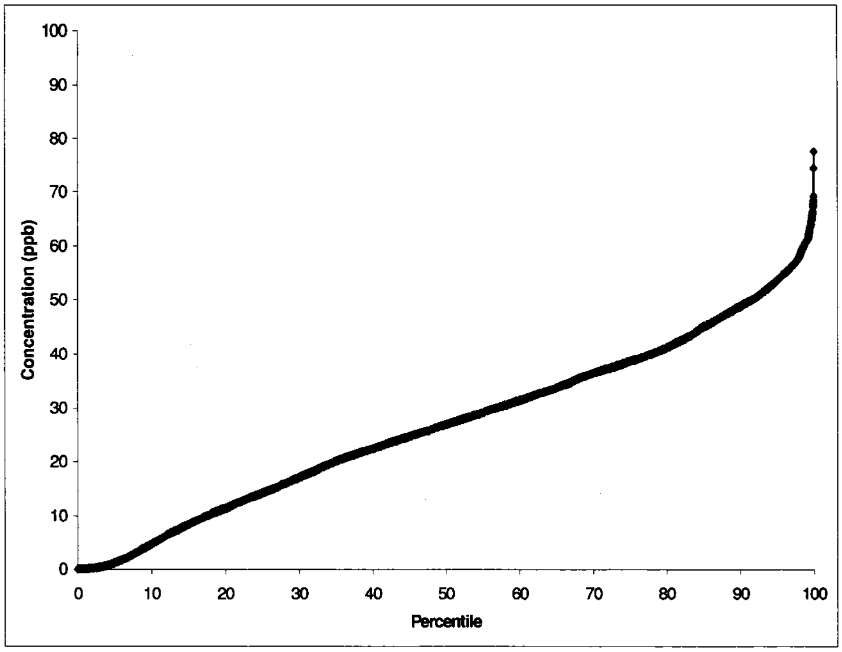

Figure 4.25 Percentile Cumulative Distribution of O_3 at Carrot Creek for 2000

Trend Detection Using Hourly Concentration

At Carrot Creek, once again the maximum one-hour average O_3 concentration (97 ppb ≈ 194 $\mu g/m^3$), recorded from 4:00 p.m. on July 17th, 2002, exceeded the guideline of 82 ppb (164 $\mu g/m^3$) for a one-hour average concentration of O_3. Although no other year recorded any exceedences, the maximum values of the rest of the years remained within a very close range of 93 to 98% of the one-hour guideline concentration. The median O_3 concentration ranged from 24 ppb to 30 ppb (48 to 60 $\mu g/m^3$). At Carrot Creek also, the lower median O_3 concentrations were mostly observed from midnight to the early morning hours and higher median levels in the afternoon.

At Carrot Creek, the picture was slightly different where the trends showed an apparent decreasing tendency, steeper at the higher percentiles (Figure 2.26). But as was the case with Tomahawk, here again none of the trends proved to be statistically significant.

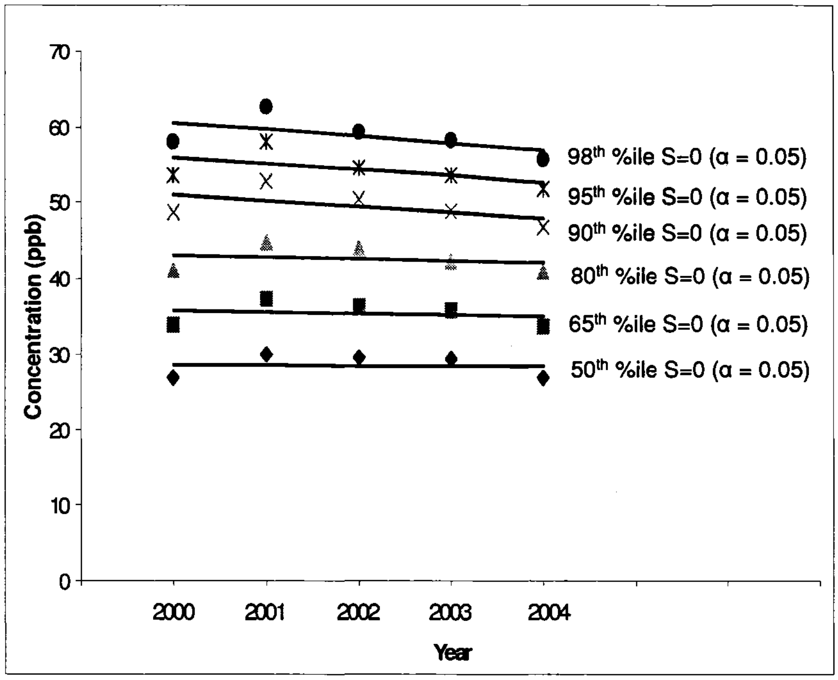

Figure 4.26 Concentration Trends for O_3 at Carrot Creek at Different Percentiles

Trend Detection Using Frequency of Exceedence

At the 50th percentile, the frequency of exceedences was highest for year 2002 (62.25%), while the years 2001 and 2003 stayed very closely (60.96% and 61.61% respectively). Like Tomahawk, this could also have been due to some meteorological conditions that could have favoured O_3 formation during these years, especially the year 2002 (after Qin et al., 2004). The year 2004 was slightly below 2000. But this distribution pattern was slightly different. From the 65th to 98th percentiles, the year 2001 now remained the year with the highest frequency of exceedence. At these percentiles, a decrease was observed for the years that followed. The lowest frequency was observed at the year 2004, although, the 98th percentile in 2000 showed the lowest frequency.

As expected, with the application of the approach of frequency of exceedence, identical results were obtained for ozone. The trends have been presented in Figure 4.27. Except for 50th, the rest of percentiles showed decreasing trends. Statistically all of them failed to prove significant. A summary of the results is also available in Table 4.1. Thus the findings supported the conclusion from the previous approach that no significant change has taken place in the ozone concentration during the study period.

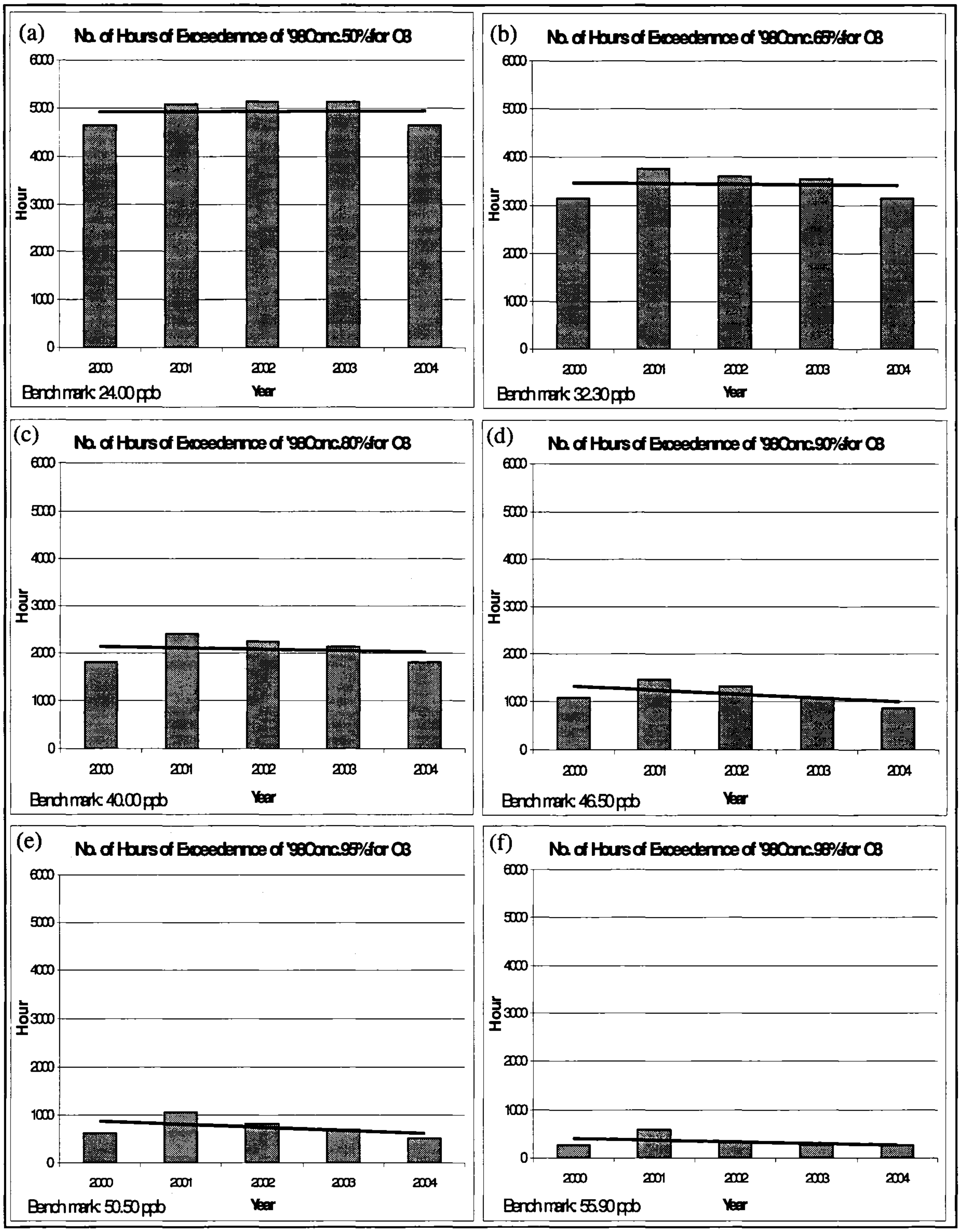

Figure 4.27 Trend Detection for O_3 at Carrot Creek Using frequency of Exceedence of Various Benchmark Concentration Each year, (a) 50%, (b) 65%, (c) 80%, (d) 90%,(e) 95%, (f) 98%

4.2.2.2 Sulphur Dioxide (SO_2)

Cumulative Frequency Distribution

The cumulative distribution for SO_2 at Carrot Creek was quite similar to Tomahawk. Here also, the hourly concentrations for SO_2 were typically very low. The data for each year were sorted individually from smallest to largest to obtain a cumulative frequency distribution. A general pattern of distribution was clear from the cumulative frequency distributions for 2000, 2001, 2002, 2003, and 2004. A sample has been presented in Figure 4.28. (For all distributions please refer to Appendix C). 20% of all data lay very closely to 0 ppb. A very mild but steady increase followed after the 20th percentile. The chart indicated that 80% of the data were below 2 ppb (5 $\mu g/m^3$). Up to 95%, the change was rapid but not too great. Variation at the 98th percentile was not significantly large either except that the year 2000 went higher than any others.

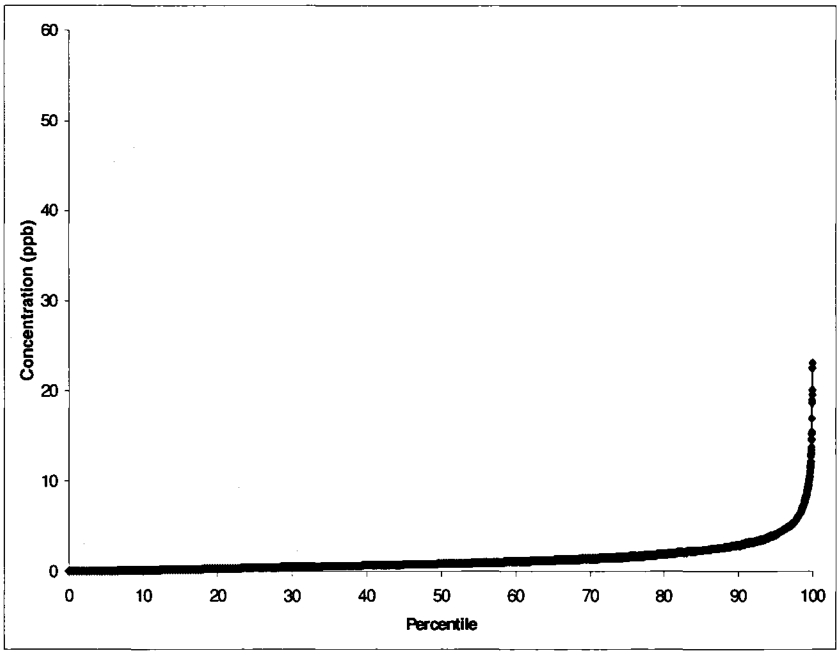

Figure 4.28 Percentile Cumulative Distribution of SO_2 at Carrot Creek for 2000

Trend Detection Using Hourly Concentration

At Carrot Creek, SO_2 concentrations were typically low and never exceeding Alberta's one-hour guideline. On average about 14% of the data was non-detects each study year. The maximum the SO_2 levels were even lower than at Tomahawk (2000-2004). The maximum one-hour concentration of 54 ppb (144 μg/m^3) was measured at 12:00 noon on May 28th, 2004, which is about 34% of the one-hour guideline for SO_2. Those in the other years ranged between 12 to 19% only of the one-hour guideline. However, the median SO_2 levels appear to be a little higher and with more variation than Tomahawk, 1 ppb (3 μg/m^3) as the highest median on 2000.

When trend analysis was conducted over the 5 years, similarities were pronounced between this station and the previous, with some variations in the details. Trends at Carrot Creek appeared more well-defined; decreasing through all percentiles (Figure 4.29). Statistically the trends at 50th, 65th, 80th and 90th percentiles proved to be significant trends.

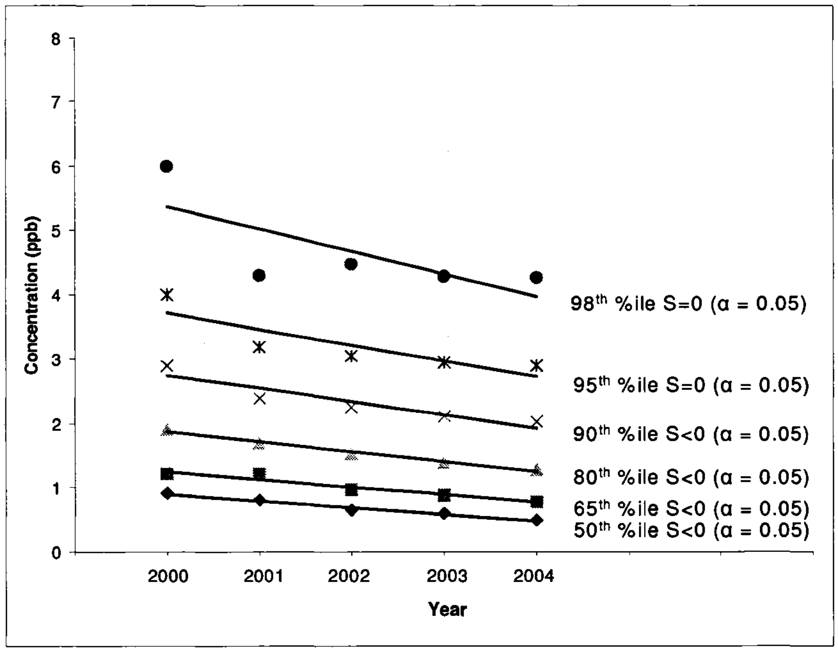

Figure 4.29 Concentration of SO_2 at Carrot Creek at Different Percentiles

Trend Detection Using Frequency of Exceedence

A clear decrease in the number of hours of exceedence was observed from the 2000 to 2004 (Figure 4.30). Only the year 2002 topped 2001 at the 95th and 98th percentiles, while 2003 proved to be higher than both 2002 and 2001 at the 98th percentile.

Nonetheless, the year 2000 was higher than any other year by a significant margin at all percentiles. Compared to that, 2004 showed significantly lower frequencies.

Trend detection using the frequency of exceedence of benchmark percentiles provided identical results. Trends at Carrot Creek decreased through all percentiles (Figure 4.30), among which trends at the 50th, 65th, 80th and 90th percentiles were significant decreasing trends ($\alpha = 0.05$) (Table 4.1). A lack of statistically significant trends was observed at higher percentiles (95th and 98th).

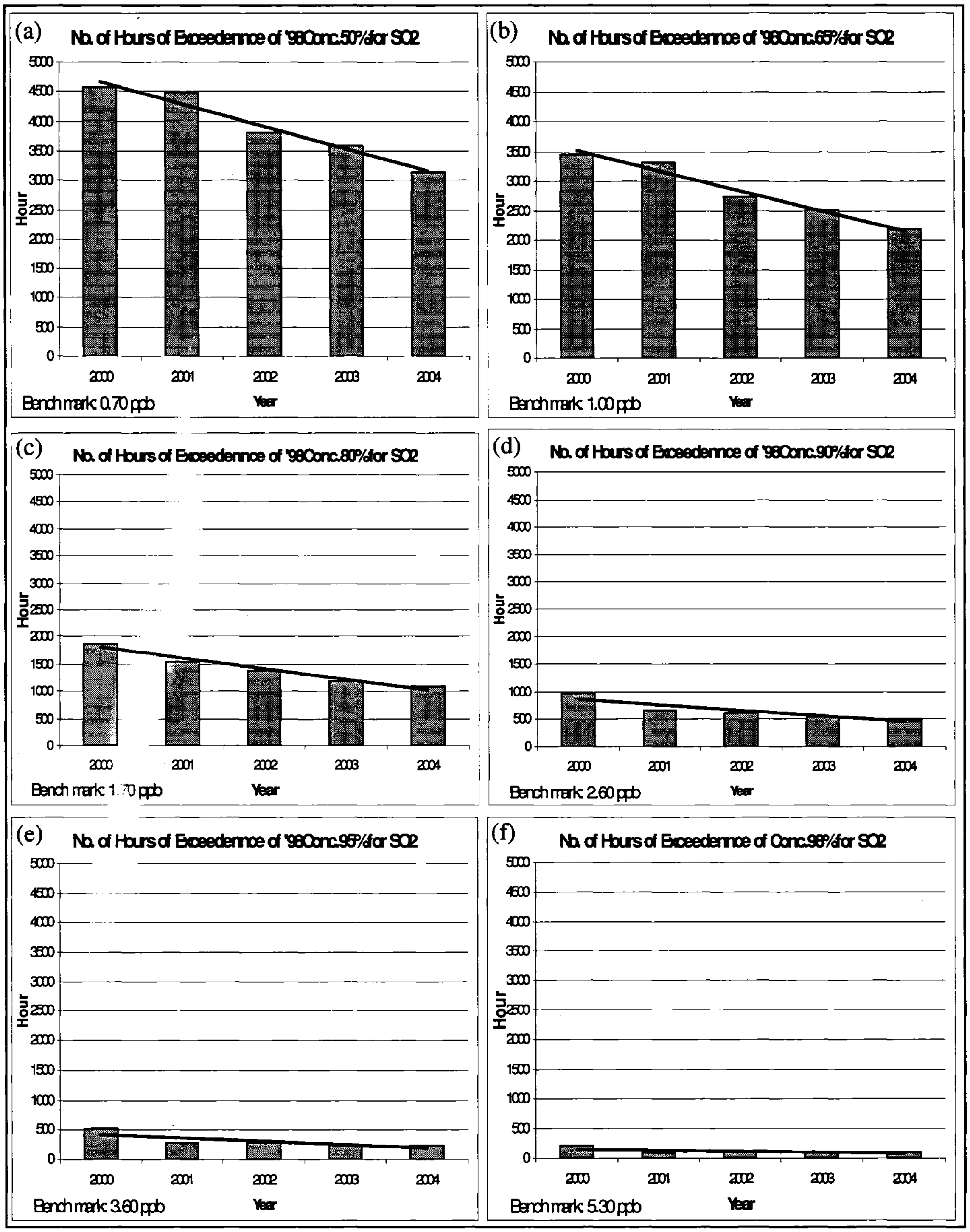

Figure 4.30 Trend Detection for SO_2 at Carrot Creek Using Frequencies of Exceedence of Various Benchmark Concentration Each Year, (a) 50%, (b) 65%, (c) 80%, (d) 90%, (e) 95%, (f) 98%.

4.2.2.3 Nitrogen Dioxide (NO_2)

Cumulative Frequency Distribution

The cumulative distribution pattern for NO_2 varied somewhat between years. The values were also a little higher in ranges than at Tomahawk. For all of the years, 90% of the data fell within the range of 17 ppb (33 $\mu g/m^3$); except 2003 (20 ppb) and 90% fell within 10 ppb (19 $\mu g/m^3$), but again, year 2003, in general, had higher values at most of the percentiles. Year 2001 also showed very high values only at the highest percentiles (Figure 4.31; for all distributions please refer to Appendix C). Changes were not drastic before the 90th percentile for any of the years, indicating reasonably good air quality with respect to NO_2 prevailing most of the time

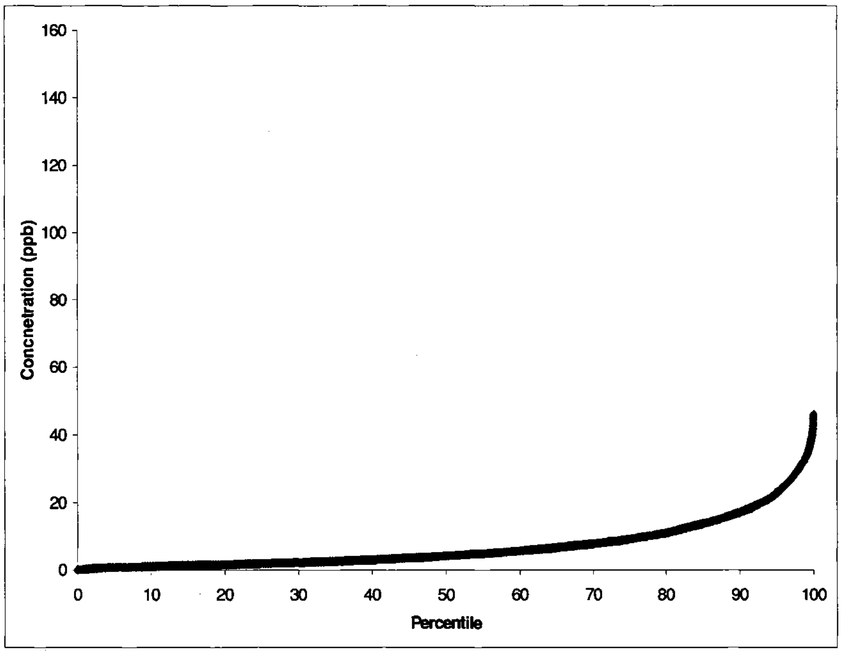

Figure 4.31 Percentile Cumulative Distribution of NO_2 at Carrot Creek for 2001

Trend Detection Using Concentration

At Carrot Creek, NO_2 levels were below Alberta's one-hour guideline. The maximum NO_2 levels were much higher than at Tomahawk. The maximum one-hour concentration of 155 ppb (296 $\mu g/m^3$) was measured at 5:00 pm on May 19th, 2003, which is about 73% of the one-hour guideline for NO_2. The second highest was also quite high (139 ppb $\approx$ 265 $\mu g/m^3$), about 66% of the one-hour guideline. The rest however was much lower, 52 ppb (99 μg/m^3) or less. The median NO_2 levels also were a little higher than at Tomahawk with 2003 showing the highest value close to 6 ppb (11 μg/m^3) in 2003, as the highest. The rest lay closely ranged, 4 ppb (8 μg/m^3) being the minimum. The percentile concentrations at Carrot Creek were markedly higher in 2003 than any other years.

In trend analysis, a little different picture was observed at Carrot Creek. Here, an increasing trend was observed up to the 90th percentile and then a decreasing trend at the 95th and 98th percentiles (Figure 4.32). None of the trends proved to be statistically significant, leading to the conclusion that no significant change with respect to the concentration of NO_2 has taken place over the study period of 5 years.

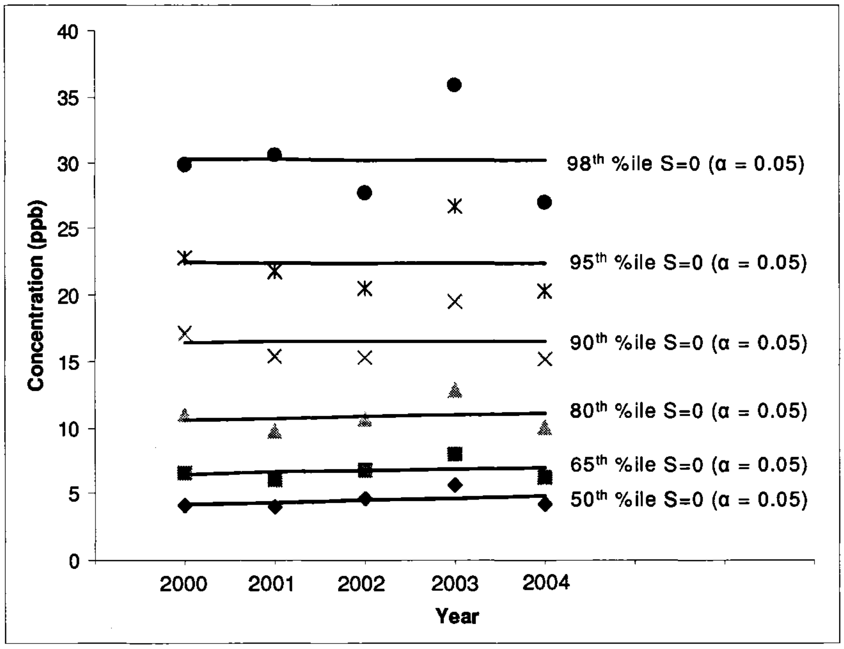

Figure 4.32 Concentration Trends for NO_2 at Carrot Creek at Different Percentiles

Trend Detection Using Frequency of Exceedence

At the 50th percentile, the frequency of exceedence increased gradually from 2000 to 2003, then dropped in 2004. From the 65th percentile, the picture changed slightly as 2001 showed a consistently lower frequency than did the other years. It was, in fact, the lowest in the 65th, 80th, 90th and 95th percentiles. Only at the 98th percentile, did 2002 show the lowest frequency. As in the case of hourly concentrations, there has also been an increase in the number of hours of exceedence of the benchmark concentration in the year 2003; however, the concentrations never exceeded the hourly standard of 212 ppb.

The approach of "frequency of exceedence" generated the same results for the NO_2 trend analysis at both stations. In this approach also, increasing trends were observed up to the 90th percentile and then a decreasing trend at the 95th and 98th percentiles (Figure 4.33). None of the trends proved to be statistically significant (Table 4.1), leading to the conclusion that no significant change has been taking place with respect to the concentration of NO_2 over the study period of 5 years.

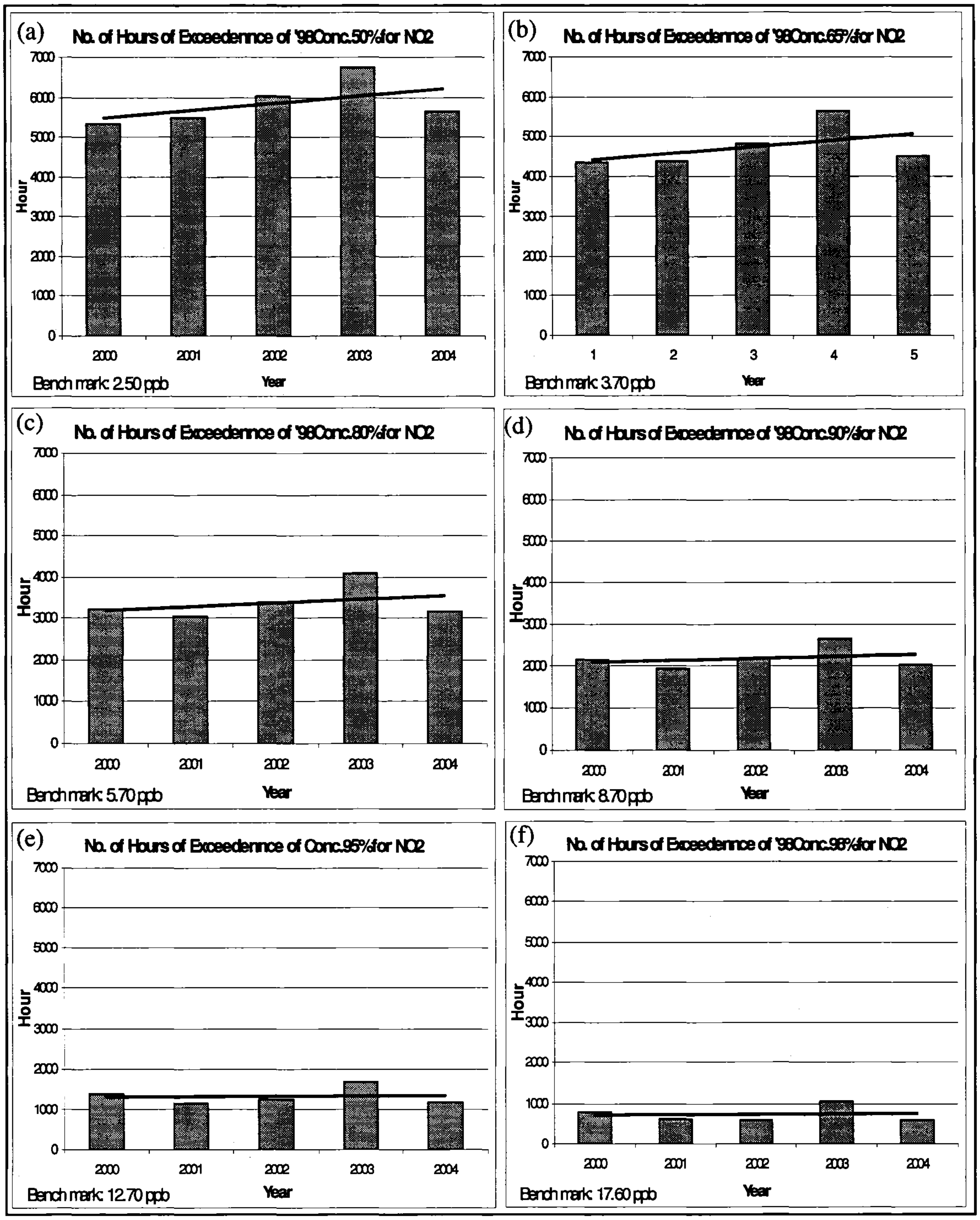

Figure 4.33 Trend Detection for NO_2 at Carrot Creek Using Frequencies of Exceedence of Various Benchmark Concentration Each Year, (a) 50%, (b) 65%, (c) 80%, (d) 90%. (e) 95%, (f) 98%

Table 4.1 Statistically Significant Trends Obtained from Frequency of Exceedence Approach for O_3, SO_2, NO_2 and $PM_{2.5}$ at Tomahawk and Carrot Creek

Stations	**Tomahawk**		**Carrot Creek**	
Statistical tests / **Pollutants**	**t-test**	**F-test**	**t-test**	**F-test**
O_3	*	*	*	*
SO_2	65%(-), 80%(-), 90%(-)	65%(-), 80%(-), 90%(-)	50%(-),65%(-), 80%(-), 90%(-)	50%(-), 65%(-), 80%(-), -0%(-)
NO_2	65%(-), 80%(-), 90%(-)	65%(-), 80%(-), 90%(-)	*	*
$PM_{2.5}$	*	*	*	*

Note :

%	percentile
*	no significant trend
-ve sign	decreasing trends
+ve sign	increasing trends

CHAPTER 5 : DISCUSSION

5.1 OZONE (O_3)

The diurnal behaviour of O_3 at both the Tomahawk and the Carrot Creek station closely corresponds to that of turbulent mixing layer and conforms to the general behaviour of ground-level O_3 in a rural area where it is determined by the interaction of source and sink mechanism (Angle and Sandhu, 1986). The characteristic diurnal ozone concentration patterns (i.e. low levels in early morning and peak levels in mid-afternoon) are due to more-dominant vertical convective mixing during day time hours and the absence of that mixing during night time and early morning hours (He et al., 2005).

During day time vertical convective mixing, ozone is brought down from the upper layers of the atmosphere, which leads to the highest ozone concentrations at the ground level between 3:00 pm to 5:00 pm (He et al., 2005), the steady period of maximum mixing height. At this period ground-level O_3 concentrations may approach that in the tropospheric reservoir in the air (Angle and Sandhu, 1986).

Crossing this period, the mixing layer ceases to grow and collapses at sunset. Angle and Sandhu (1986) further relate that generally at night, an inversion, present over the plain, prevents downward transport of O_3 and facilitates surface destruction. Destruction of ozone from physical contact with surface vegetation accumulates during the early hours of the next morning and achieves a decrease in the ambient concentrations at ground level. About 3 hours after sunrise, this nocturnal inversion is replaced by a mixing layer which again transports momentum and other properties from the troposphere to the surface.

At Carrot Creek, the dip after sunset appears to indicate more scavenging effects than at Tomahawk. The behaviour of diurnal O_3 was compared to that observed for NO_2. The trend in the NO_2 data appears to correspond to similar increasing/decreasing levels of O_3. The data shows a dip in the concentrations during the period 10:00 to 18:00 hours. The effect of this reduction in NO_2 could have been the reason for the decline in local O_3 scavenging, thus resulting in an apparently higher percentile concentration of O_3 (Fuentes and Dann, 1994).

The little "weekday/weekend" effect is not unexpected at stations like Tomahawk or Carrot Creek, which are largely rural areas, i.e., where variation of activities between weekdays and weekends is not great. The ''weekend effect'' on ozone reported in the literature are mostly observed in urban areas or urban-influenced areas, which could be attributed to different emission patterns at weekend and on weekday (Altshuiler et al., 1987; Qin et al., 2004). Both NO_x and VOCs emission sources are reduced at the weekend; however, it is likely that the weekend effect on O_3 becomes weak with distance from urban areas or areas with greater anthropogenic emissions (Qin et al., 2004).

The seasonal patterns at Tomahawk and Carrot Creek reflect the contribution of photochemically generated O_3 from sunshine and anthropogenic and natural precursors (Jo, et al., 2000; Su et al., 2005). The elevated O_3 concentrations during the summer season at these stations could be the result of a combination of locally formed O_3 and O_3 that had been transported over long distances (Fuentes and Dann, 1994). During the summer, especially around July, data shows much more variability than that of late winter or around March (standard deviation is higher for the data in July than April). Therefore, despite the maximum being in July, the overall variability of the data lowers the average.

Fuentes and Dann (1994), who observed a similar event at rural locations in Eastern Canada, suggested that the higher O_3 concentrations recorded during the spring at this location might reflect the impact of O_3 transport from the stratosphere. In the northern hemisphere there is increased transport of stratospheric O_3 into the free troposphere during the spring (Fuentes and Dann, 1994). Fuentes and Dann (1994) have further stated that because of the longer lifetime of O_3 during the winter, accumulation of anthropogenically produced O_3 may contribute to the spring O_3 maximum recorded in the lower troposphere of the northern hemisphere. A similar seasonal pattern to the present study was also found over much of the USA and Europe (Logan, 1985; Feister and Balzer, 1991).

The spring maximum and autumn minimum are consistent with the known behaviour of the tropospheric reservoir of O_3, which is in phase with the O_3 content of the lower stratosphere (Singh et al., 1980). However, the reason behind the second peak observed at Carrot Creek is not clear. It is present in 4 out of 5 years individually as well as in the composite. It may be that the tropospheric reservoir is increased from October to January (Angle and Sandhu, 1986). No such secondary peak was observed at Tomahawk. The little differences between the concentrations between the two areas may be attributed to the combined effects of O_3 precursor emissions and meteorological conditions (Jo et al., 2000).

The results of the short-term trend analysis shows that at both Tomahawk and Carrot Creek stations air quality remained unchanged with respect to O_3 concentration as none of the trends exhibited any statistically significant change. This result is not unexpected at rural sites, where the influence of local and regional sources of anthropogenic pollutant is not very high compared to cities. The majority of O_3 at rural locations in west central Alberta results from natural processes (He et al., 2005). These processes include transport from the "ozone-rich" upper atmosphere and organic compounds (from vegetation) reacting with NOx in presence of sunlight to form ozone (CASA, 2003).

CASA (2003) also reports that O_3 concentrations approaching or exceeding the Canada-wide Standard (CWS) in several areas in the province, including Hightower Ridge, Violet Grove and Carrot Creek, was the case only if the higher O_3 concentrations were determined to be caused by natural sources or sources outside of Alberta. Sandhu (1999) relates that in Alberta in general, ozone formation is relatively suppressed, as the meteorology is not favorable for it. High temperatures and shallow mixing depths necessary for ozone formation do not exist. This position supports observations made earlier by Peake and Fong (1990) that under the climatological and meteorological conditions existing in Alberta, exceedences are more likely in remote areas, than in cities or in areas under the direct influence of urban and industrial emissions. Therefore, the exceedences observed during the current study periods do not signify unexpected occurrences.

The results of the short-term trend analysis in this study are also consistent with that observed by others. Wolff et al., (2001) reviewed trends in the concentrations of O_3 over

North America and reported that in Canada (Ontario, Alberta, and British Columbia) trends of mean daily maximum one-hour O_3 concentrations at urban sites showed mixed trends with a majority of sites showing an increase from 1980 to 1993. However, Wolff et al. (2001) reported that trends appear to decrease from 1985 to 1993 or showed no significant change at the 95% level at most regionally representative sites.

5.2 SULPHUR DIOXIDE (SO_2)

The decreasing trends for SO_2 observed at both stations were difficult to explain as the trends lacked consistency with respect to statistical significance; trends from the 50th to the 90th percentiles proved to be statistically significant, while the higher two percentiles (95th and 98th) proved insignificant ($\alpha = 0.05$). However, it was noticeable that for the majority of the time both stations displayed similar decreasing trends (50th to 90th percentile). Higher readings were observed to be mostly isolated occurrences with short durations.

In Alberta, it is estimated that 51% of SO_2 emissions are produced by upstream oil and gas industries while power plants and oil sands produce about 25% and 18% of SO_2 emissions respectively (Environment Canada, 2004). Other sources include gas plant flares, oil refineries, pulp and paper mills and fertilizer plants. As the activities of oil and gas plants exist within the range of the two stations studied, the decreasing trends at both stations can be partially explained by the successful effort of the Alberta Energy and Utility Board (EUB) for reducing sulphur related flaring and venting. A summary of the actual reductions for the past five years has been reported, which shows a gradual increase in percentage reduction for flaring and venting. In the year 2004 alone, EUB reported flared volumes to be 72% less than the 1996 flaring baseline, and the vented volumes to be 49% less than the 2000 venting baseline. This gradual decrease compares well with the decrease in the SO_2 concentration observed at the stations.

5.3 NITROGEN DIOXIDE (NO_2)

The seasonal variation for the average hourly NO_2 concentrations was determined so as to check whether the previously identified O_3 concentration trend corresponded to similar increasing/decreasing levels of NO_2. The NO_2 concentrations at both rural sites were typically low; however, a distinct seasonal pattern was observed which contrasted well with those trends observed for O_3.

The decreasing composite trend for NO_2 at Tomahawk is difficult to explain. More information and study are necessary to determine its origin. NO_2 concentrations at Tomahawk was likely to be affected by emissions from nearby power plants, while the primary source of oxides of nitrogen in the Carrot Creek area was emissions from processes related to the gas plants located at close proximity to the station. At Carrot Creek, even though the maximum concentrations stayed below the relevant standard over the study period, both the maximum and median concentrations were still higher than at Tomahawk for all of the years. Besides oil and gas plants, the Carrot Creek station had other possible influences, it is near a major highway and the higher average NO_2 concentrations reflect emissions from motor vehicle traffic as well as farm equipment operating near the site (WCAS, 2004). The relatively high percentile concentrations in 2003 might have been due to an exceptional meteorological condition pertaining to that year, leading to high oxidant concentrations (Carslaw, 2005).

5.4 PARTICULATE MATTER ($PM_{2.5}$)

Temporal variations in $PM_{2.5}$ concentration can be influenced by a variety of anthropogenic and meteorological factors (Sandhu, 1998). At Tomahawk, the diurnal pattern of $PM_{2.5}$ did not show a significant trend, which complies with the rural character of the site. Only a mild peak might have been observed during night-time. Hien et al. (2002) reported the highest $PM_{2.5}$ levels at night to be part of a distinct diurnal concentration cycle during radiational inversions. Similarly, the low weekday concentrations could be explained by the fact that, being rural, the monitoring site has less of the common weekday pollution sources (traffic, industry, etc.) (Vassilakos et al., 2005). Additionally, the prevailing concentrations, which are observed to be higher during some weekends, could be an effect of plumes from the nearby power plants which were operating continuously.

The observed absence of a seasonal trend or the lack of proper understanding of it could be due to the short data history (2000-2004). It might be insufficient to exhibit any underlying seasonal trend. For the inconsistent high summer values, an association with forest fire during the study period is suspected. Su et al., (2004b), suggests that isolated high values such as those observed at this station may subterfuge any seasonal trend that might exist.

The winter high (not higher than in the summer) could be a result of various factors, e.g., lower mixing heights at this time of the year, and also higher energy consumption as heating is higher, along with more rampant wood burning (Brook et al., 1997). When Namdeo and Bell (2005) performed a similar study at two rural locations in the UK under the influence of anthropogenic activities, they made a clear observation that at both urban and rural sites, the proportion of fine particles was greater in the winter than in the summer. They concluded that better dispersion of pollutants in the hotter months is likely to be the reason for lower concentrations of $PM_{2.5}$ during the summer.

The Tomahawk station is located in an agricultural area and hence, the major source of particulates at monitoring locations during this survey was likely agriculture dust, soil dust, and road dust from traffic traveling on roads adjacent to the monitoring locations. The station is also about 30 to 40 km from four coal-fired power plants. Sulphate and nitrate derived from such industrial emissions of SO_2 and NO_x were considered the major constituents of the $PM_{2.5}$ for the area (WCAS, 2004). It was expected that local topographical and meteorological conditions, as well as emission sources, would affect particle concentrations at this location (Cheng et al., 2000); however, the trend results of this study indicated otherwise. These findings support that background concentrations at Tomahawk are low, where local anthropogenic sources are relatively few in number and small in emissions. The findings are consistent with those reported by Namdeo and Bell (2005), who reported that particulate levels were low and almost unchanged at rural sites, reflecting the prevailing background conditions.

CHAPTER 6 : FINDINGS & CONCLUSION

6.1 FINDINGS

The study was conducted through analyzing the hourly concentrations of O_3, SO_2, NO_2, and $PM_{2.5}$, using data over a period of 5 to 8 years. The analyses revealed the following:

- Peak hourly "averaged" concentrations for O_3 occurred between 2:00 pm and 5:00 pm in the range of 36 to 40 ppb (72 to 80 $\mu g/m^3$) at the two stations. The highest averaged concentrations occurred at the higher elevation station, Carrot Creek. The lowest averaged concentrations occurred during the morning hours around 6:00 am to 7:00 am, again at Carrot Creek. For $PM_{2.5}$ at Tomahawk, two peaks were observed in the diurnal cycle, one around 9:00 am and the second, a slightly higher one, around 8:00 pm.

- Peak "averaged" monthly concentrations for O_3 occurred in the early spring for both stations, although the maximum monthly concentrations are observed in the summer. Again, in both cases, Carrot Creek showed higher concentration.

- No distinct weekly or monthly trends in the hourly average for $PM_{2.5}$ were observed at the Tomahawk station. Only one exceedence was recorded with a very high value of 121 $\mu g/m^3$ in May, 2002.

- At Tomahawk, statistically significant decreasing trends were observed for SO_2 at most of the percentiles examined. For O_3 and $PM_{2.5}$, none of the trends proved to be statistically significant indicating no change in air quality.

- For Carrot Creek, SO_2 exhibited a clear and statistically significant decreasing trend in most cases, while O_3 and NO_2 displayed no statistically significant change in air quality.

- The statistically significant decreasing trends observed for SO_2 compare well with the decrease in the sulfur related flaring and venting volumes of the upstream oil and gas industries. The statistically significant decreasing trends observed for

NO_2 at Tomahawk could not be explained. The findings support that background concentrations of O_3 and $PM_{2.5}$ are low where local anthropogenic sources are relatively few in number and small in emissions.

An ultimate objective in this study was to develop and examine statistical procedures for trend detection that are straightforward and easy to implement. In this study, both approaches (concentration trends and frequencies of exceedences) were kept simple and the results obtained show that they complemented each other well as they produced similar results. In view of that, the methods examined here can be used as demonstrated to evaluate changes in air quality at monitoring stations in Alberta.

6.2 RECOMMENDATIONS

The main recommendation would be to increase the length of the study period. The period of this particular study over which trends were examined was rather short (less than a decade). The changes or lack of changes observed might not indicate what may happen over the long term. Another recommendation would be to make the meteorological data available along with the hourly concentrations as it may facilitate a greater understanding of the changes taking place.

REFERENCES

Alberta Environment. (2001). Quarterly Air Quality Reports. Retrieved July 11, 2005, from www3.gov.ab.ca/env/air/airqual/quart.html.

Alberta Environment. (2005a). Alberta Ambient Air Quality Objectives. Alberta Environment, Edmonton, AB. Retrieved July 11, 2005, from http://www3.gov.ab.ca/env/protenf/approvals/factsheets/ABAmbientAirQuality.pdf

Alberta Environment, (2005b). About Air Quality. Retrieved June 8, 2005, from http://www3.gov.ab.ca/env/air/Info/aboutaq.html.

Altshuiler, A. P. (1987). Estimation of the Natural Background of Ozone Present at Surface Rural Locations. Journal of Air Pollution Control Association, 37:1409-1417.

Air monitoring Directive (AMD), (1989). Monitoring and Reporting Procedures for Industry, Alberta Environment, 403/427-5883.

Angle, R.P., and Sandhu, H.S. (1986). Rural Ozone Concentrations in Alberta, Canada. Atmospheric Environment, 20(6):1221-1228.

Barrie, L.A., and Hoff, R.M. (1985). Five Years of Air Chemistry Observations in the Canadian Arctic. Atmospheric Environment, 19: 1995-2010.

Bates, D. (1991). The Effects of Ozone on Plants and Humans. In the Air and Waste Management Association Tropospheric Ozone and the Environment 3; Papers from an International Conference. Air and Waste Management Association, Pennsylvania, held March 19-22, 1990 in Los Angeles, CA.

Blanchard, C. L. (1999). Methods of Attributing Ambient Air Pollutants to Emission Sources. Annual Review Energy Environment, 24:329-65.

Bower, J. (1997). Ambient Air Quality Monitoring. In R.E. Hester and R.M. Harrison (Eds.), Air Quality Management, The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, UK, 41-65pp.

Brook, J.R., Dann, T.F., and Burnett, R.T. (1997). The Relationship among TSP, PM_{10}, $PM_{2.5}$, and Inorganic Constituents of Atmospheric Particulate Matter at Multiple Canadian Locations. Journal of Air & Waste Management Association, 47:2-19.

Burnett, R.T., Cakmak, S., and Brook, J.R. (1998). The Effect of the Urban Air Pollution Mix on Daily Mortality Rates in 11 Canadian Cities. Canadian Journal of Public Health, 89(3):152-156.

Carslaw, D. (2005). Evidence of an Increasing NO_2/NO_x Emissions Ratio from Road Traffic Emissions. Atmospheric Environment, 39:4793-4802.

CASA, (2003). Clean Air Strategic Alliance. Guidance Document for the Management of Fine Particulate Matter and Ozone in Alberta. Clean Air Strategic Alliance, Edmonton, AB. 92 pp.

CASA, (2005). Clean Air Strategic Alliance, Edmonton, AB. Retrieved May, June, July, 2005, from http://www.casadata.org/.

CCME, (2000). Canada Wide Standards for Particulate Matter (PM) and Ozone. Canadian Council of Ministers of Environment, Winnipeg, M.B.

CEPA/FPAC WGAQOG, (1999). Canadian Environmental Protection ACT Federal/Provincial Working Group on Air Quality Objectives and Guidelines. National Ambient Air Quality Objectives for Ground-level Ozone Science Assessment Document, Catalogue No. En42-17/702-1999E. Health Canada and Environment Canada, Downsview, ON and Ottawa, ON.

CEPA/FPAC, (1999). National Ambient Air Quality Objectives for Particulate Matter. A Report by CEPA/FPAC Working Group on Air Quality Objectives and Guidelines, Ottowa, ON.

Cheng, L., Sandhu, H.S., Angle, R.P., and Myrick, R.H. (1998). Characteristics of Inhalable Particulate Matter in Alberta Cities. Atmospheric Environment, 32:3835-3844.

Cheng, L., Sandhu, H.S., Angle, R.P., McDonald, K.M., and Myrick, R.H. (2000). Rural Particulate Matter in Alberta, Canada. Atmospheric Environment, 34(20):3365-3372.

Cho, K.D., and Peirce J.J. (2005). Nitric Oxide Emissions from the Soil to Lower Levels of the Troposphere. Environmental Engineering Science, 22(1):46-57.

Chow, J.C., Engelbrecht, J.P., Watson, J.G., Wilson, W.E., Frank, N.H., and Zhu, T. (2002). Designing Monitoring Networks to Represent Outdoor Human Exposure. Chemosphere, 49:961-978.

Colls, J. (1997). Air Pollution: An Introduction, Published by E&FN SPON, An Imprint of Chapman & Hall, London, UK.

Colvile, R.N., Hutchinson, E.J., Mindell, J.S., and Warren, R.F. (2001). The Transport Sector as a Source of Air Pollution. Atmospheric Environment, 35:1537-1565.

Daum, P.H., Kelly, T.J., Tanner, R.L., Tang, X.,Anlauf, K., Bottlenheim, J., Brice, K.A., and Wiebe, H.A.(1989). Winter Measurements of Trace Gas and Aerosol Composition at a Rural Site in Southern Ontario. Atmospheric Environment, 23(1):161-173.

de Nevers, N. (2000). Air Pollution Control Engineering, McGraw-Hill Companies, Inc., New York, NY.

DeGaetano, A., and Doherty, O. (2004). Temporal, Spatial and Meteorological Variations in Hourly $PM_{2.5}$ Concentration Extremes in New York City. Atmospheric Environment, 38:1547-58.

Delfino, R.J., Murphy-Moulton, A.M., Burnett, R.T., Brook, J.R., and Becklake, M.R. (1997). Effects of Air Pollution on Emergency Room Visits for Respiratory Illness in Montreal, Quebec. American Journal of Respiratory and Critical Care Medicine, 155:586-576.

Demerjian, K.L. (2000). A Review of National Monitoring Networks in North America. Atmospheric Environment, 34:1861-1884.

Desauziers, V. (2004). Traceability of Pollutant Measurements for Ambient Air Monitoring. Trends in Analytical Chemistry, 23(3):252-260.

Deslauriers, M. (1996). Canadian Emissions Inventory of Criteria Air Contaminants (1990). Environmental Protection Series Report EPS 5/AP/7E, February, Pollution Data Branch, Environmental Protection Service, Environment Canada, Ottawa, ON, 75 pp.

Eatough, D.J., Richter, B.E., Eatough, N.L., and Hansen, L.D. (1981). Sulfur Chemistry in Smelter and Power Plant Plumes in the Western US. Atmospheric Environment, 15(10-11):2241-2253.

Elsom, D. (1987). Atmospheric Pollution: Causes, Effects and Control Policies, Basil Blackwell Ltd., New York, NY. 319pp.

Environment Canada, 2000, (2004) Criteria Air Contaminant Emissions Inventory Summaries (2000). Pollution Data Branch, Environment Canada. Retrieved June 7, 2005, from http://www.ec.gc.ca/pdb/ape/ape_tables/sox2000_e.cfm.

Environment Canada, (2005). Clean Air. Retrieved June 9, 2005, from http://www.ec.gc.ca/cleanair-airpur/Pollution_Issues-WSD61E229E-1_En.htm.

Envirotools (2005). Nitrogen Oxides. Retrieved July 29, 2005, from http://www.envirotools.org/factsheets/contaminants/nitrogenoxides.shtml.

Energy and Utility Board (EUB), (2005). Upstream Petroleum Industry Flaring and Venting Report : Industry Performance for Year Ending December 31, 2004, Alberta Energy and Utilities Board, 640-5 Avenue S.W., Calgary, Alberta.

Feister, U., and Balzer, K. (1991). Surface Ozone and Meteorological Predictors on a Subregional Scale. Atmospheric Environment, 25(9):1781-1790.

Fenn, M.E., Haeuber, R., Tonnesen, G.S., Baron, J.S., Grossman-Clarke, S., Hope, D., Jaffe, D.A., Copeland, S., Geiser, L., Rueth, H.M., and Sickman, J.O. (2003). Nitrogen Emissions, Deposition, and Monitoring in the Western United States. Bioscience, 53(4):391-403.

Freeman, G., and Haydon, G.B. (1964). Emphysema after Low-level Exposure to Nitrogen Dioxide. Archives of Environmental Health, 8:125-128.

Freudenrich, C.C. (2002). How Ozone Pollution Works. Retrieved June 8, 2005, from http://science.howstuffworks.com/ozone-pollution1.htm.

Fuentes, J.D., and Dann, T.F. (1994). Ground-Level Ozone in Eastern Canada: Seasonal Variations, Trends, and Occurrences of High Concentrations. Journal of the Air and Waste Management Association, 44:1019-1026.

Gehrig, R., and Buchmann, B., (2003). Characteriszing Seasonal Variations and Spatial Distributions of Ambient PM_{10} and $PM_{2.5}$ Concentrations Based on Long-term Swiss Monitoring Data. Atmospheric Environment, 37:2571-2580.

Gilbert, R.O. (1987). Statistical Methods for Environmental Pollution Monitoring, Van Nostrand Reinhold Company Inc., New York, NY.

Godish, T. (2004). Air Quality, Lewis Publishers, Boca Raton, Fla.

Gold, D.R., Litonjua, A., Schwartz, J., Lovett, E., Larson, A., Nearing, B., Allen, G., Verrier, M., Cherry, R., and Verrier, R.L. (2000). Ambient Pollution and Heart Rate Variability. Circulation, 101:1267-1273.

Günes, M., (2005). A Simple Evaluation of SO_2 and PM Data on Ambient Air Quality. Energy Source, 27:729-740.

Harnett, D.L. (1982). Statistical Methods. Addison-Wesley Publishing Company, Inc. Philippines.

Hays, W.L., and Winkler, R.L. (1971). Statistics: Probability, Inference, and Decision Holt, Rinehart and Winston, Inc. Austin, Texas, USA.

He, Y., Selvaraj, M., Kindzierski, W.B., and Gamal El-Din, M. (2005). Investigation of Factors Affecting Ambient O_3 Concentrations in West Central Airshed Society Zone, Alberta. Report Prepared for West Central Airshed Society, Drayton Valley, Alberta. January 2005.

Health Canada, (2005). Regulations, Health and Air Quality Science Assessment. Retrieved July 11, 2005, from http://www.hc-sc.gc.ca/hecs-sesc/air_quality/regulations.htm.

Hess, A., Iyer, H., and Malm, W. (2001). Linear Trend Analysis: A Comparison of Methods. Atmospheric Environment, 35:5211-5222.

Hien, P.D., Bac, V.T., Tham, H.C., Nhan, D.D., and Vinh, L.D. (2002). Influence of Meteorological Conditions on $PM_{2.5}$ and $PM_{2.5-10}$ Concentrations during the Monsoon Season in Hanoi, Vietnam. Atmospheric Environment, 36:3473-3484.

Hirsch R.M., Slack J.R. and Smith R.A. (1982). Techniques of Trend Analysis for Monthly Water Quality Data. Water Resources Research, 18(1):107-121.

Hirsch, R.M., and Slack, J.R. (1984). A Nonparametric Trend Test for Seasonal Data with Serial Dependence. Water Resources Research, 20(6):727-732.

Hirsch, R.M., Alexander, R.B. and Smith, R.A. (1991). Selection of Methods for the Detection and Estimation of Trends in Water Quality. Water Resources Research, 27(5):803-813.

Hueglin, C., Gehriga, R., Baltenspergerb, U.,Gyselc, M., Monnd, C., and Vonmonta, H. (2005). Chemical Characterisation of $PM_{2.5}$, PM_{10} and Coarse Particles at Urban, Near-City and Rural Sites in Switzerland. Atmospheric Environment, 39:637-651.

Jacobson, M.Z. (1999). Fundamental of Atmospheric Modeling. Cambridge University Press, Cambridge, UK.

Jaecker-Voirol, A., and Mirabel, P. (1989). Heteromolecular Nucleation in the Sulphuric Acid-water System. Atmospheric Environment, 23:2053-2057.

Jin, Y., Veiga, M.C., and Kennes, C. (2005). Bioprocesses for the Removal of Nitrogen Oxides from Polluted Air, Journal of Chemical Technology and Biotechnology, 80:483–494.

Jo, W.K., Yoon, I.H., and Nam, C.W. (2000). Analysis of Air Pollution in Two Major Korean Cities: Trends, Seasonal Variations, Daily 1-Hour Maximum versus other Hour-Based Concentrations, and Standard Exceedences. Environmental Pollution, 110:11-18.

Johnson, B. 2005. Email communication with W. Kindzierski, Department of Civil & Environmental Engineering, University of Alberta, June 2005. West Central Airshed
Society, Drayton Valley, AB.

Jones, C. (1996). New $PM_{2.5}$ Standards Ensnare More Than Just Particulates. Power, November/December; 57-60.

Katrinak, K.A., Rez, P., Perkes, P.R., and Buseck, P.R. (1993). Fractal Geometry of Carbonaceous Aggregates form An Urban Aerosol. Environmental Science & Technology, 27:539-547.

Kellogg, W.W., Cadle, R.D., Allen, E.R., Lazrus, A.L., and Matell, E.A. (1972). The Sulfur Cycle. Science, 175:587-596.

Kelly, N.A., Wolff, G.T., and Ferman, M.A. (1984). Sources and Sinks of Ozone in Rural Areas. Atmospheric Environment, 18:1251-1266.

Kendall, M.G. (1938). A New Measure of Rank Correlation. Biometrika, 30:81-93.

Kindzierski, W., and Sembaluk, S. (2001). Indoor/Outdoor Relationship of SO_2 in a Rural and Urban Community in Alberta. Canadian Journal of Civil Engineering, 28(Suppl.1):163-169.

Klemm, O., and Lang, H. (1999). Trends of Air Pollution in the Fichtelgebirge Mountains. Environmental Science and Pollution Research, 6(4):193-199.

Korhonen, P., Kumala, M., Laaksonen, A., Viisanen, Y., McGraw, R., and Seinfeld, J.H. (1999). Ternary Nucleation of H_2SO_4, NH_3 and H_2O in the Atmosphere. Journal of Geophysical Research, 104:26349-26353.

Kundzewicz, W.Z., and Robson, A.J. (2004). Change Detection in Hydrological Records—A review of the methodology. Hydrological Sciences, 49(1):7-19.

Künzli N., Kaiser, R., Medina, S., Studnicka, M., Chanel, O., and Filliger, P. (2000). Public-Health Impact of Outdoor and Traffic-Related Air Pollution: A European Assessment. Lancet, 356:795-801.

Laakso, L., Hussein, T., Aarnio, P., Komppula, M., Hiltunen, V., Viisanen, Y., Kulmala, M. (2003). Diurnal and Annual Characteristics of Particle Mass and Number Concentrations in Urban, Rural and Arctic Environments in Finland. Atmospheric Environment, 37:2629-2641.

Lipfert, F.W., and Hammerstrom, T. (1992). Temporal Patterns in Air Pollution and Hospital Admissions. Environmental Research, 59:374-399.

Lettenmaier, D. P. (1988). Multivariate Nonparametric Tests for Trend in Water Quality. Water Resources Research, 24(3):503-512.

Libiseller, C., Grimvall, A., Walden, J., and Saari, H. (2005). Meteorological Normalisation and Non-parametric Smoothing for Quality Assessment and Trend Analysis of Troposhperic Ozone Data. Environmental Monitoring and Assessment, 100:33-52.

Loftis, J. C., Taylor, C. H., Newell, A. D., and Chapman, P. L. (1991). Multivariate Trend Testing Lake Water Quality. Water Resources Bulletin, 27(3):461-473.

Loftis, J. C., Ward R. C., Phillips, R. D., and Taylor C. H. (1989). An Evaluation of Trend Detection Techniques for Use in Water Monitoring Programs, EPA/600/3-89/037, U.S. Environmental Protection Agency, Corvallis, Oregon.

Logan, J.A. (1985). Tropospheric Ozone: Seasonal Behaviour, Trends and Anthropogenic Influences. Journal of Geophysical Research, 90:10473-10482.

Mann, H.B. (1945). Nonparametric Test against Trend. Econometrica, 13:245-259.

McConnell, R., Berhane, K., Gilliland, F., London, S., Islam, T., Gauderman,W., Avol, E., Margolis, H., and Peters, J. (2002). Asthma in Exercising Children Exposed to Ozone: A Cohort Study. Lancet, 359:386-391.

Massart, D.L., Smeyers-Verbeke, J., Rius, F.X. (1989). Method Validation: Software to Compare the Slopes of Two Calibration Lines with Different Residual Variance, Trends in Analytical Chemistry (Personal Edition), 8(2): 49-51.

Maroni, M., Seifert, B., and Lindvall, T. (1995). Indoor Air Quality: A comprehensive Reference Book, Elsevier Science, New York, NY. 1049pp.

Mauzerall, D.L., Sultan, B., Kim, N., Bradford, D.F. (2005). NO_x Emission from Large Point Sources: Variability in Ozone Production, Resulting Health Damages and Economic Costs. Atmospheric Environment, 39:2851-2866.

Meyer, B. (1983). Indoor Air Quality, Addison-Wesley Publishing Company Inc. Reading, MA.

Moore, D.S., and McCabe, G.P. (1999). Introduction to the Practice of Statistics. W.H. Freeman and Company, New York, NY.

Moreno, T., Gibbons, W., Jones, T., and Richards, R. (2003). The Geology of Ambient Aerosols: Characterising Urban and Rural/Coastal Silicate $PM_{10-2.5}$ and $PM_{2.5}$ Using

High-volume Cascade Collection and Scanning Electron Microscopy. Atmospheric Environment, 37:4265-4276.

Mustafa, M.G. (1994). Health Effects and Toxicology of Ozone and Nitrogen Dioxide. Advances in Environmental Science and Technology, 28:351-404.

Namdeo, A., and Bell, M.C., (2005). Characteristic and Health Implications of Fine and Coarse Particulate at Roadside, Urban Background and Rural Sites in UK. Environment International, 31:565-573.

North American Research Strategy for Tropospheric Ozone Synthesis Team (NASTRO), (2000). An Assessment of Tropospheric Ozone Pollution: A North American Perspective. Retrieved June 9, 2005, from http;// www.cgenv.com/Nastro

Neuberger, M., Moshammer, H., and Kundi, M. (2002). Declining Ambient Air Pollution and Lung Function Improvement in Austrian Children. Atmospheric Environment, 36:1733-1736.

Newman, L. (1981). Atmospheric Oxidation of Sulfur Dioxide: A Review as Viewed from Power Plant and Smelter Plume Studies. Atmospheric Environment, 15(10-11):2231-2239.

Önöz, B., and Bayazit, M. (2003). The Power Test of Statistical Tests for Trend Detection. Turkish Journal of Engineering & Environmental Sciences, 27:247-251.

Pease, B. (1999). Sulfur Dioxide Product Profile, Environmental Defense Fund, New York, NY. Retrieved July 3, 2005, from www.scorecard.org/cheical-rpfiles/uses.tel?edf-substances-id=7446%2d09%2d5.

Peake, E., and Fong, B.D. (1990). Ozone Concentrations at a Remote Mountain Site and at Two Regional Locations in Southwestern Alberta. Atmospheric Environment, 24A(3): 475-480.

Pio, C.A., and Lopes, D.A. (1998). Chlorine Loss from Marine Aerosol in a Coastal Atmosphere. Journal of Geophysical Research, 103:25263-25272.

Pope III, C.A., Burnett, R.T., Thun, M.J., Calle, E.E., Krewski, D., Ito, K., Thruston, G.D. (2002). Lung Cancer, Cardiopulmonary Mortality and Long-Term Exposure to Fine Particulate Air Pollution. Journal of the American Medical Association, 287(9):1132-1141.

Prybutok, V.R., Yi, J., and Mitchell, D. (2000). Comparison of Neural Network Models with ARIMA and Regression Models for Prediction of Houston's Daily Maximum Ozone Concentrations. European Journal of Operational Research, 122:31-40.

Putaud, J.P., Raes, F., Van Dingenen, R., Baltensperger, U., Brüggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Hüglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Müller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Ten Brink, H., Tørseth, K., Wiedensohler, A., (2004). A European Aerosol Phenomenology-2: Chemical Characteristics of Particulate Matter at Kerbside, Urban, Rural and Background Sites in Europe. Atmospheric Environment, 38:2579-2595.

Qin, Y., Tonnaesen, G.S., and Wang, Z., (2004). One-hour and Eight-hour Averaged Ozone in the California South Coast Air Quality Management District: Trends in Peak Values and Sensitivity to Precursors. Atmospheric Environment, 38:2197-2207.

Querol, X., Alastuey, A., Lopez-Soler, A., Plana, F., Puicercus, J.A., Ruiz, C.R., Mantilla, E., and Juan, R. (1998). Seasonal Evolution of Atmospheric Suspended Particles around a Coal-fired Power Station: Chemical Characterization. Atmospheric Environment, 32 (4):719-731.

Sandhu, H.S. (1998). Ambient Particulate Matter in Alberta, Report Prepared for Science and Technology Branch, Alberta Environment, Edmonton, AB.

Sandhu, H.S. (1999). Ground-Level Ozone in Alberta. Alberta Environmental Protection, Edmonton, AB.

Sawyer, C.N., McCarrt, P.L., and Parkin, G.F. (2003). Chemistry for Environmental Engineering and Science, McGraw-Hill Companies, Inc. New York, NY.

Schlensinger, R.B. (2000). Nitrogen Oxide. In M. Lippmann (Eds.), Environmental Toxicants: Human Exposure and their Health Effects, John Wiley & Sons, Inc. New York, NY, 595-638pp.

Seinfield, J.H. (1989). Urban Air Pollution: State of The Science. Science, 243:745-763.

Seinfield, J.H., and Padis, S.N. (1997), Atmospheric Chemistry and Physics. From Air Pollution to Climate Change. John Wyley & Sons, Inc., Toronto, ON, 1326 pp.

Sen, P.K., (1968). Estimates of Regression Coefficient Based on Kendall's tau. Journal of American Statistical Association, 63:1379-1389.

Singh, H.B., Viezee, W., Johnson, W.B., and Ludwig, F.L. (1980). The Impact of Stratospheric Ozone on Tropospheric Air Quality. Journal of Air Pollution Control Association, 30:1009-1017.

Sioss, L.L., and Smith, I.M. (2000). PM_{10} and $PM_{2.5}$: An International Perspective. Fuel Processing Technology, 65-66:127-141.

Slini, T., Kaprara, A., Karatzas, K., and Moussiopoulos, N. (2006). PM_{10} Forecasting for Thessaloniki, Greece. Environmental Modeling and Software, 21:559-565.

Smith, G., Coulston, J., Jepsen, E., and Prichard, T. (2003). A National Ozone Biomonitoring Program Results from Field Surveys of Ozone Sensitive Plants in Northeastern Forests (1994–2000). Environmental Monitoring and Assessment, 87:271-291.

Smith, W.H. (1990). Air Pollution and Forests, Interactions between Air Contaminants and Forest Ecosystems. 2nd edition, Springer-Verlag, New York, NY.

Socolow, R.H. (1999). Nitrogen Management and the Future of Food: Lessons from the Management of Energy and Carbon. Proceedings of the National Academy of Sciences of the United States of America, May 25, 1999, 96(11): 6001–6008.

Spiegel, M.R. (1961). Theory and Problem of Statistics, Schaum's Outline Seriese, Schaum Publishing CO. New York, NY.

Stern, A.C., Wohlers, H.C., Boubel, R.W., and Lowry, W.P. (1973). Fundamentals of Air Polution. Academic Press, Inc., New York, NY.

Stern, B.R., Raizenne, M.E., Burnett, R.T., Jonea, L., Kearney, J., and Franklin, C.A. (1994). Air Pollution and Childhood Respiratory Health: Exposure to Sulfate and Ozone in 10 Canadian Rural Communities, Environmental Research, 66:125-142.

Su, D., El-Din, A.G., Gamal El-Din, M., Idriss, A., and Wiens, B., (2004a). Investigation of Historical Data Patterns for Ozone and Related Compounds in Edmonton and Calgary and their Application to Modeling Ground-Level Ozone, In: Proceedings of 12th Cold Regions Engineering Conference and Expo, Edmonton, Alberta, Canada, CD, 17p.

Su, D., El-Din, A.G., Gamal El-Din, M., Idriss, A., and Wiens, B., (2004b). Historical $PM_{2.5}$ Monitoring Data Trends in Edmonton and Calgary: Investigation of Their Potential Use for $PM_{2.5}$ Modeling, In: Proceedings of 12th Cold Regions Engineering Conference and Expo, Edmonton, Alberta, Canada, CD, 19p.

Su, D., Gamal El-Din, M., El-Din, A.G., and Idriss, A., (2005). Systematic Development of an Artificial Neural Network Model for Real-Time Prediction of Ground-Level Ozone in Edmonton, Alberta, Canada. Journal of Air and Waste Management Association, 55:1847-1857.

Suh, H.H., Bahadori, T., Vallarino, J., Spengler, J.D. (2000). Criteria Air Pollutants and Toxic Air Pollutants. Environmental Health Perspectives, 108:625-633.

Taylor, M.R., Rubin, E. S., and Hounshell, D. A. (2005). Control of SO_2 Emissions from Power Plants: A Case of Induced Technological Innovation in the U.S. Technological Forecasting & Social Change, 72:697-718.

Theli, H. (1950). A Rank-invariant Method of Linear and Polynomial Regression Analysis, 1,2 and 3, Koninalijke Nederlandse Akademie van Weinenschatpen, Proceedings, Vol. 53:386-392,521-525,1397-1412.

Tomás-Alonso, F. (2005). A New Perspective about Recovering SO_2 Offgas in Coal Power Plants: Energy Saving. Part III. Selection of the Best Methods. Energy Sources, 27:1051–1060.

Touloumi, G., Katsouyanni, K., Zmirou, D., Schwartz, J., Spix, C., Ponce de Leon, A., Tobias, A., Quennel, P., Rabczenko, D., Bacharova, L., Bisanti, L., and Vonk, J.M. (1997). Short-term Effects of Ambient Oxidant Exposure on Mortality: A Combined Analysis within the APHEA Project. American Journal of Epidemiology, 54:99-120.

Tucker, W.G. (2000). An Overview of $PM_{2.5}$ Sources and Control Strategies. Fuel Processing Technology, 65-66:379-392.

Turalio Ĝlu, F. S. (2005). An Assessment on Variation of Sulphur Dioxide and Particulate Matter in Erzurum (Turkey). Environmental Monitoring and Assessment, 104:119-130.

United States Agency for Toxic Substances & Disease Registry (US ATSDR), Research Triangle Institute and Science International Inc., (1998a). Toxicological Profile for Sulfur Dioxide, US Department of Health and Human Services, Agency for Toxic Substance, Atlanta, GA.

United States Agency for Toxic Substances & Disease Registry (US ATSDR), Research Triangle Institute and Science International Inc., (1998b). Toxicological Profile for Oxides of Nitrogen, US Department of Health and Human Services, Agency for Toxic Substance, Atlanta, GA.

US Environmental Protection Agency (USEPA), (1993). Quality Assurance Handbook for Air Pollution Measurement Systems, Volume 1- A Field Guide to Environmental Quality Assurance, EPA-600/R-94/038a, Office of Research and Development, Atmospheric Research and Exposure Assessment Laboratory, US Environmental Protection Agency, Research Triangle Park, NC 27111.

US Environmental Protection Agency (USEPA), (1996). Air Quality Criteria for Ozone and Related Photochemical Oxidants-Volume I, II & III, EPA/600/P-93/004aF, Office of Research and Development, US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency (USEPA), (1997). $PM_{2.5}$ Composition and Sources, Prepared for FCFA National and Regional Strategies Workgroup, Prepared by Emission, Monitoring and Analysis Division, Office of Air Quality Planning and Standards, US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency (USEPA), (1999). National Air Quality and Emissions Trend Report, US Environmental Protection Agency, Washington, DC.

US Environmental Protection Agency (USEPA), (2000). PM – How Particulate Matter Affects The Way We Live And Breath, Published by The US EPA Office of Air Quality Planning and Standards. US Environmental Protection Agency, Washington, DC. Retrieved June 10, 2005, from http://www.epa.gov/air/urbanair/pm/hlth1.html/.

US Environmental Protection Agency (USEPA), (2001) National Air Quality and Emissions Trends Report, EPA 454/R-01-004, Office of Research and Development, US Environmental Protection Agency, Research Triangle Park, NC 27111.

US Environmental Protection Agency (USEPA), (2002), Guidance on Choosing a Sampling Design for Environmental Data Collection for Use in Developing a Quality Assurance Project Plan. EPA QA/G-5S, Office of Research and Development, Washington, DC

US Environmental Protection Agency (USEPA), (2003). National Ambient Air Quality Standards (NAAQS), US Environmental Protection Agency, Washington, DC. Retrieved June 29, 2006, from http://www.epa.gov/air/criteria.html.

US Environmental Protection Agency, (2005a). Basic Information about Ground Level Ozone: How Ground-level Ozone Affects the Way We Live & Breathe. Retrieved July 14, 2005, from http://www.epa.gov/air/urbanair/ozone/index.html

US Environmental Protection Agency, (2005b). Human Health and Environmental Effects of Emission from Power Generation. Retrieved July 14, 2005, from www.epa.gov/airmarket.

US Environmental Protection Agency(USEPA), (2005c). Control Emission Technologies. Retrived June 8, 2005, from http://www.epa.gov/apti/course422/ce1.html.

U.S. Environmental Protection Agency (USEPA), (2006). EPA's Efforts to Reduce NOx. Retrieved May 2, 2006, from http://www.epa.gov/air/urbanair/nox/effrt.html.

U.S. PIRG Education Fund (2005), Pollution on the Rise: Local Trends in Power Plant Pollution. U.S. PIRG Education Fund, Washington, DC

Vassilakos, Ch., Saraga, D., Maggos, Th., Michopoulos, J., Pateraki, S., and Helmis, C.G., (2005). Temporal Variations of $PM_{2.5}$ in the Ambient Air of a Suburban Site in Athens, Greece. Science of the Total Environment, 349:223-231.

Vedal, S., (1995). Health Effects of Inhalable Particles: Implications for British Columbia, Prepared for the Air Resources Branch, British Columbia Ministry of Environment, Lands and Parks, Victoria, BC.

Vedal, S. (1996). Evaluation of Health Impacts due to Fine Inhalable Particles ($PM_{2.5}$). Contract Report Prepared from Health Canada, Final Report November 1996. Ministry of Public Works and Government Services, Ottawa.

Wang, K.Y., Shallcross, D.E., Hadjinicolaou, P. and Giannakopoulos, C. (2004). Ambient Vehicular Pollutants in the Urban Area of Taipei: Comparing Normal with Anomalous Vehicle Emissions. Water, Air, and Soil Pollution, 156(1):29-55

Wang, W., Van Gelder, P.H.A.J.M., and Vrijiling, J.K. (2005). Trend and Stationary Analysis for Streamflow Process of Rivers in Western Europe in the 20th Century, IWA International Conference on Water Economics, Statistics, and Finance, Rethymo, Greece, 8-10 July, 2005.

WCAS, (2004). West Central Airshed Society, Annual Report-2004. West Central Airshed Society, Drayton Valley, Alberta. Retrieved January 27, 2006, from http://www.wcas.ca/documents/WCAS_AR_2004.pdf

WCAS, (2005). West Central Airshed Society, Objectives. West Central Airshed Society, Drayton Valley, Alberta. Retrieved June 26, 2005, from http://www.wcas.ca/objectives/overview.html.

Weatherhead, E.C., Reinsel, G.C., Tiao, G.C., Meng, X.L., Choi, D., Cheang, W.K., Keller, T., Deluisi, J., Wuebbles, D.J., Kerr, J.B., Miller, A.J., Oltmans, S.J., and Frederick, J.E. (1998). Factors Affecting the Detection of Trends: Statistical Considerations and Applications to Environmental Data. Journal of Geophysical Research, 103(D14): 17149-17162.

Wichmann, H.E., and Peters, A. (2000). Epidemiological Evidence of the Effects of Ultrafine Particle Exposure. Philosophical Transactions of the Royal Society of London Series A, 358:2751-2769.

Williams, D.J., Carras, J.N., Milne, J.W., and Heggie, A.C. (1981). The Oxidation and Long-range Transport of Sulphur Dioxide in a Remote Region. Atmospheric Environment, 15(10-11):2255-2262.

World Health Organization (WHO), (1997). Assessment of Exposure to Indoor Air Pollutants, WHO Regional Publication, European Series, No.78, Copenhagen.

World Health Organization (WHO), (2000). Air Quality Guidelines, World Health Organization, Health Documentation Services, WHO Regional Office for Europe, Copenhagen.

World Health Organization (WHO), (2003). Health aspects of air pollution with particulate matter, ozone and nitrogen dioxide, World Health Organization, Health Documentation Services, WHO Regional Office for Europe, Copenhagen.

Wolff, G.T., Dunker, A.M., Rao, S.T., Porter, P. S. and Zubenko, I.G. (2001). Ozone Air Quality over North America: Part 1 – A Review of Reported Trends. Journal of Air and Waste Management Association, 51:273-282.

Zhang, Y. (2005). Indoor Air Quality, CRC Press, Boca Raton, FL.

APPENDIX A : DETECTION LIMITS OF POLLUTANTS AND STATISTICAL ANALYSIS OF POLLUTANT DATA

Table- A.1 Detection Limits and Statistical Analysis of Monitoring Data of the Pollutants at Tomahawk

Station	Pollutants	Detection Limit	Statistics	1997	1998	1999	2000	2001	2002	2003	2004
Tomahawk	O_3	1.0 ppb	% Completeness	87.01	85.38	49.03	94.39	92.19	94.43	91.59	94.68
			Maximum	73.50	74.40	70.50	75.20	80.30	97.02	82.70	70.49
			Minimum	0.00	0.00	0.40	0.00	0.00	0.00	0.00	0.00
			Median	29.75	27.30	35.60	28.60	30.60	30.88	31.29	29.21
			% Non-detects	0.41	0.41	0.05	0.66	0.69	0.98	0.24	0.42
	SO_2	0.2 ppb	% Completeness	93.73	92.23	57.47	92.71	93.23	94.28	91.83	95.06
			Maximum	56.40	23.20	22.60	33.90	29.40	52.04	37.67	24.86
			Minimum	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
			Median	0.60	0.60	0.60	0.50	0.60	0.60	0.62	0.57
			% Non-detects	24.64	20.23	20.82	34.95	18.17	16.95	15.00	19.05
	NO_2	0.05 ppb	% Completeness		55.65	60.83	93.86	91.92	94.28	91.37	94.74
			Maximum		39.20	35.20	36.70	38.70	38.70	31.74	58.08
			Minimum		0.00	0.10	0.00	0.00	0.00	0.00	0.00
			Median		3.10	3.00	3.40	3.40	3.21	3.26	2.74
			% Non-detects		0.74	0.00	6.69	6.86	0.05	0.09	0.62
	$PM_{2.5}$	0.1 $\mu g/m^3$	% Completeness				58.80	95.26	98.03	94.22	94.33
			Maximum				37.30	55.90	121.25	55.85	50.02
			Minimum				0.00	0.00	0.00	0.00	0.00
			Median				4.40	2.08	2.98	3.35	2.63
			% Non-detects				1.47	7.77	5.44	8.42	13.99
	PM_{10}	0.1 $\mu g/m^3$	% Completeness				45.81	53.65	98.81	95.05	96.19
			Maximum				196.80	187.20	214.38	148.58	171.10
			Minimum				0.00	0.05	0.00	0.00	0.00
			Median				8.20	9.50	9.07	9.10	8.31
			% Non-detects				0.72	0.00	0.76	0.65	4.64

Table- A.2 Detection Limits and Statistical Analysis of Monitoring Data of the Pollutants at Carrot Creek

Station	Pollutants	Detection Limit	Statistics	1997	1998	1999	2000	2001	2002	2003	2004
Carrot Creek	O_3	1.0 ppb	% Completeness		63.53	65.91	93.88	94.87	94.87	94.94	94.74
			Maximum		77.40	58.20	77.50	77.00	93.77	76.45	80.39
			Minimum		0.00	0.00	0.00	0.00	0.00	0.00	0.00
			Median		24.00	29.60	26.90	29.90	29.51	29.38	26.84
			% Non-detects		5.95	2.68	4.50	4.68	3.78	4.15	4.57
	SO_2	0.2 ppb	% Completeness		64.12	65.76	94.46	94.52	94.38	95.08	93.39
			Maximum		18.50	47.70	23.10	18.80	29.48	24.46	54.04
			Minimum		0.00	0.00	0.00	0.00	0.00	0.00	0.00
			Median		0.70	0.80	0.90	0.80	0.64	0.59	0.50
			% Non-detects		15.83	7.67	12.25	5.70	13.73	17.54	23.71
	NO_2	0.05 ppb	% Completeness		39.71	60.43	93.45	94.45	94.21	94.60	94.52
			Maximum		33.90	47.70	45.90	139.40	52.39	154.78	47.11
			Minimum		0.00	0.00	0.00	0.00	0.00	0.00	0.15
			Median		2.50	3.40	4.10	4.01	4.61	5.59	4.16
			% Non-detects		1.12	0.02	0.66	2.30	0.23	0.83	0.00

APPENDIX B : PERCENTILE CUMULATIVE DISTRIBUTIONS AT TOMAHAWK STATION

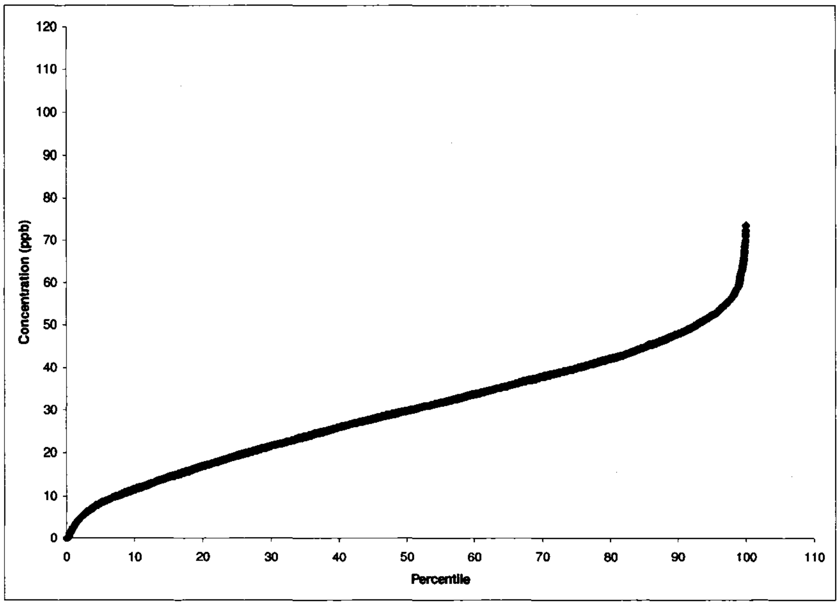

Figure- B.1 Percentile Cumulative Distribution of O_3 at Tomahawk for 1997

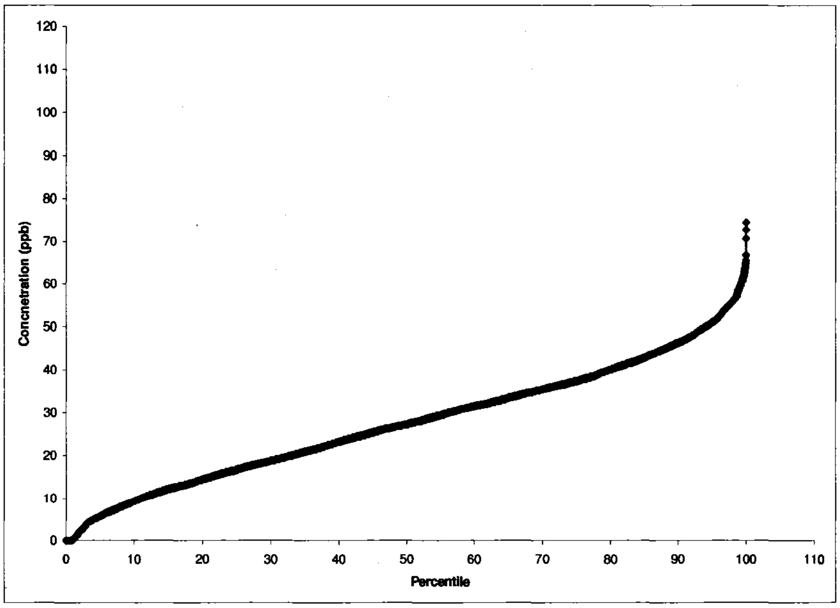

Figure- B.2 Percentile Cumulative Distribution of O_3 at Tomahawk for 1998

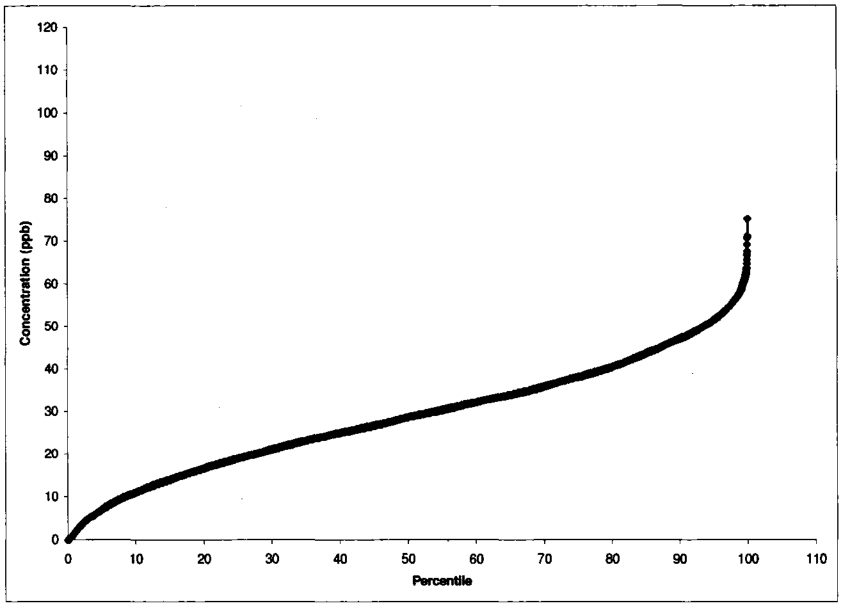

Figure- B.3 Percentile Cumulative Distribution of O_3 at Tomahawk for 2000

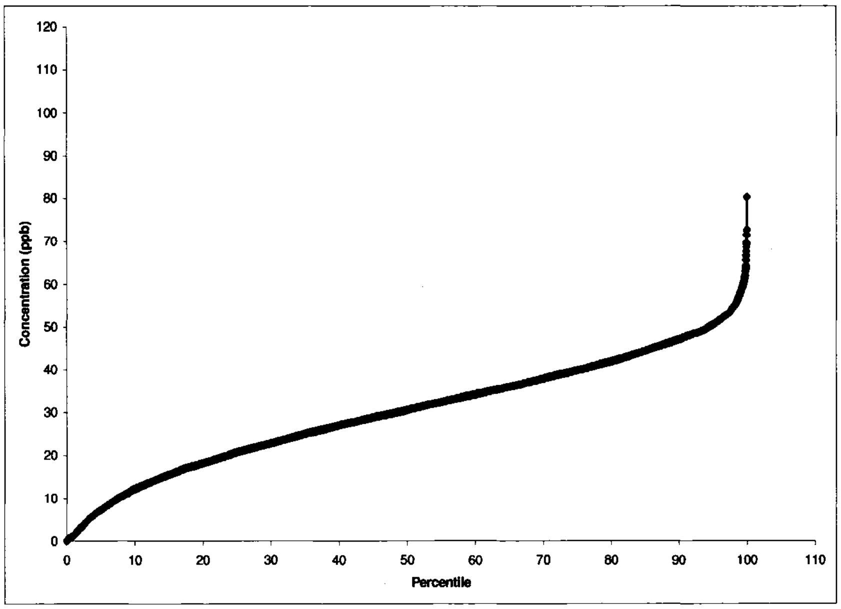

Figure- B.4 Percentile Cumulative Distribution of O_3 at Tomahawk for 2001

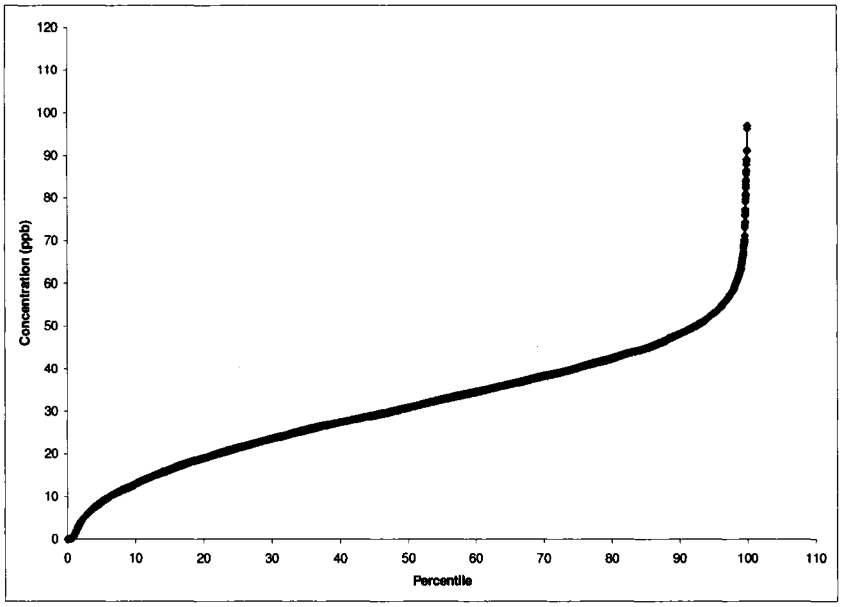

Figure- B.5 Percentile Cumulative Distribution of O_3 at Tomahawk for 2002

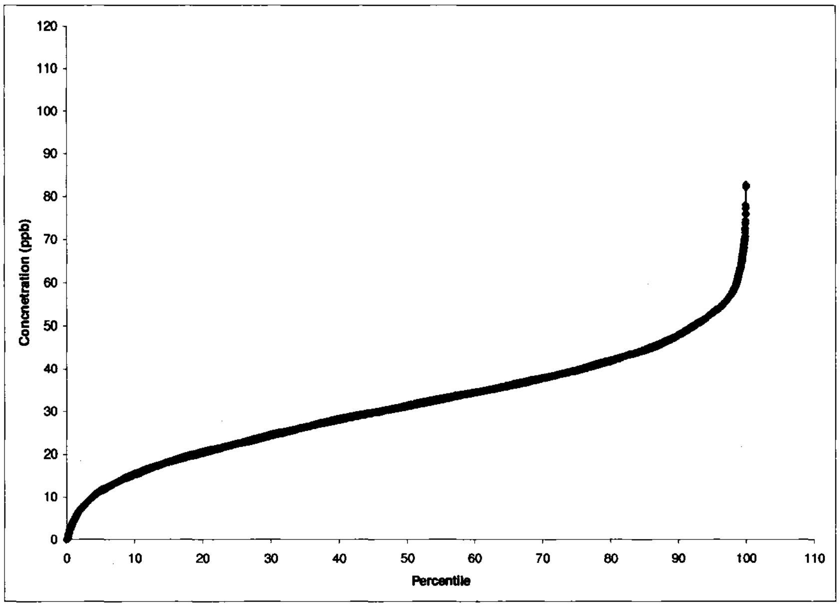

Figure- B.6 Percentile Cumulative Distribution of O_3 at Tomahawk for 2003

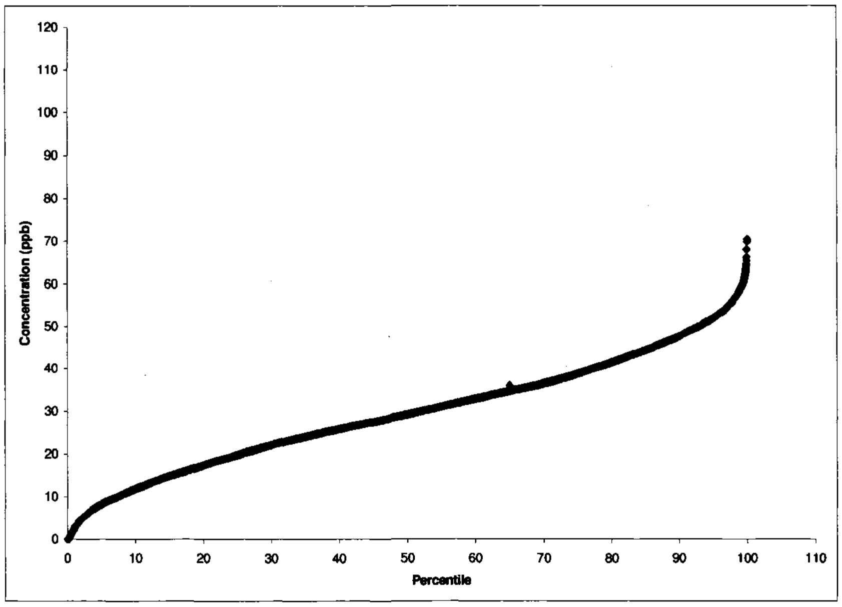

Figure- B.7 Percentile Cumulative Distribution of O_3 at Tomahawk for 2004

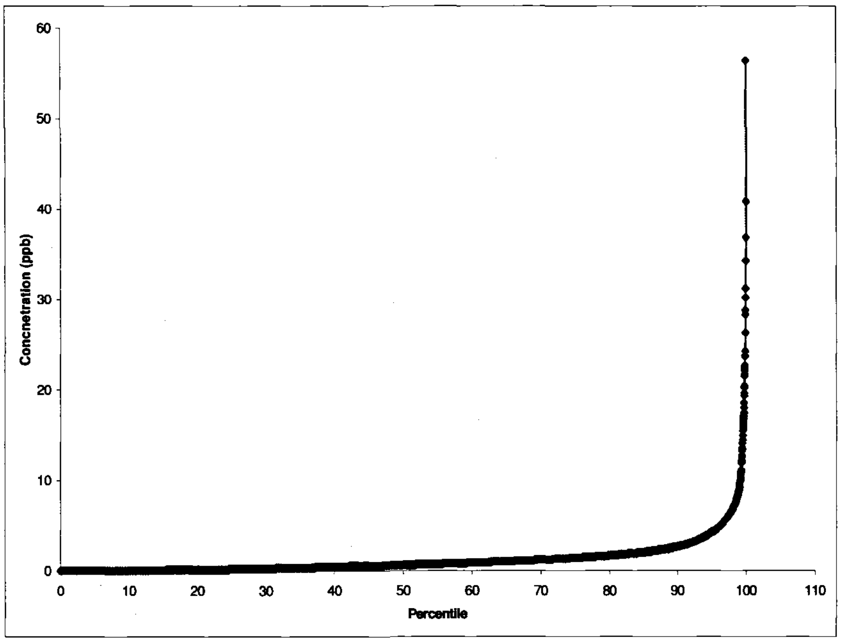

Figure- B.8 Percentile Cumulative Distribution of SO_2 at Tomahawk for 1997

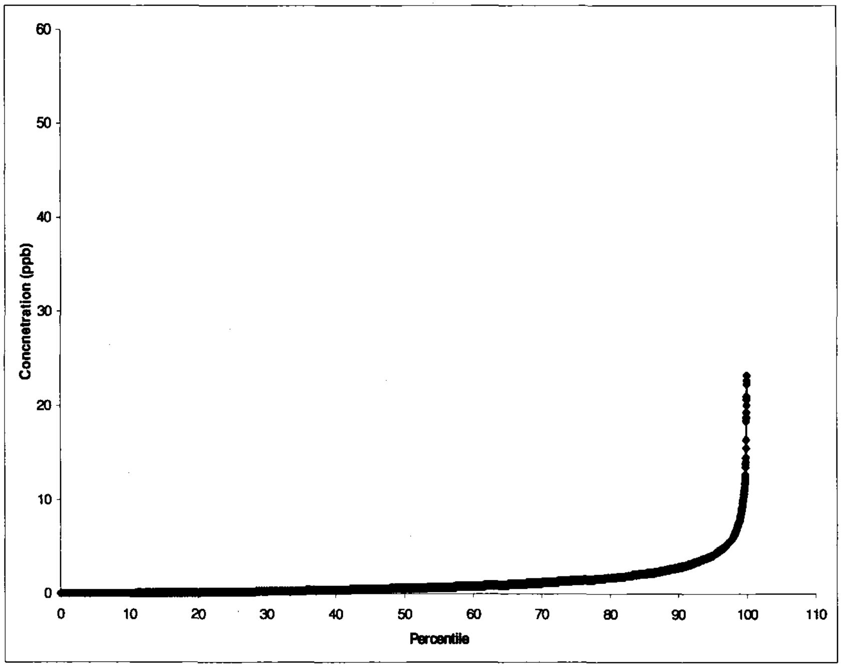

Figure- B.9 Percentile Cumulative Distribution of SO_2 at Tomahawk for 1998

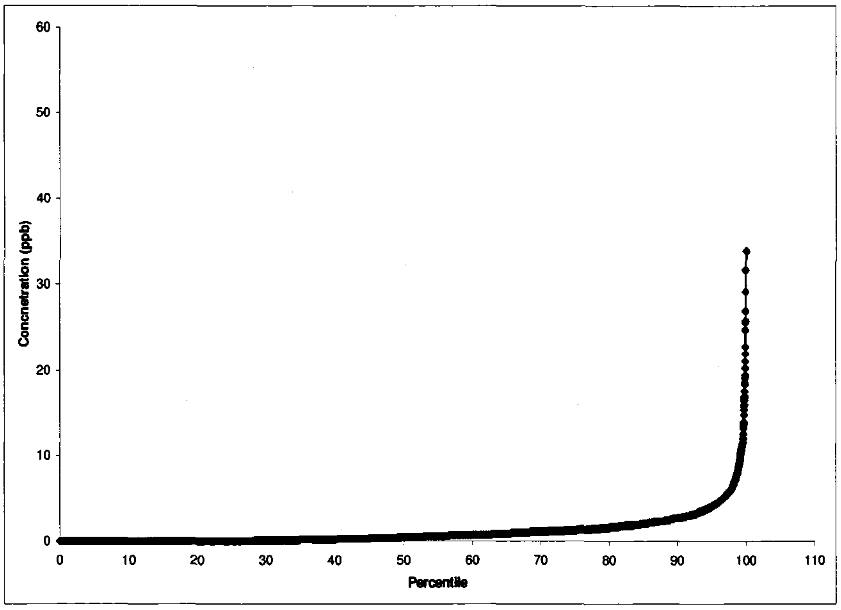

Figure- B.10 Percentile Cumulative Distribution for SO_2 at Tomahawk for 2000

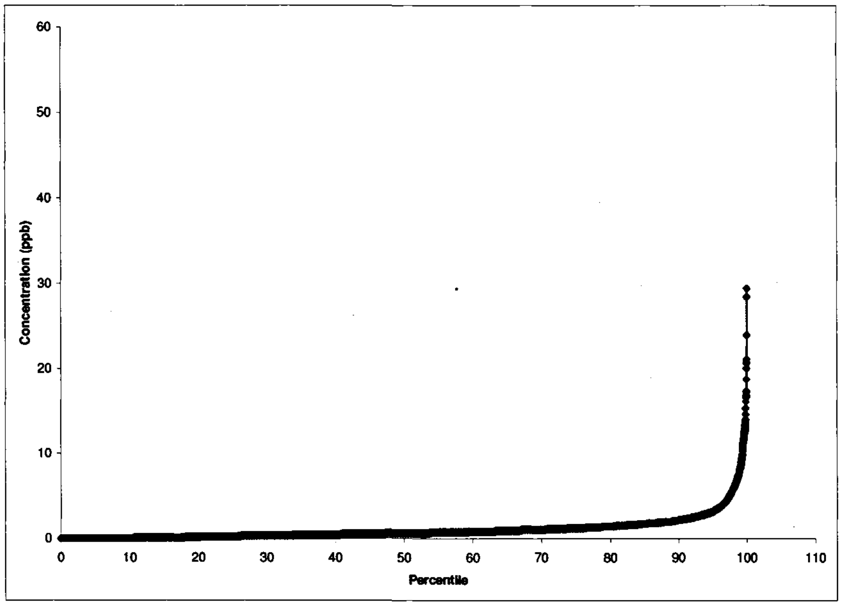

Figure- B.11 Percentile Cumulative Distribution for SO_2 at Tomahawk for 2001

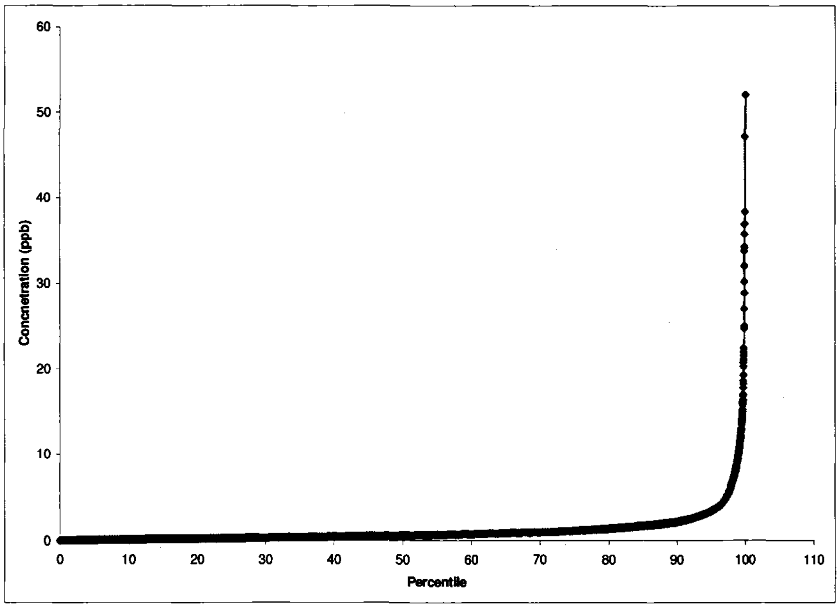

Figure- B.12 Percentile Cumulative Distribution for SO_2 at Tomahawk for 2002

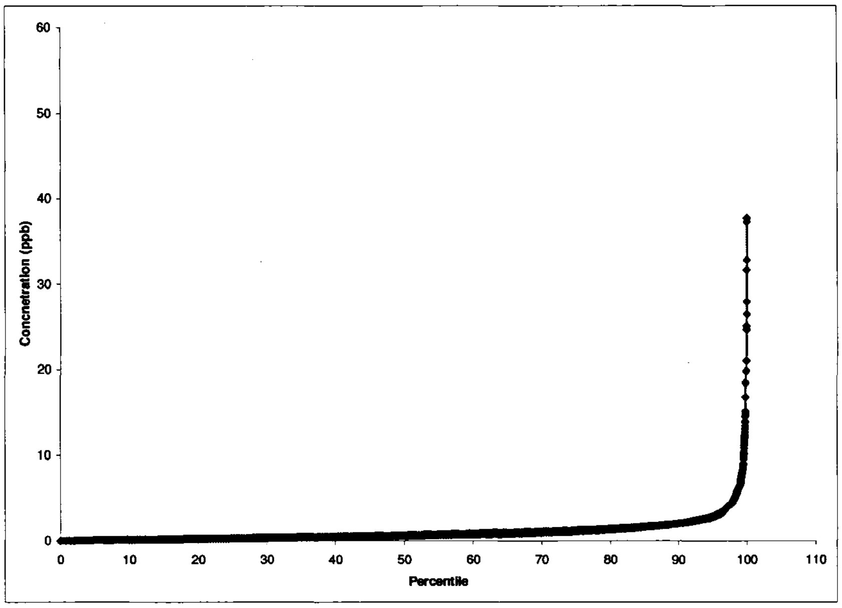

Figure- B.13 Percentile Cumulative Distribution for SO_2 at Tomahawk for 2003

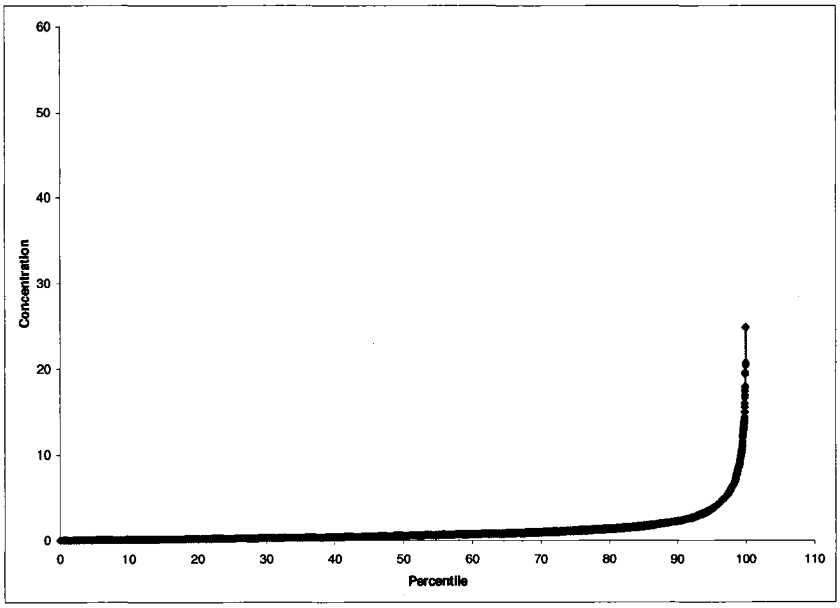

Figure- B.14 Percentile Cumulative Distribution of SO_2 at Tomahawk for 2004

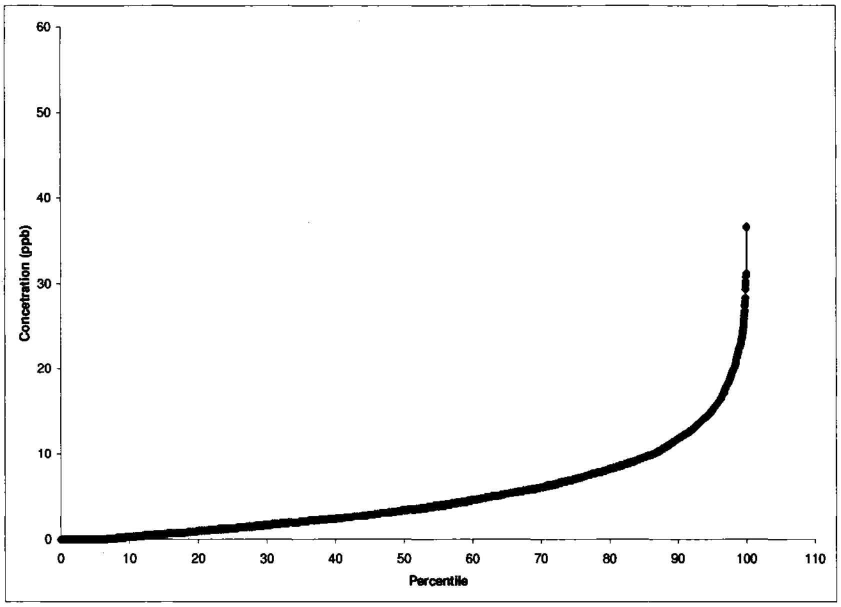

Figure- B.15 Percentile Cumulative Distribution of NO_2 at Tomahawk for 2000

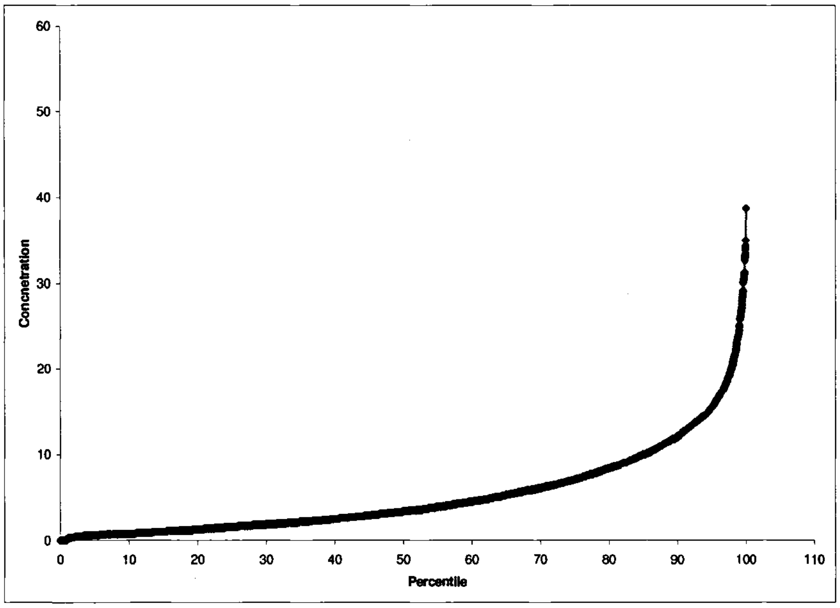

Figure- B.16 Percentile Cumulative Distribution of NO_2 at Tomahawk for 2001

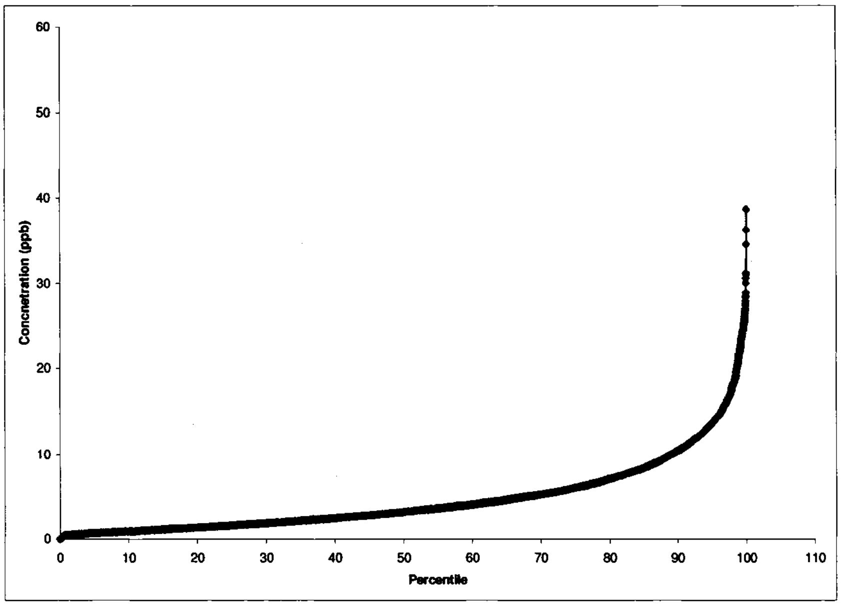

Figure- B.17 Percentile Cumulative Distribution of NO_2 at Tomahawk for 2002

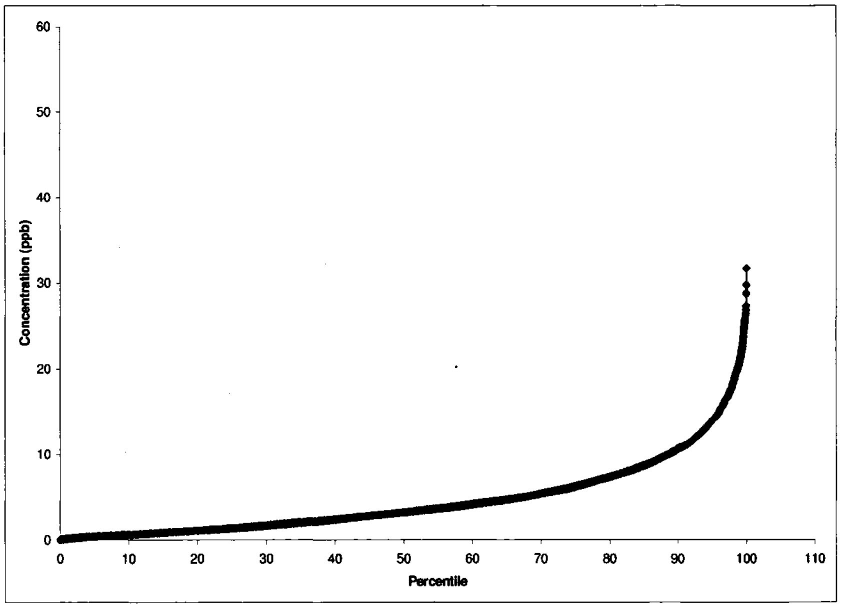

Figure- B.18 Percentile Cumulative Distribution of NO_2 at Tomahawk for 2003

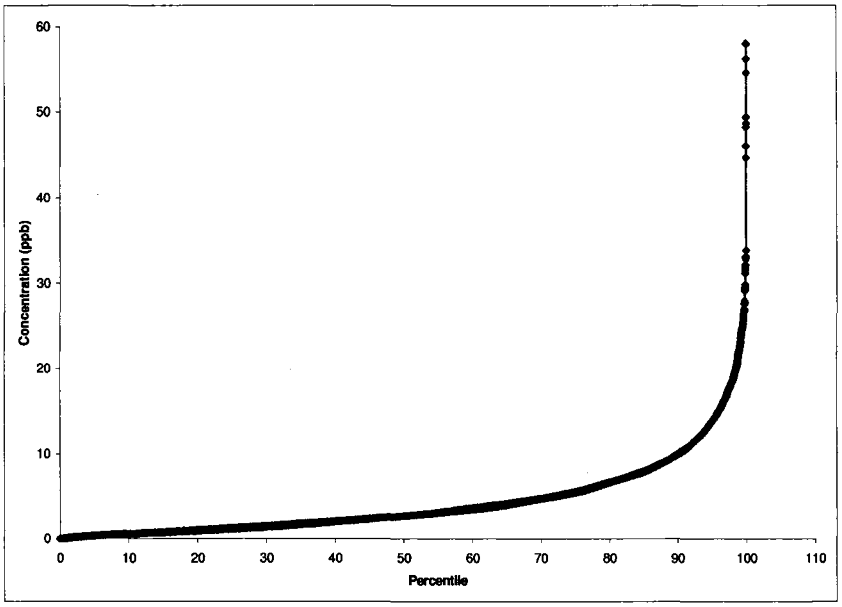

Figure- B.19 Percentile Cumulative Distribution of NO_2 at Tomahawk for 2004

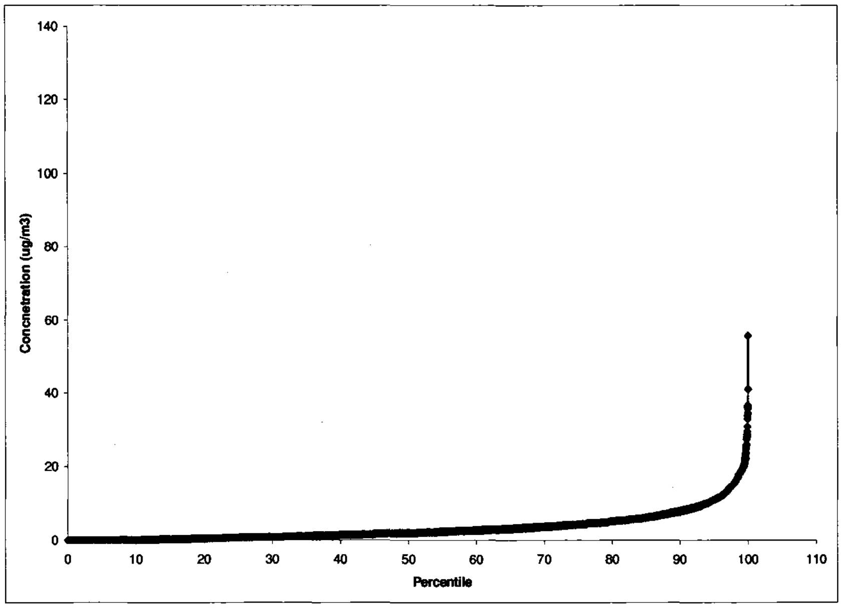

Figure- B.20 Percentile Cumulative Distribution of $PM_{2.5}$ at Tomahawk for 2001

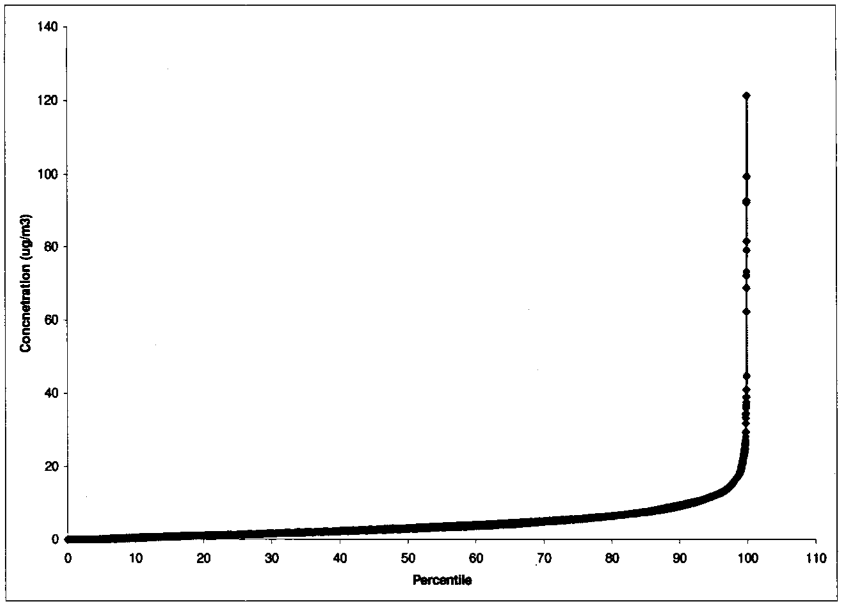

Figure- B.21 Percentile Cumulative Distribution of $PM_{2.5}$ *at Tomahawk for 2002*

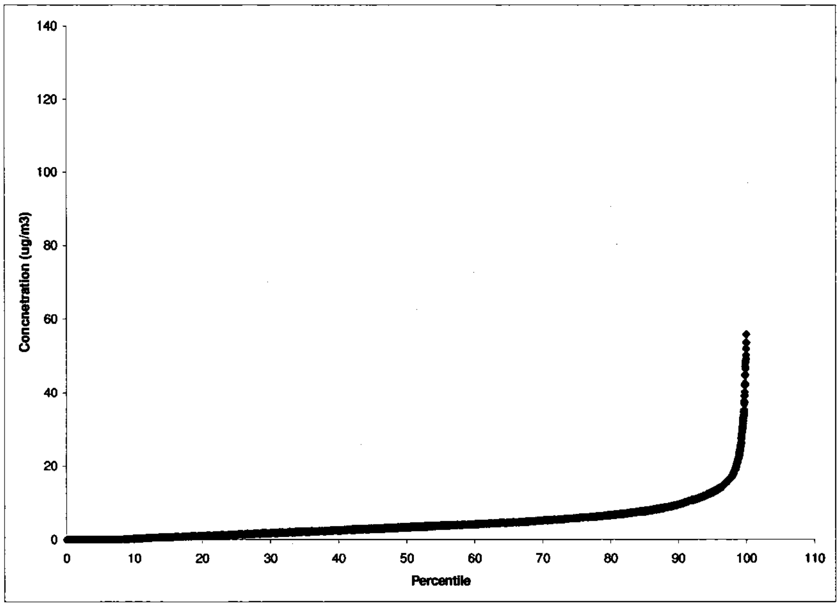

Figure- B.22 Percentile Cumulative Distribution of $PM_{2.5}$ *at Tomahawk for 2003*

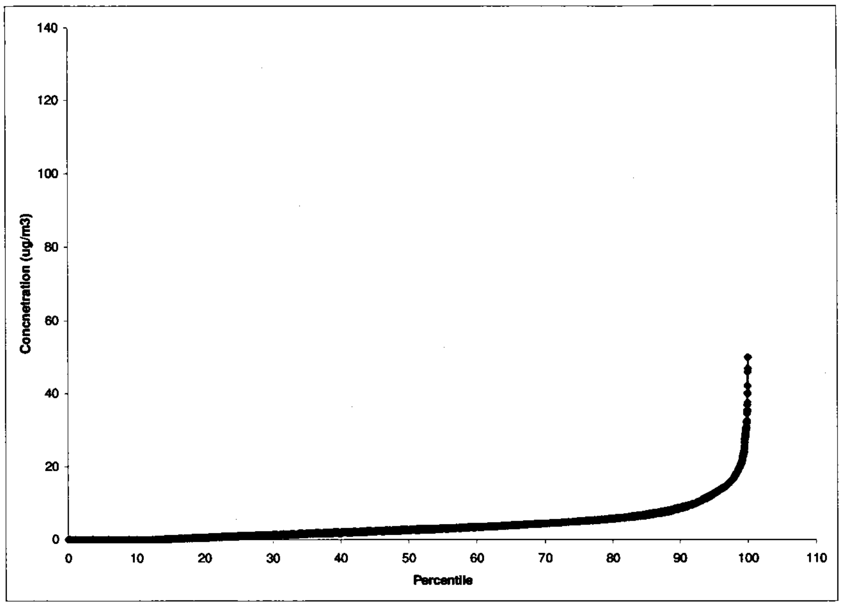

Figure- B.23 Percentile Cumulative Distribution of $PM_{2.5}$ at Tomahawk for 2004

APPENDIX C : PERCENTILE CUMULATIVE DISTRIBUTIONS AT CARROT CREEK STATION

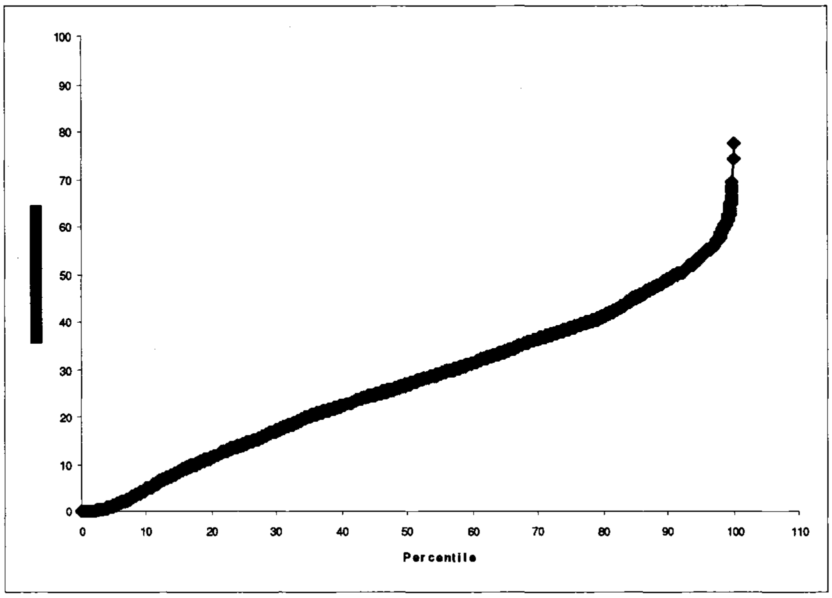

Figure- C.1 Percentile Cumulative Distribution of O_3 at Carrot Creek for 2000

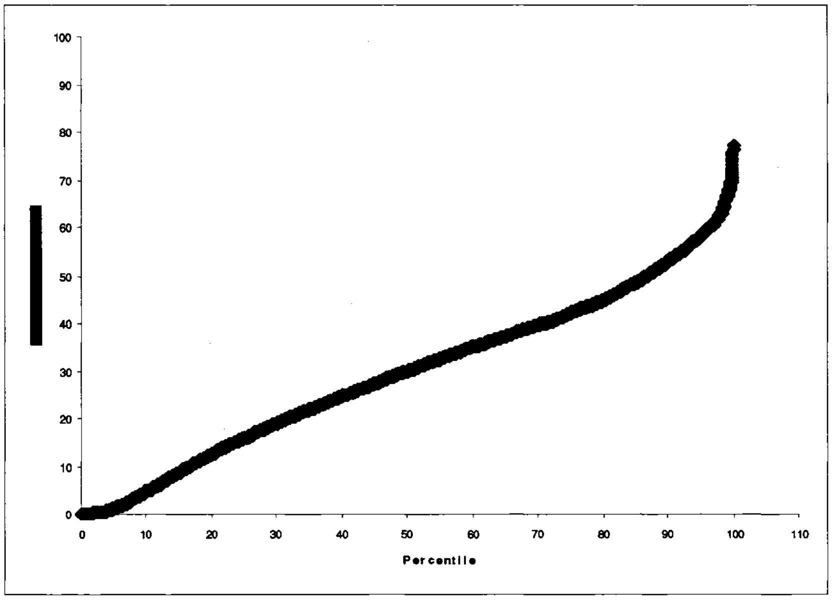

Figure- C.2 Percentile Cumulative Distribution of O_3 at Carrot Creek for 2001

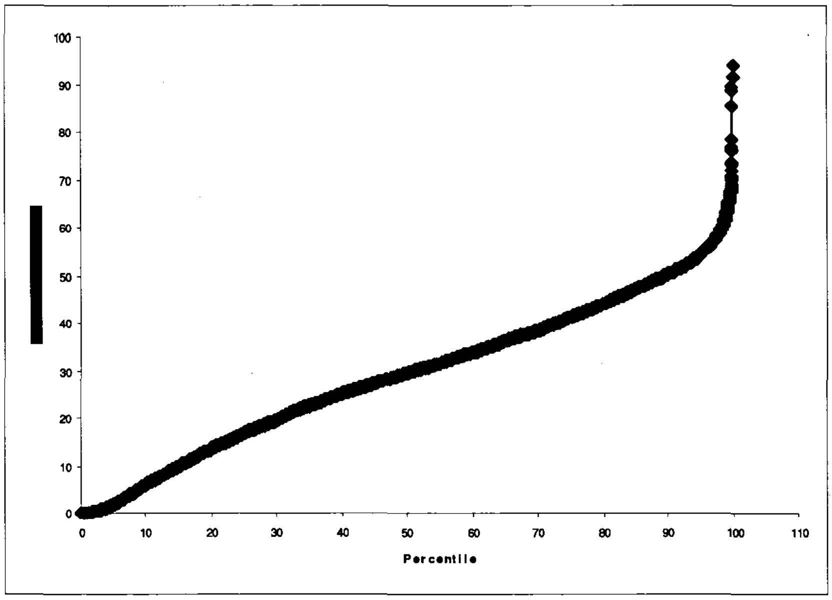

Figure- C.3 Percentile Cumulative Distribution of O_3 at Carrot Creek for 2002

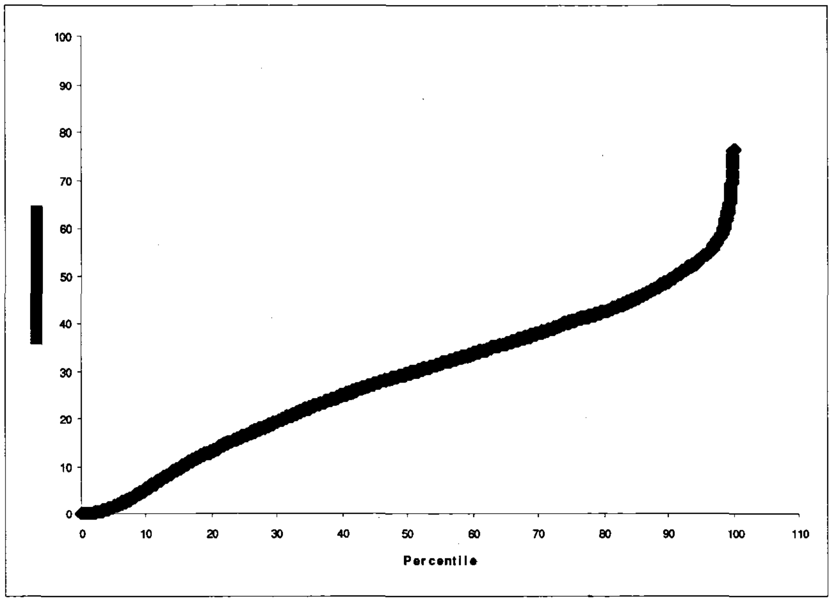

Figure- C.4 Percentile Cumulative Distribution of O_3 at Carrot Creek for 2003

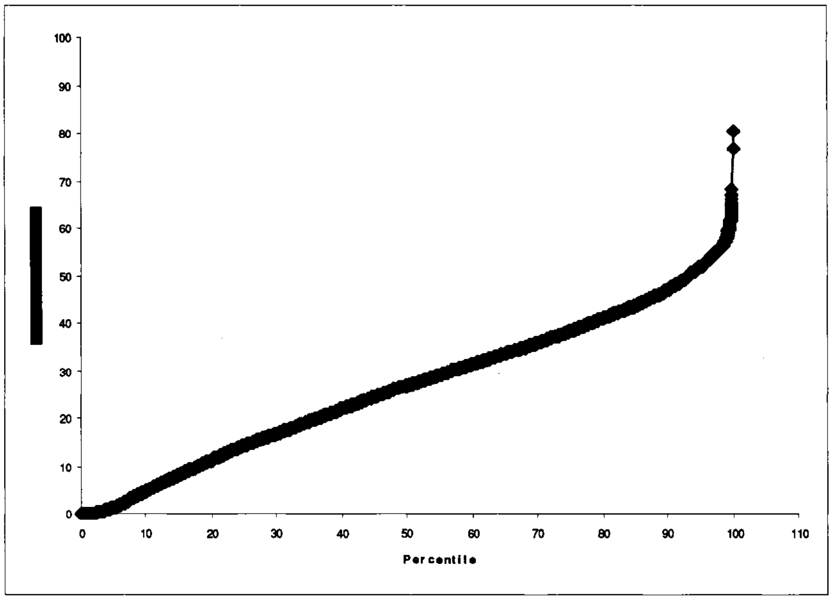

Figure- C.5 Percentile Cumulative Distribution of O_3 at Carrot Creek for 2004

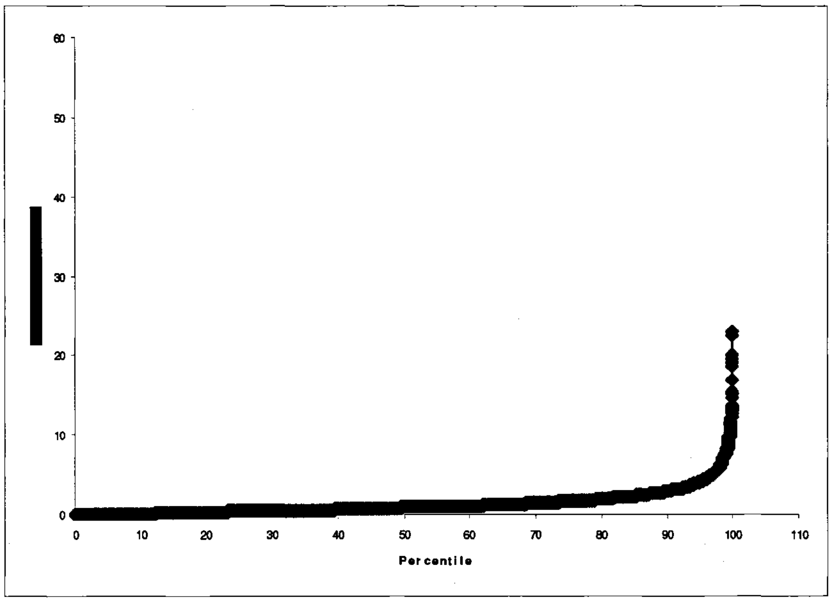

Figure- C.6 Percentile Cumulative Distribution of SO_2 at Carrot Creek for 2000

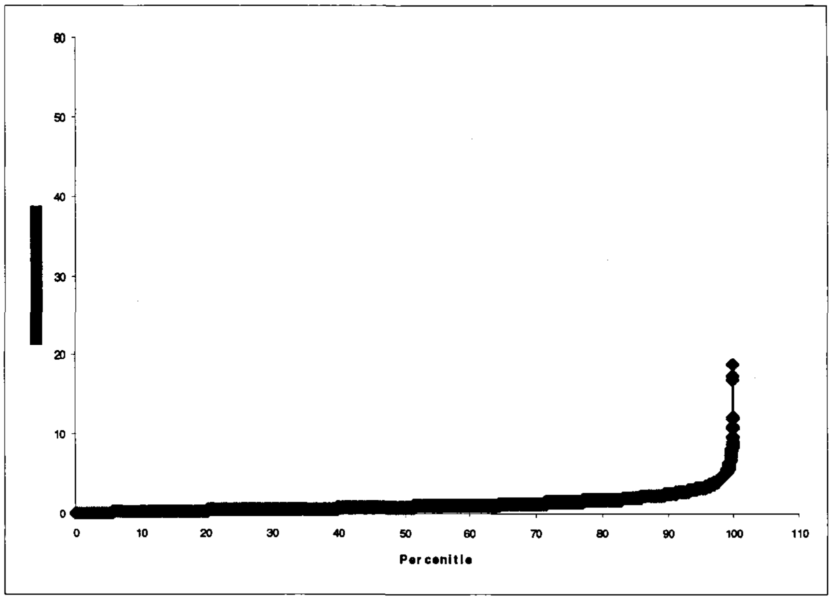

Figure- C.7 Percentile Cumulative Distribution for SO_2 at Carrot Creek for 2001

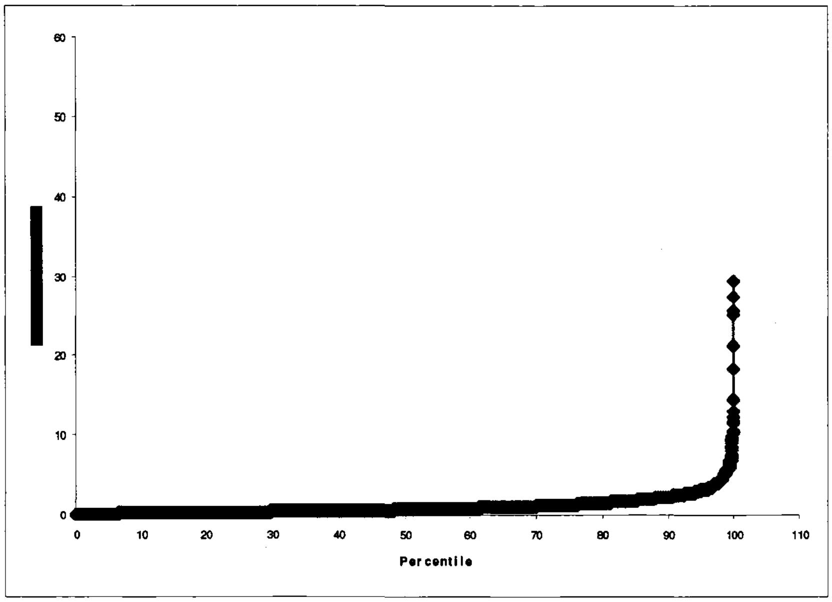

Figure- C.8 Percentile Cumulative Distribution of SO_2 at Carrot Creek for 2002

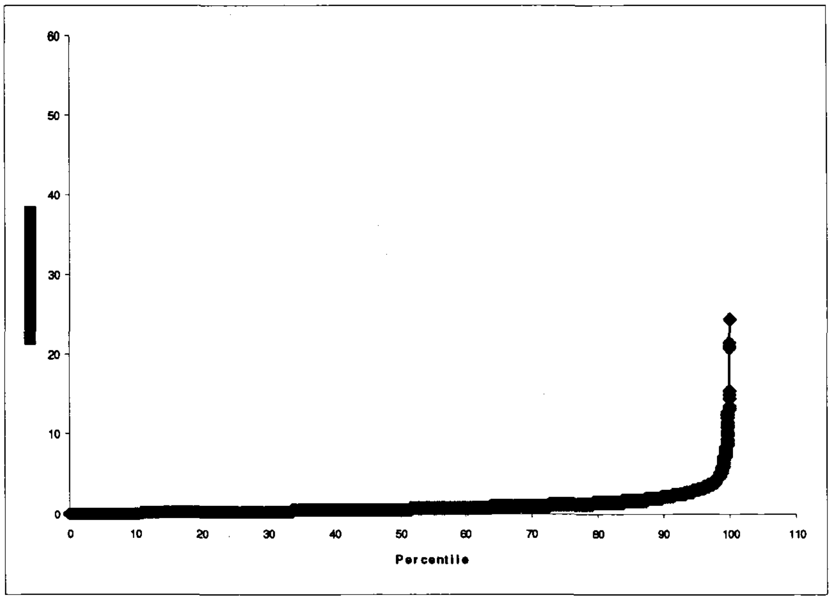

Figure- C.9 Percentile Cumulative Distribution of SO_2 at Carrot Creek for 2003

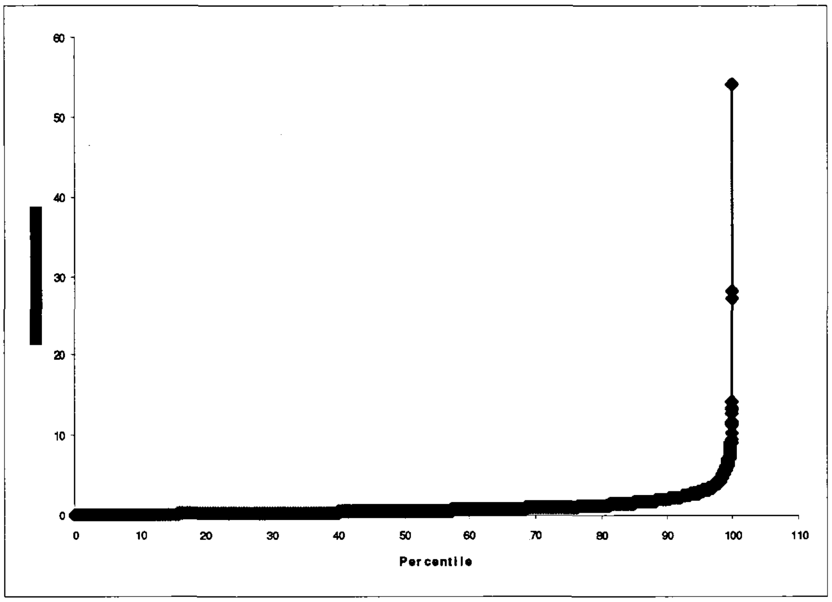

Figure- C.10 Percentile Cumulative Distribution of SO_2 at Carrot Creek for 2004

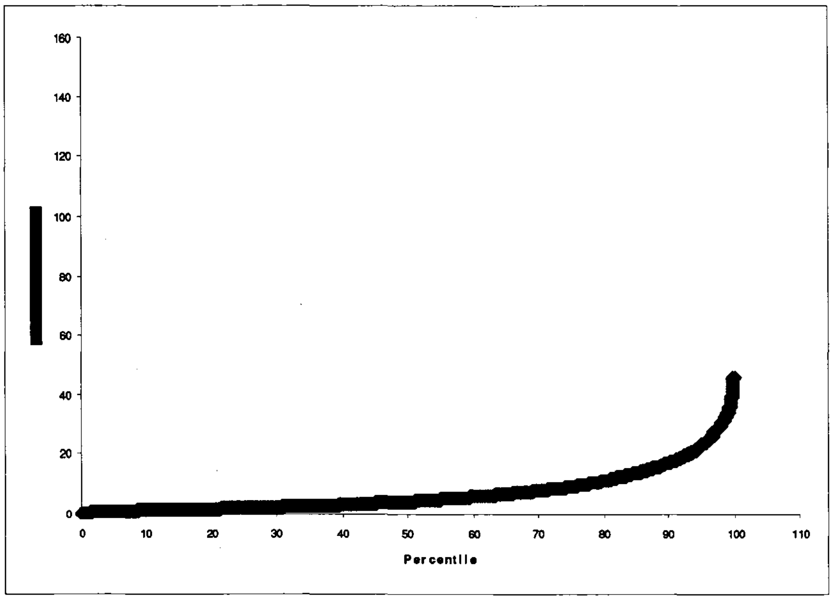

Figure- C.11 Percentile Cumulative Distribution of NO_2 at Carrot Creek for 2000

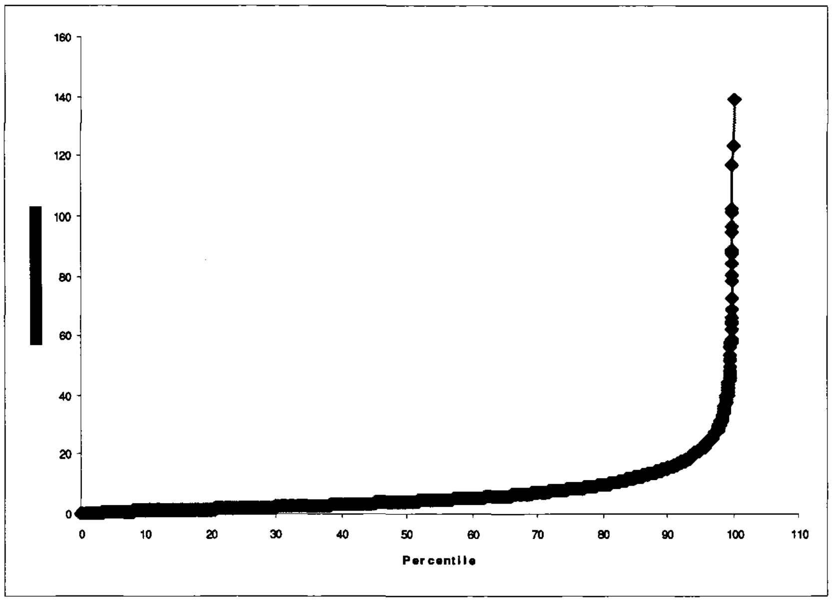

Figure- C.12 Percentile Cumulative Distribution of NO_2 at Carrot Creek for 2001

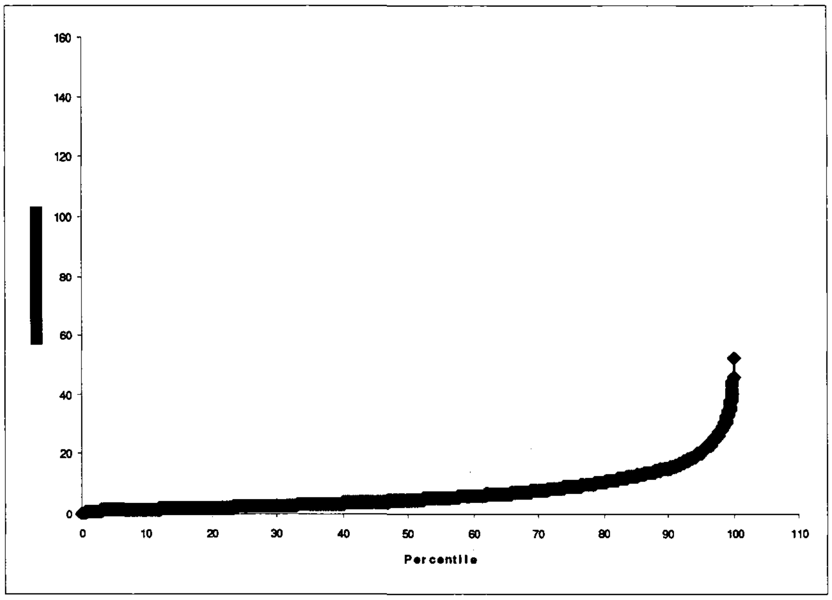

Figure- C.13 Percentile Cumulative Distribution of NO_2 at Carrot Creek for 2002

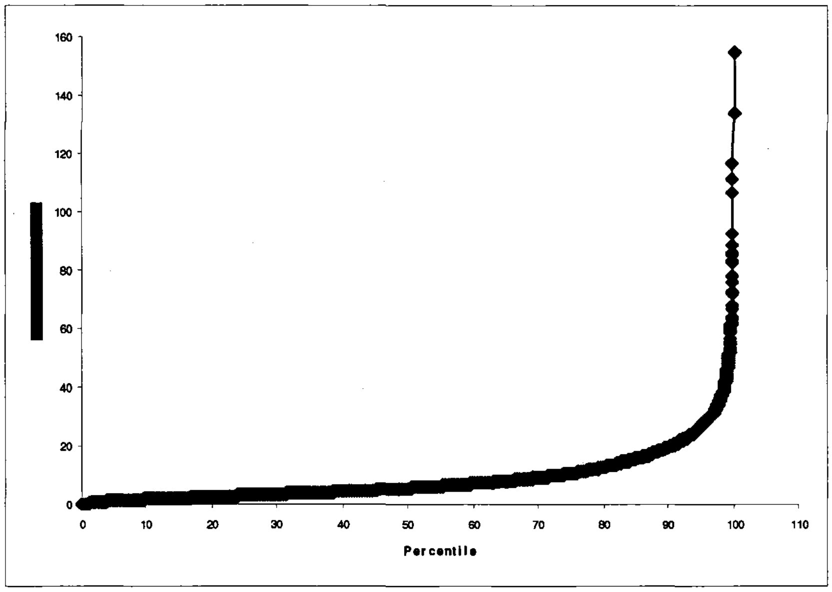

Figure- C.14 Percentile Cumulative Distribution of NO_2 at Carrot Creek for 2003

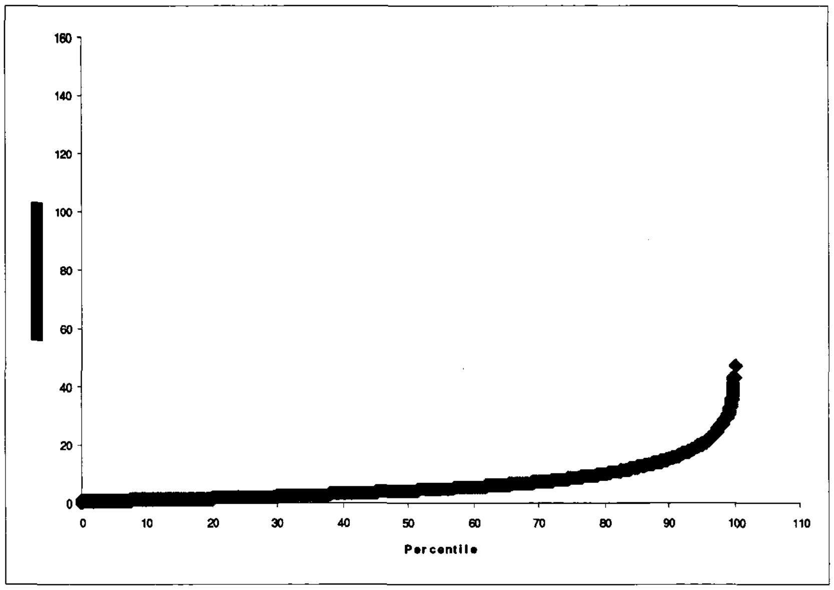

Figure- C.15 Percentile Cumulative Distribution of NO_2 at Carrot Creek for 2004

APPENDIX D : TEMPORAL VARIATION OF POLLUTANTS AT TOMAHAWK STATION

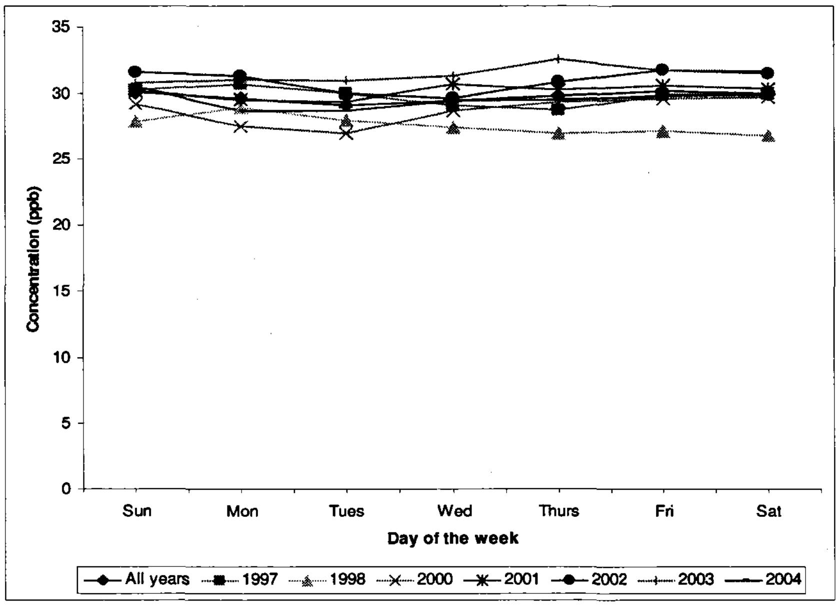

Figure- D.1 Tomahawk 1997-2004 Day of the Week Trends for O_3

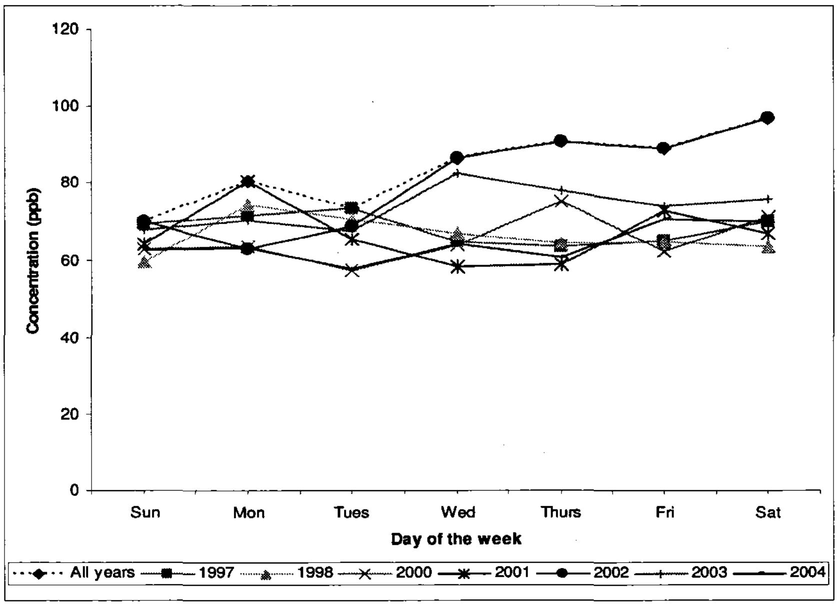

Figure- D.2 Tomahawk 1997-2004 Day of the Week Trends for O_3

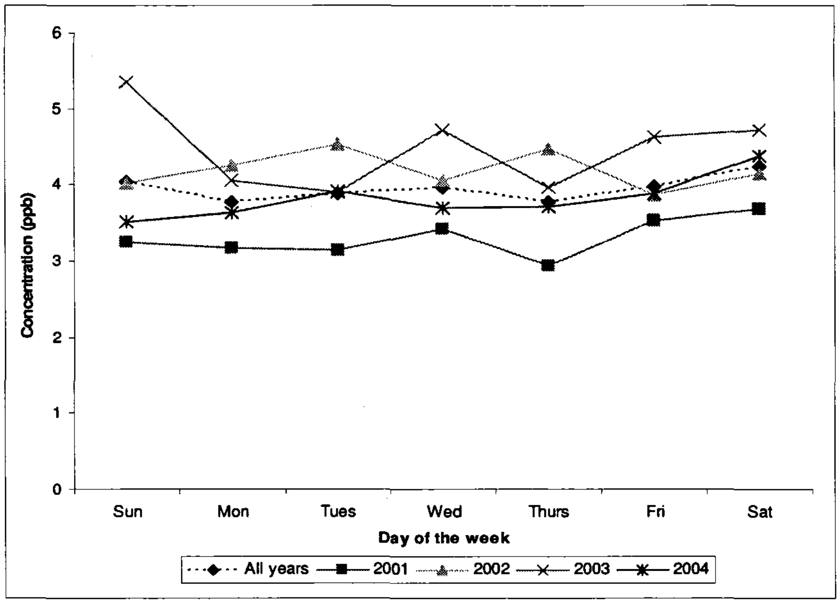

Figure- D.3 Tomahawk 1997-2004 Day of the Week Trends for $PM_{2.5}$

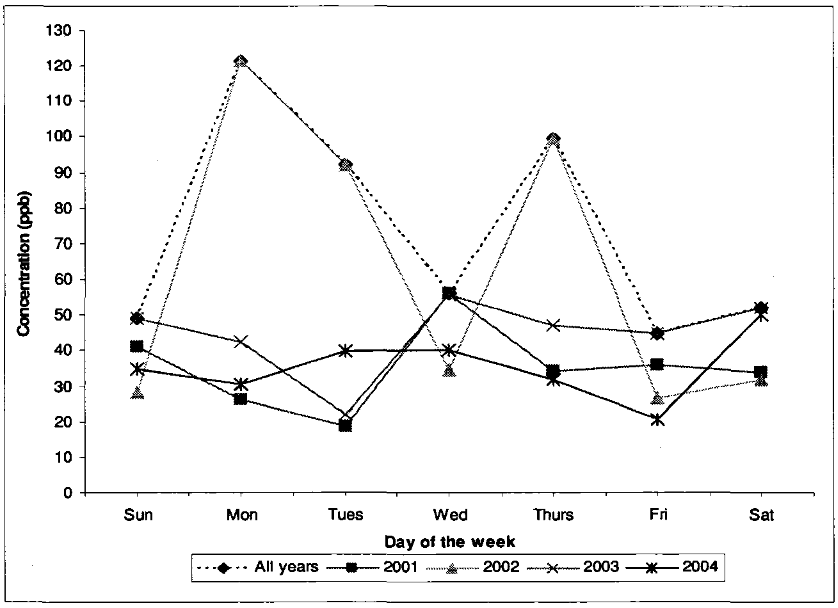

Figure- D.4 Tomahawk 1997-2004 Day of the Week Trends for $PM_{2.5}$

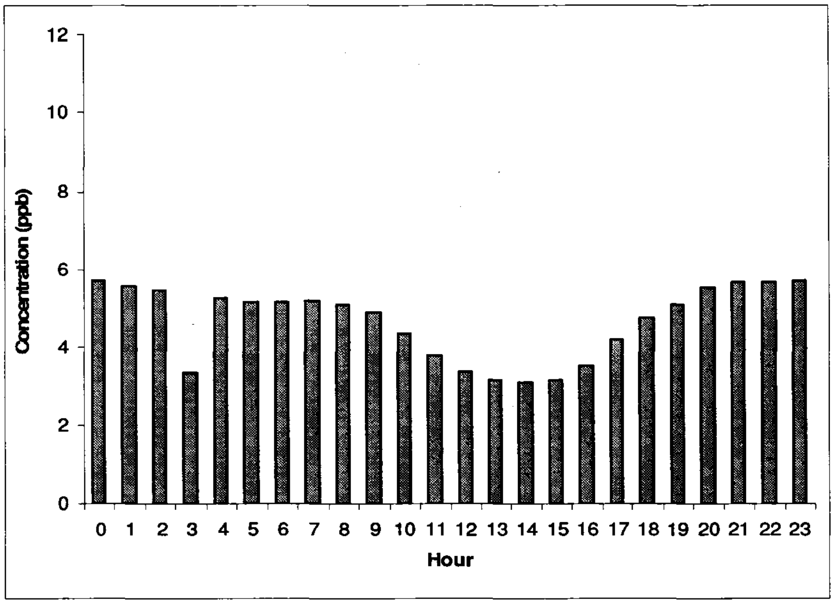

Figure- D.5 Tomahawk 1998-2004 Diurnal Hourly Average Concentration Trend for NO_2

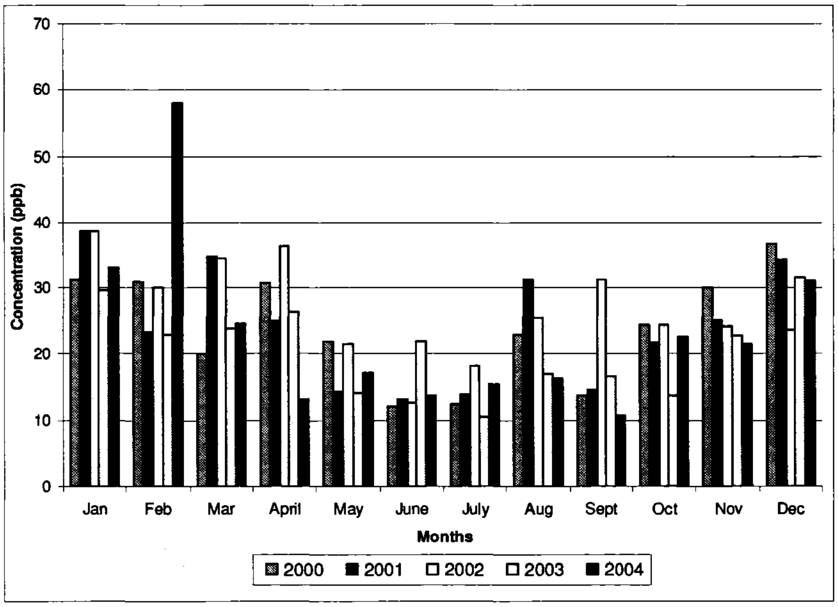

Figure- D.6 Tomahawk 2000-2004 Seasonal Trends for NO_2 (Monthly Maximum Concentrations)

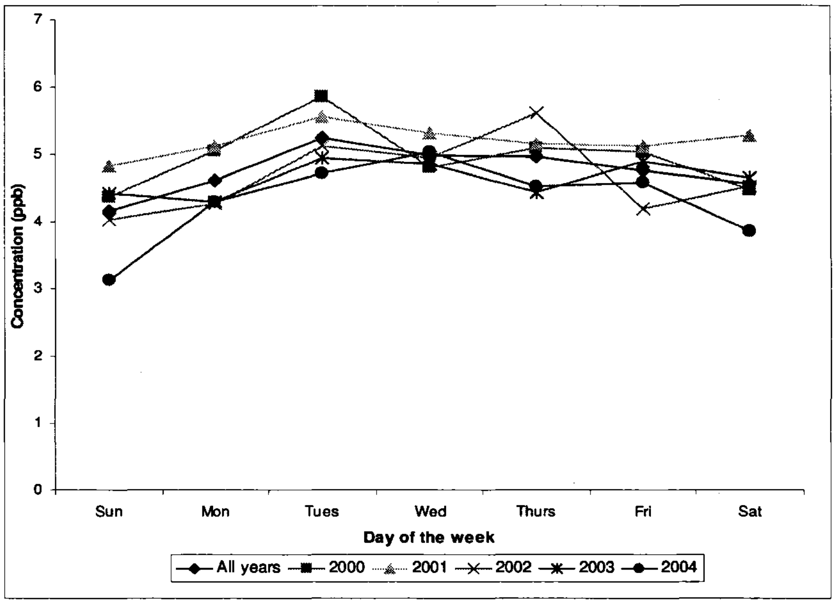

Figure D.7: Tomahawk 2000-2004 Day of the Week Trends for NO_2 (Average Hourly Concentration)

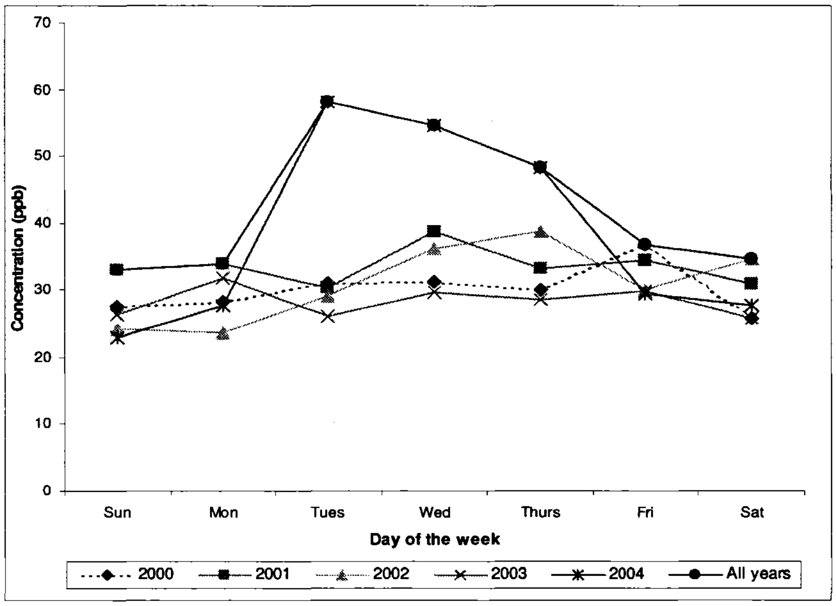

Figure D.8: Tomahawk 2000-2004 Day of the Week trends for NO_2 (Maximum hourly concentration)

APPENDIX E : TEMPORAL VARIATION OF POLLUTANTS AT CARROT CREEK STATION

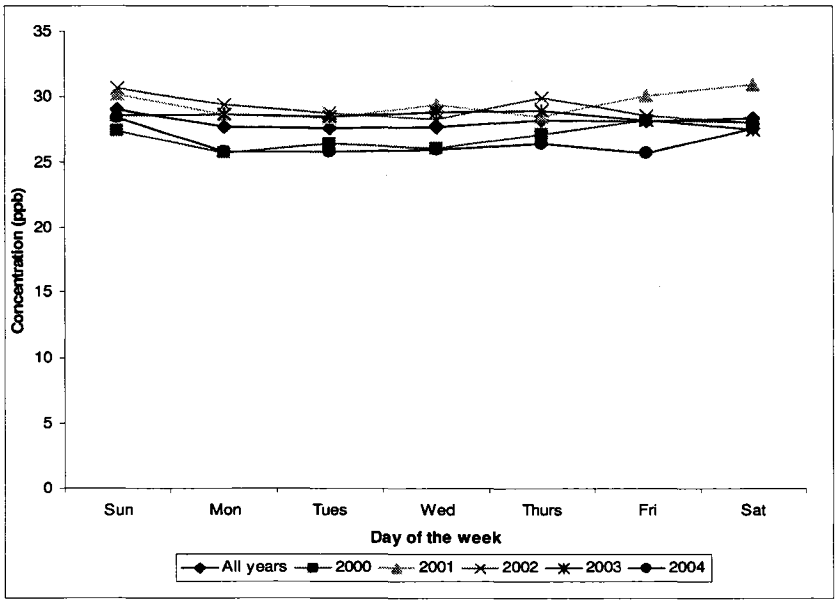

Figure- E.1 Carrot Creek 2000-2004 Day of the Week Trends for O_3 (Average Hourly Concentration)

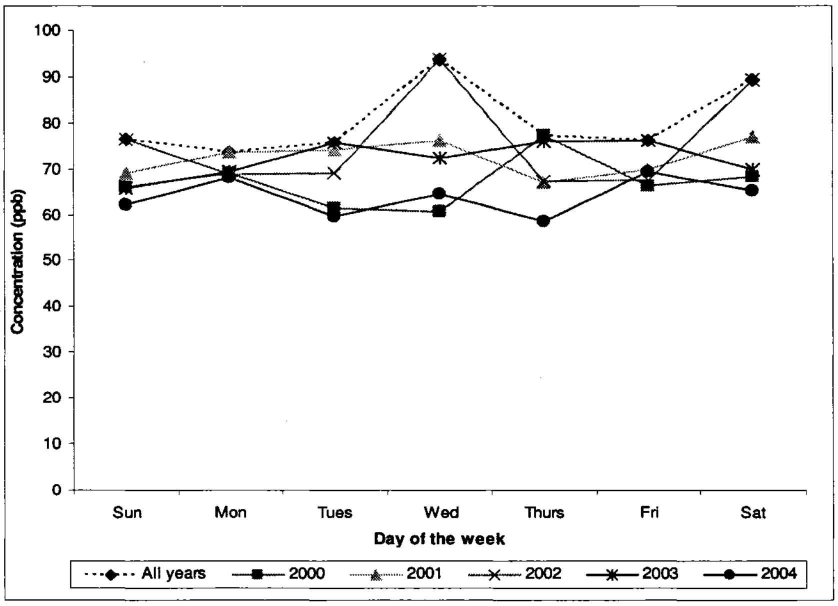

Figure- E.2 Carrot Creek 2000-2004 Day of the Week trends for O_3 (Maximum Hourly Concentration)

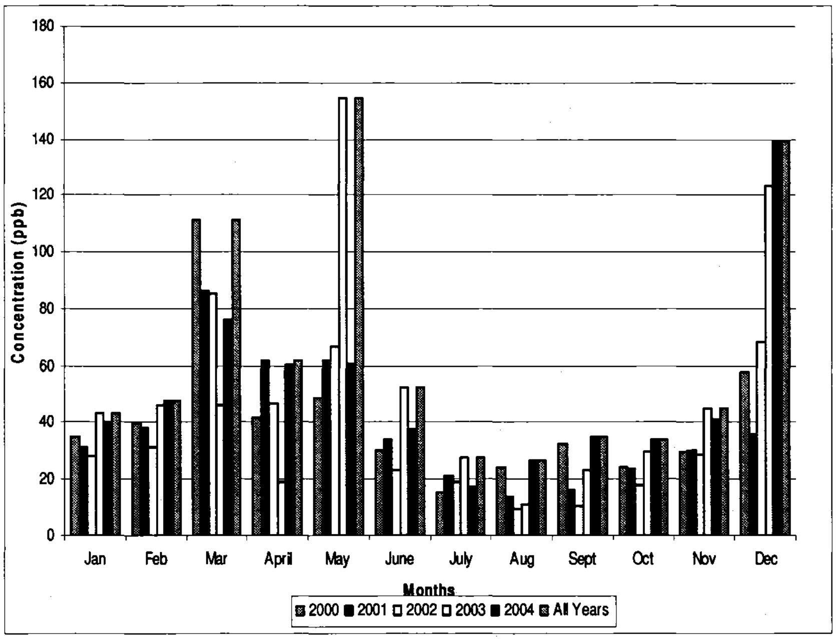

Figure E.3: Carrot Creek 2000-2004 Monthly Maximum Concentration Trends for NO_2

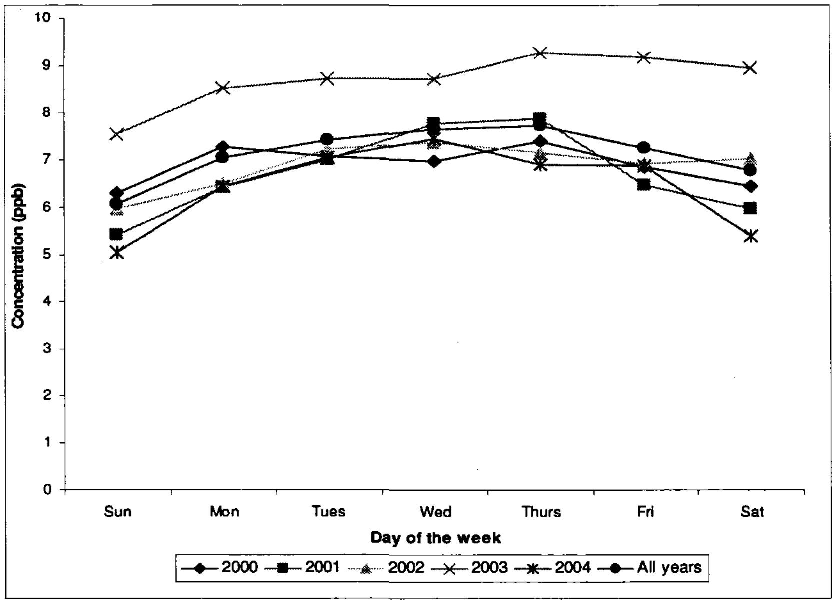

Figure E.4: Carrot Creek 2000-2004 Day of the Week Trends for NO_2

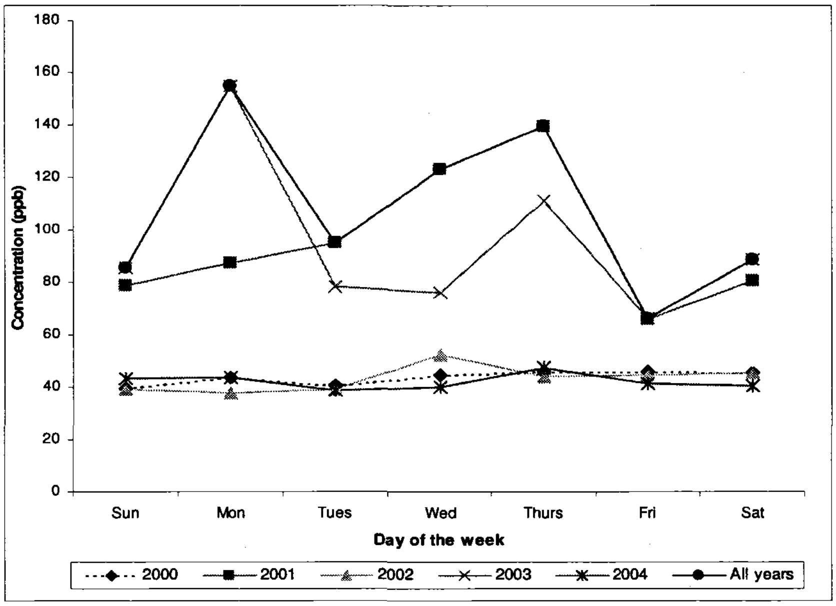

Figure E.5: Carrot Creek 2000-2004 Day of the Week trends for NO_2 (Maximum Hourly Concentration)

APPENDIX F : FREQUENCY OF EXCEEDENCE OF VARIOUS BENCHMARK CONCENTRATIONS EACH YEAR AT TOMAHAWK STATION

Table- F.1 Frequency of Exceedence of Various Benchmark Concentration of O_3 Each Year at Tomahawk

Percentile	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	1997	7622	3811	50.00
	1998	7479	3317	44.35
	2000	8291	3861	46.57
	2001	8076	4218	52.23
	2002	8272	4396	53.14
	2003	8023	4425	55.15
	2004	8317	4050	48.70
65%	1997	7622	2655	34.8
	1998	7479	2174	29.1
	2000	8291	2488	30.0
	2001	8076	2861	35.4
	2002	8272	3036	36.7
	2003	8023	2848	35.5
	2004	8317	2625	31.6
80%	1997	7622	1522.0	19.97
	1998	7479	1202.0	16.07
	2000	8291	1419.0	17.11
	2001	8076	1579.0	19.55
	2002	8272	1702.0	20.58
	2003	8023	1570.0	19.57
	2004	8317	1545.0	18.58
90%	1997	7622	755.0	9.91
	1998	7479	590.0	7.89
	2000	8291	722.0	8.71
	2001	8076	707.0	8.75
	2002	8272	851.0	10.29
	2003	8023	805.0	10.03
	2004	8317	800.0	9.62
95%	1997	7622	378.0	4.96
	1998	7479	311.0	4.16
	2000	8291	360.0	4.34
	2001	8076	287.0	3.55
	2002	8272	468.0	5.66
	2003	8023	451.0	5.62
	2004	8317	391.0	4.70
98%	1997	7622	152.0	1.99
	1998	7479	123.0	1.64
	2000	8291	144.0	1.74
	2001	8076	110.0	1.36
	2002	8272	243.0	2.94
	2003	8023	213.0	2.65
	2004	8317	161.0	1.94

Table- F.2 Frequency of Exceedence of Various Benchmark Concentrations of SO_2 Each Year at Tomahawk

Percentile	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	1997	8211	3960.0	48.23
	1998	8079	3772.0	46.69
	2000	8144	3537.0	43.43
	2001	8167	3792.0	46.43
	2002	8259	4082.0	49.42
	2003	8044	4091.0	50.86
	2004	8350	4023.0	48.18
65%	1997	8211	2782	33.88
	1998	8079	2601	32.19
	2000	8144	2574	31.61
	2001	8167	2424	29.68
	2002	8259	2404	29.11
	2003	8044	2447	30.42
	2004	8350	2428	29.08
80%	1997	8211	1534.0	18.68
	1998	8079	1546.0	19.14
	2000	8144	1517.0	18.63
	2001	8167	1192.0	14.60
	2002	8259	1219.0	14.76
	2003	8044	1128.0	14.02
	2004	8350	1223.0	14.65
90%	1997	8211	792.0	9.65
	1998	8079	801.0	9.91
	2000	8144	810.0	9.95
	2001	8167	550.0	6.73
	2002	8259	596.0	7.22
	2003	8044	445.0	5.53
	2004	8350	632.0	7.57
95%	1997	8211	391.0	4.76
	1998	8079	365.0	4.52
	2000	8144	372.0	4.57
	2001	8167	253.0	3.10
	2002	8259	274.0	3.32
	2003	8044	189.0	2.35
	2004	8350	326.0	3.90
98%	1997	8211	162.0	1.97
	1998	8079	130.0	1.61
	2000	8144	145.0	1.78
	2001	8167	122.0	1.49
	2002	8259	157.0	1.90
	2003	8044	77.0	0.96
	2004	8350	138.0	1.65

Table- F.3 Frequency of Exceedence of Various Benchmark Concentrations of NO_2 Each Year at Tomahawk

Percentile	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	2000	8245	4319	52.38
	2001	8052	4225	52.47
	2002	8259	4239	51.33
	2003	8001	4142	51.77
	2004	8322	3768	45.28
65%	2000	8245	3495	42.39
	2001	8052	3403	42.26
	2002	8259	3219	38.98
	2003	8001	3203	40.03
	2004	8322	2862	34.39
80%	2000	8245	2432	29.50
	2001	8052	2401	29.82
	2002	8259	2056	24.89
	2003	8001	2073	25.91
	2004	8322	1850	22.23
90%	2000	8245	1375	16.68
	2001	8052	1417	17.60
	2002	8259	1102	13.34
	2003	8001	1123	14.04
	2004	8322	1009	12.12
95%	2000	8245	623	7.56
	2001	8052	675	8.38
	2002	8259	472	5.71
	2003	8001	483	6.04
	2004	8322	473	5.68
98%	2000	8245	258	3.13
	2001	8052	265	3.29
	2002	8259	180	2.18
	2003	8001	185	2.31
	2004	8322	213	2.56

Table- F.4 Frequency of Exceedence of Various benchmark Concentrations of $PM_{2.5}$ Each Years at Tomahawk

Percentile	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	2001	8345	2043	24.48
	2002	8587	2882	33.56
	2003	8254	3065	37.13
	2004	8286	2502	30.20
65%	2001	8345	1465	17.56
	2002	8587	2085	24.28
	2003	8254	2208	26.75
	2004	8286	1760	21.24
80%	2001	8345	979	11.73
	2002	8587	1391	16.20
	2003	8254	1412	17.11
	2004	8286	1139	13.75
90%	2001	8345	638	7.65
	2002	8587	906	10.55
	2003	8254	922	11.17
	2004	8286	768	9.27
95%	2001	8345	426	5.10
	2002	8587	549	6.39
	2003	8254	633	7.67
	2004	8286	549	6.63
98%	2001	8345	259	3.10
	2002	8587	291	3.39
	2003	8254	377	4.57
	2004	8286	362	4.37

APPENDIX G : FREQUENCY OF EXCEEDENCE OF VARIOUS BENCHMARK CONCENTRATIONS EACH YEAR AT CARROT CREEK STATION

Table- G.1 Frequency of Exceedence of Various benchmark Concentrations of O_3 Each Years at Carrot Creek

Percentiles	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	2000	8246	4652	56.42
	2001	8311	5066	60.96
	2002	8264	5144	62.25
	2003	8317	5124	61.61
	2004	8322	4655	55.94
65%	2000	8246	3142	38.10
	2001	8311	3772	45.39
	2002	8264	3593	43.48
	2003	8317	3564	42.85
	2004	8322	3154	37.90
80%	2000	8246	1811	21.96
	2001	8311	2418	29.09
	2002	8264	2249	27.21
	2003	8317	2126	25.56
	2004	8322	1813	21.79
90%	2000	8246	1072	13.00
	2001	8311	1456	17.52
	2002	8264	1330	16.09
	2003	8317	1081	13.00
	2004	8322	873	10.49
95%	2000	8246	631	7.65
	2001	8311	1040	12.51
	2002	8264	811	9.81
	2003	8317	689	8.28
	2004	8322	519	6.24
98%	2000	8246	256	3.10
	2001	8311	579	6.97
	2002	8264	313	3.79
	2003	8317	261	3.14
	2004	8322	264	3.17

Table- G.2 Frequency of Exceedence of Various Benchmark Concentrations of SO_2 Each Year at Carrot Creek

Percentiles	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	2000	8297	4574	55.13
	2001	8280	4479	54.09
	2002	8268	3801	45.97
	2003	8329	3598	43.20
	2004	8203	3136	38.23
65%	2000	8297	3449	41.57
	2001	8280	3302	39.88
	2002	8268	2729	33.01
	2003	8329	2511	30.15
	2004	8203	2170	26.45
80%	2000	8297	1878	22.63
	2001	8280	1547	18.68
	2002	8268	1392	16.84
	2003	8329	1184	14.22
	2004	8203	1099	13.40
90%	2000	8297	982	11.84
	2001	8280	658	7.95
	2002	8268	611	7.39
	2003	8329	557	6.69
	2004	8203	519	6.33
95%	2000	8297	520	6.27
	2001	8280	277	3.35
	2002	8268	278	3.36
	2003	8329	245	2.94
	2004	8203	253	3.08
98%	2000	8297	216	2.60
	2001	8280	80	0.97
	2002	8268	103	1.25
	2003	8329	106	1.27
	2004	8203	102	1.24

Table- G.3 Frequency of Exceedence of Various Benchmark Concentrations of NO_2 Each Years at Carrot Creek

Percentiles	Year	Total Hours	No. of Hours Exceeded	% of Hours Exceeded
50%	2000	8209	5332	64.95
	2001	8274	5477	66.20
	2002	8253	6016	72.89
	2003	8287	6756	81.53
	2004	8303	5623	67.72
65%	2000	8209	4348	52.97
	2001	8274	4388	53.03
	2002	8253	4835	58.58
	2003	8287	5646	68.13
	2004	8303	4510	54.32
80%	2000	8209	3234	39.40
	2001	8274	3053	36.90
	2002	8253	3395	41.14
	2003	8287	4078	49.21
	2004	8303	3164	38.11
90%	2000	8209	2153	26.23
	2001	8274	1930	23.33
	2002	8253	2186	26.49
	2003	8287	2643	31.89
	2004	8303	2021	24.34
95%	2000	8209	1369	16.68
	2001	8274	1150	13.90
	2002	8253	1233	14.94
	2003	8287	1674	20.20
	2004	8303	1170	14.09
98%	2000	8209	767	9.34
	2001	8274	629	7.60
	2002	8253	596	7.22
	2003	8287	1038	12.53
	2004	8303	600	7.23

APPENDIX H : SAMPLE CALCULATION FOR TESTING SIGNIFICANT OF SLOPE

Sample Calculation for Testing Significant of Slope by t-Test:

Station: Tomahawk

Pollutant: SO_2

Trend at 90th Percentile: $y = -0.0993x + 2.8552$

Table- H.1 Calculations for t-test

Year	x	$x-\bar{x}$	$(x-\bar{x})^2$	y	$\hat{y}$	$y-\hat{y}$	$(y-\hat{y})^2$	Sum of Squares of Error (or Residuals), *SSE* = $\sum(y-\hat{y})^2$
1997	1	-3.71	13.80	2.70	2.76	-0.06	0.00	0.00
1998	2	-2.71	7.37	2.70	2.66	0.04	0.00	0.00
2000	4	-0.71	0.51	2.70	2.46	0.24	0.06	0.06
2001	5	0.29	0.08	2.20	2.36	-0.16	0.03	0.03
2002	6	1.29	1.65	2.15	2.26	-0.11	0.01	0.01
2003	7	2.29	5.22	2.02	2.16	-0.14	0.02	0.02
2004	8	3.29	10.80	2.24	2.06	0.18	0.03	0.03
	$\bar{x}$ =4.71			**$\bar{y}$ =2.39**			$\sum$=0.15	$\sum$ = 0.15 df = (n-2) =5

$$\text{SSE} = \sum(y-\hat{y})^2 = 0.15$$

$$s_e = \sqrt{\frac{1}{n-2}\sum(y_i-\hat{y})^2} = \sqrt{\frac{SSE}{n-2}} = 0.175$$

$$s_b = s_e\sqrt{\frac{1}{\sum_{i=1}^{n}(x_i-\bar{x})^2}} = 0.028$$

$$t_0 = t_{(n-2)} = \frac{b-\beta}{s_b} = -\,3.56$$

$$t_c = 2.571$$

Here, $t_0 > t_c$ [Absolute value of t_0]

Therefore, H_0 : β=0 is rejected, indicating that slope is "Significant".

Sample Calculation for Testing Significant of Slope by F-Test:

Station: Tomahawk

Pollutant: SO_2

Trend at 90th Percentile: $y = -0.0993x + 2.8552$

Table- H.2 Calculations for F-test

Year	x	$x-\bar{x}$	$(x-\bar{x})^2$	y	$\hat{y}$	$y-\hat{y}$	$(y-\hat{y})^2$	Sum of Squares of Error (or Residuals), *SSE* = $\sum(y-\hat{y})^2$	Sum of Squares of Regression, SSR = $\sum(\hat{y}-\bar{y})^2$
1997	1	-3.71	13.80	2.70	2.76	-0.06	0.00	0.00	0.14
1998	2	-2.71	7.37	2.70	2.66	0.04	0.00	0.00	0.07
2000	4	-0.71	0.51	2.70	2.46	0.24	0.06	0.06	0.01
2001	5	0.29	0.08	2.20	2.36	-0.16	0.03	0.03	0.00
2002	6	1.29	1.65	2.15	2.26	-0.11	0.01	0.01	0.02
2003	7	2.29	5.22	2.02	2.16	-0.14	0.02	0.02	0.05
2004	8	3.29	10.80	2.24	2.06	0.18	0.03	0.03	0.11
	$\bar{x}$ =4.71			$\bar{y}$ =**2.39**			Σ=0.15	Σ = 0.15 df = (n-2) =5	Σ = 0 df = 1

$$MSR = \frac{SSR}{1} \quad = 0.39$$

$$MSE = \frac{SSE}{n-2} \quad = 0.03$$

$$F_0 = \frac{MSR}{MSE} \quad = 12.65$$

$$F_{(0.05,1,5)} \quad = 6.61$$

Here, $F_0 > F_c$

Therefore, H_0 : β=0 is rejected, indicating that slope is "Significant".

Verification of the t-test and F-test by "Regression Tool" in Excel :

Station: Tomahawk

Pollutant: SO_2

Trend at 90th Percentile: $y = -0.0993x + 2.8552$

Table- H.3 Regression by Excel

Regression Statistics	
Multiple R	0.846603
R Square	0.716736
Adjusted R Square	0.660083
Standard Error	0.175299
Observations	7

ANOVA

	df	SS	MS	F	Significance F
Regression	1	0.388775	0.388775	12.65138762	0.016268
Residual	5	0.153649	0.03073		
Total	6	0.542424			

	Coefficients	Standard Error	t Stat	P-value	Lower 95%	Upper 95%	Lower 95.0%
Intercept	2.855204	0.147347	19.37735	6.75333E-06	2.476436	3.233972	2.476436
X Variable 1	-0.099299	0.027917	-3.556879	0.016268318	-0.171062	-0.027535	-0.171062