



University of Alberta

**Ambient Air Quality Trends
in West Central Airshed Society Zone**

Final Report

Prepared for:

West Central Airshed Society
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Executive Summary

Ambient air monitoring can be used to determine the status of air quality, and to understand deviations from natural background levels and changes over time (trends). Responding to public perceptions and concerns about air quality remains a challenge and requires sound assessment. It is of great interest to know whether changes in air quality have occurred over time in areas where economic development is on going and continuous air monitoring is conducted. Assessment of trends offers a sound scientific approach for responding to public perceptions and concerns about air quality and establishing whether or not change is occurring.

The objective of this study was to examine the extent to which concentrations of ambient air quality parameters have changed (trends) over a period of 7 to 8 years at two West Central Airshed Society (WCAS) stations in central Alberta: i) Tomahawk (from 1997 to 2004) and ii) Carrot Creek (from 1998 to 2004). These stations are on the eastern side of the airshed within elevations 700 to 1000 m above sea level. While they are both located in predominantly rural areas, anthropogenic activities – oil and gas wells, gas processing plants, coal-fired power plants – occur in the area.

Pollutants studied include ozone, nitrogen dioxide, sulphur dioxide and fine particulate matter. The methodology for examining trends consisted of two approaches. The first approach consisted of examining trends in annual percentiles in the mid-to-upper-range (50th to 98th percentile) of hourly concentration distributions. The second approach examined trends in annual frequencies (number of hours) in which various benchmark concentrations were exceeded. Assuming these summary statistics to be linear, hypothesis testing at a significance level (α) = 0.05 was conducted on best-fit lines to check whether slopes were greater or less than zero to indicate trends.

Ozone (O₃)

The diurnal behaviour of O₃ at both Tomahawk and Carrot Creek station closely corresponded to that of turbulent mixing layer and conformed to the general behaviour of

ground-level O₃ in rural areas – where it is strongly influenced by the interaction of source and sink mechanisms. Seasonal monthly average and monthly maximum patterns at Tomahawk and Carrot Creek appear to reflect the contribution of photochemically-generated O₃ from sunshine and natural and anthropogenic precursors.

Results of trend analysis showed that – at both Tomahawk and Carrot Creek stations – air quality remained unchanged with respect to O₃. None of the trends exhibited any statistically significant change. This is not unexpected at rural sites, where the influence of local and regional sources of anthropogenic pollutant is not high compared to cities.

Sulphur Dioxide (SO₂)

Hourly SO₂ concentrations are considered low at the two WCAS stations and trend analysis clearly indicated that they are decreasing. In investigating possible causes for this change, the Alberta Energy and Utilities Board (EUB) has been working with the oil and gas industry in Alberta to reduce solution gas flaring and venting and documenting annual volumes of solution gas flared and vented since 1999. These data show continuously reduced flared and vented solution gas volumes in the WCAS zone. These data offer a reasonable explanation for decreasing hourly SO₂ concentration trends observed at the Tomahawk and Carrot Creek stations.

Nitrogen Dioxide (NO₂)

Seasonal variation of average monthly NO₂ concentrations showed an expected approximate inverse relationship to seasonal variation of average monthly O₃ concentrations. Specifically, maximum monthly average NO₂ concentrations during November, December, and January corresponded to minimum monthly average O₃ concentrations. While NO₂ concentrations are much lower compared to O₃, scavenging reactions between O₃ and oxides of nitrogen and decreased reactivity of NO₂ in winter months offer plausible explanations for seasonal variation of average monthly NO₂ concentrations.

Trend analysis showed that hourly NO₂ concentrations decreased at Tomahawk and did not change at Carrot Creek during the period of study. Not enough information is known about

whether any differences exist among NO_x source emissions in close proximity to these stations that might offer plausible explanations for the change (or lack thereof) observed.

Fine Particulate Matter (PM_{2.5})

At Tomahawk, the diurnal pattern of PM_{2.5} concentrations did not show any substantive trend, consistent with the rural character of the site. Lack of a temporal trend suggested that the air monitoring station is influenced by mostly rural activities of low importance. PM_{2.5} concentrations are not monitored at Carrot Creek.

The period of study over which trends were observed is acknowledged to be short (less than a decade). Changes or lack of changes observed do not necessarily provide an indication of what may happen over the long term. Results of this study are indicating that air quality is unchanged for O₃ and PM_{2.5} and improving in the case of SO₂. The former condition would be expected for rural areas with little or no strong source emission influences. The latter condition is consistent with reduced solution gas flaring and venting in the region of study.

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List of Abbreviations

AAQG	Ambient Air Quality Guideline
AMD	Air Quality Monitoring Directive
AQM	Air Quality Monitoring
AQOG	Air Quality Objectives and Guidelines
ATSDR	Agency for Toxic Substances & Disease Registry
CASA	Clean Air Strategic Alliance
CCME	Canadian Council of Ministers of Environment
CO	Carbon monoxide
CWS	Canada-Wide Standard
EPA	Environmental Protection Agency
EUB	Energy and Utilities Board
GIS	Geographic Information System
MK	Mann-Kendall
MSE	Mean square 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 Plan
SK	Seasonal Kendall
SO ₂	Sulphur dioxide
SO _x	Oxides of sulphur
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
USEPA	US Environmental Protection Agency
UV	Ultraviolet
VOCs	Volatile Organic Compounds
WCAS	West Central Airshed Society
WHO	World Health Organization

1 Introduction

Air quality issues are among the most difficult environmental problems currently faced by societies as more and more studies report impacts of atmospheric pollution on human health and the environment (Desauziers, 2004). Air pollution can originate from many different sources – stationary sources (large factories and smaller sources such as dry cleaners and degreasing operations); mobile sources (cars, buses, planes, trucks, and trains); and naturally occurring sources such as windblown dust and forest fires. All of these contribute to air pollution.

Ozone (O₃), nitrogen dioxide (NO₂), sulphur dioxide (SO₂) are known respiratory irritants and prolonged exposure to these gases may be 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; US EPA, 1999). Epidemiological studies, which rely on data from stationary ambient monitoring sites, have reported statistical associations between particulate matter (PM) and adverse health outcomes including cardiovascular effects (US EPA, 1999; Wichmann and Peters, 2000). Responding effectively to concerns about air quality is a challenge for many regions and it requires sound assessment and innovative strategic and tactical advice. Accordingly, it is of great interest to know whether a change in air quality has occurred over the years.

Changes to air quality are often assessed by examination of collected real-time measurements of ambient level pollutants at different sites. It is important to keep records of air quality measurements to check compliance or non-compliance with air quality standards. However, only evaluating and reporting monitoring data to assess compliance 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).

Trend analysis tries to identify underlying longer-term trends and help in prediction of the future based on past data (Blanchard, 1999). In Alberta, air quality issues are mostly local in nature, both in their causes and solutions required. The present study focuses on air quality at two West Central Airshed Society (WCAS) monitoring stations: Tomahawk and Carrot Creek. Both stations largely represent rural west-central Alberta. In general, rural air quality is affected by agricultural practices such as use of fertilizers, burning of wastes, and raising cattle, as well as the transport of pollutants from other areas (Barrie and Hoff, 1985; Kelly et al., 1984). However, input of anthropogenic emissions in recent years (e.g., oil and gas plants, coal fired power plants) in these relatively remote areas can also influence concentrations of air pollutants (Seinfeld, 1989).

1.2 Objectives of Study

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 air quality concentration trends at selected WCAS air monitoring stations. This was accomplished by using simple linear regression for analyzing trends in historical ambient air quality data.
- To identify whether and to what extent the hourly 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 WCAS zone encompasses approximately 46,000 square kilometres in west central Alberta (Figure 1). The zone is 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 eastern boundary of the airshed is the Capital Region of Alberta (Edmonton and surrounding area). The eastern half of the airshed is characterized by gently rolling terrain with greater anthropogenic activities (e.g., gas plants and coal fired power plants) and residential acreage developments.

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 areas remote from man-made emission sources. The location of two stations selected for this study – Tomahawk and Carrot Creek – are shown in Figure 1. Both stations are located in the eastern half of the airshed.

Tomahawk Station – The Tomahawk station (WCAS Station no. 901) is located about 25 km northeast of Drayton Valley, Alberta near the community of Tomahawk (at latitude 53° 22' 12" N and longitude 115° 11' 26" W). The area is about 793 m above sea level. Land use surrounding the station is predominantly pastured. Roadway influences for the station include a paved highway about 700m away with traffic volume of about 200 vehicles per hour. Other sources identified are four coal fired power plants about 30 to 40 km away from the station.

Carrot Creek Station – The Carrot Creek station (WCAS Station No: 903) is located north of Highway 16, approximately 40 km east of Edson (at latitude 53° 36' 26" and longitude 115° 52' 37"). This area is higher in elevation than Tomahawk, about 860 m above sea level. Land use is characterized as pasture. Apart from Highway 16, the nearest roadway influence includes a gravel municipal road, about 200 m from the station with a traffic volume of 10 vehicles per hour. Three gas plants are located within a distance of 5 to 15 km from the station.

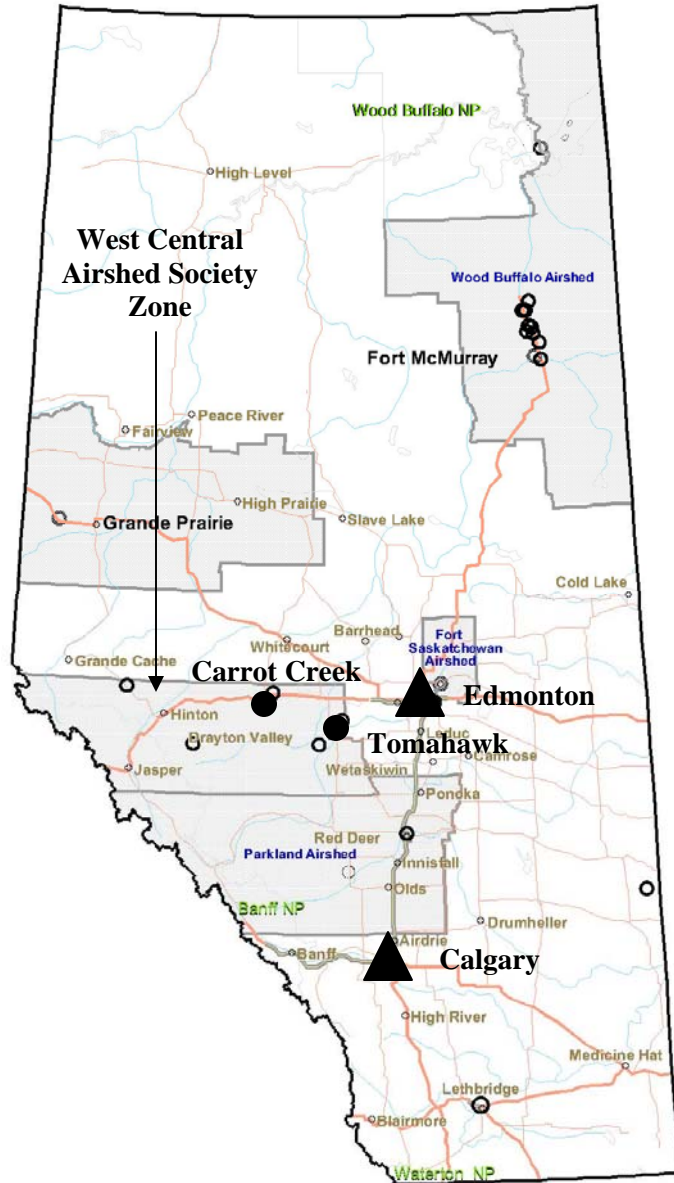


Figure 1 Province of Alberta showing West Central Airshed Society Zone and location of Carrot Creek and Tomahawk air monitoring stations.

2 Background Information

2.1 Air Quality

Air pollution indicates 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 on longer time scale, depending on concentration of pollutants, which in turn depends on the magnitude of emissions from individual sources, density of emissions, topography, and stability of the atmosphere.

The US Environmental Protection Agency (US EPA, 2003) uses six “criteria pollutants” as indicators of air quality – ozone (O₃), carbon monoxide (CO), nitrogen dioxide (NO₂), sulphur dioxide (SO₂), particulate matter (PM), and lead (Pb). For each of these, US EPA (2003) 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 – SO₂, NO₂, CO, suspended particulates, and O₃ (Environment Canada, 2005).

Air quality criteria are defined as scientifically 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):

- **Maximum Desirable** defines the long-term goal for air quality and provides a basis for an anti-degradation policy for the country and for continuing development of control technology.
- **Maximum Acceptable** is intended to provide adequate protection against effects on soil, water, vegetation, material, animals, visibility, and personal comfort and well-being.
- **Maximum Tolerable** denotes time-based concentrations of air contaminants beyond which, due to a diminishing margin of safety, appropriate action is required without delay to protect health of the general population.

The Canadian Council of Ministers of the Environment (CCME) endorsed new national air quality standards for PM and O₃ in June 2000 (CCME, 2000). These new standards, termed Canada-Wide Standards (CWSs) are in addition to air quality objectives discussed above.

2.2 Ambient Air Quality Monitoring

Air quality monitoring is often used to determine air pollution levels in urban or rural environments. Chow et al. (2002) highlighted the importance of monitoring networks to represent exposure of large populations to outdoor air. The purpose of monitoring is not however limited to collecting data only. It provides important information required by scientists,

policy-makers, and planners for making informed decisions on managing and improving the environment. Monitoring fulfils a controlling role in this process, providing 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 air quality management. Monitoring often needs to be used in combination with other objective assessment techniques – including modeling, emission measurements and inventories, interpolation, mapping, and interpretation (Bower, 1997). 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). On the other hand, models can provide a powerful tool for interpolation, prediction, and optimization of control strategies. However they are effectively useless without being properly validated by real-world monitoring data. Therefore reliance on modeling alone is equally unsound.

2.2.1 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 take into account an array of issues including statutory requirement, policy and strategy development, local or national planning, measurement against standards, identification/quantification of risk, and public awareness (Bower, 1997). Bower (1997) summarized typical monitoring functions as follows:

- Identifying impacts 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 air quality management, 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 quantification to identify potential future problems or assess progress against management/control targets

Influence of local/national issues and objectives determine the layout and operation of an air monitoring network. This in turn helps in establishing (Bower, 1997; WHO, 1997): a targeted and cost-effective quality assurance program (QAP), an optimally designed network, a list of priority pollutants as well as methods to measure them, and requirements for data management and reporting.

2.2.2 Quality Assurance And Control

Quality assurance (QA) and quality control (QC) are essential parts of any air monitoring system. US EPA (1993) defines quality assurance as a set of activities that are designed in such a way to ensure 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 (US EPA, 1993). Bower (1997) defines QA/QC as a program of activities that guarantee that 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 collected are fit for an intended purpose. Major QA/QC objectives are to ensure (Bower, 1997):

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

2.3 Properties, Sources, and Monitoring of Pollutants

2.3.1 Ground-Level Ozone

In establishing ambient air quality standards, regulations are introduced to set limits on the emissions of pollutants in such a way that they cannot exceed prescribed maximum values (US EPA, 1999). Ozone is unique among pollutants, as it is not emitted directly into the air; rather it results from complex chemical reactions in the atmosphere. To track and predict ozone, one must create an understanding of not only ozone itself but also the conditions that contribute to its formation.

Formation of Ground Level Ozone

Ozone is a gas that occurs both in the Earth's upper atmosphere and at ground level. Unlike many air pollutants, ground-level ozone is not emitted directly into the air; it is formed by oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) – which in the presence of heat and sunlight – react to form ozone. Tropospheric ozone is largely man-made; a result of air pollution from fossil fuel combustion activities in urban areas. Automobile exhaust and industrial emissions release nitrogen oxide gases and VOCs. These gases 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 night.

Ground-level ozone is a primary constituent of smog along with fine particulate matter. Various meteorological parameters affect the atmospheric ozone balance. Changing weather patterns

contribute to yearly differences in ozone concentrations from area to area (US EPA, 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 (US EPA, 1996).

Factors Affecting Formation of Ground-Level Ozone

Sources of NO_x and VOCs (precursor compounds) have been found to be both anthropogenic and natural. Table 1 presents examples of such sources. NO_x are largely formed in combustion processes, from nitrogen present in the fuel source. Consequently, emissions from transportation, stationary source fuel combustion sources, industrial processes, and solid waste disposal processes are some of the main human activities responsible for NO_x (US EPA, 1996). Natural sources, on the other hand, include lightning strikes, soils, wildfires, stratospheric intrusion, and evaporation over large bodies of water (US EPA, 1996). VOCs are equally emitted in large quantities from deciduous vegetation and conifers. Evaporative and combustion processes are anthropogenic sources of VOCs.

Meteorological Factors

In the atmosphere, several meteorological parameters affect the balance of ozone. Ultraviolet radiation, wind speed, and temperature influence chemical reactions that occur in the atmosphere (US EPA, 1996). In addition surface scavenging and atmospheric mixing and transport process can alter the ozone balance (US EPA, 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, in fact, required as an energy source to power the photochemical reaction in ozone formation. However the amount of UV in any given location is a function of season, cloud cover and atmospheric conditions.

Ozone Monitoring

Ozone is continuously measured using an ultra-violet (UV) light process. Sampled air is exposed to UV light, which is absorbed by O_3 . Therefore, the amount of UV light absorbed is roughly proportional to the amount of O_3 in a sample; that is, the more UV light is absorbed, the greater the amount of O_3 present in a sample (CASA, 2005).

2.3.2 Sulphur Dioxide

Sources of Sulphur Dioxide

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.

Table 1 Major anthropogenic activities that contribute urban levels of ozone precursor compounds (after US EPA, 1996).

Category	NO _x 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	

Atmospheric SO₂ is produced from both natural and anthropogenic sources. Natural sources of SO₂ are from volcanic eruptions. Anthropogenic sources of SO₂ can be divided into industrial sources, domestic sources, and vehicular sources. Industrial sources of SO₂ are produced from combustion of fossil fuel such as coal and oil (Taylor et al., 2005; Tomás-Alonso, 2005). On the ground SO₂ oxidizes to sulphates which are vital component of plant nutrients (Meyer, 1983).

Emissions of SO₂ are related to the sulphur content of fossil fuel and total amount of fossil fuel that is consumed. Thus emissions of SO₂ are related to population density of an area (US ATSDR, 1998). Stern et al. (1994) reported studies conducted from October 1985 to March 1986 in Saskatchewan and Ontario comparing outdoor rural and urban SO₂ concentrations as a result of long-range transport of air pollutants from industrial sites. It was observed that in five rural communities in Saskatchewan, the mean outdoor SO₂ concentration was 1.1 µg/m³, while the SO₂ concentration in five urban communities located in southwestern Ontario averaged 5.5 µg/m³.

In another study conducted by Kindzeriski and Sembaluk (2001), indoor and outdoor concentrations of SO₂ were measured in late fall for five weeks in the urban center of Sherwood Park and rural community of Boyle, Alberta. It was found that the rural community of Boyle (indoor: 0.5 µg/m³; outdoor: 4.3 µg/m³) had consistently lower concentrations of SO₂ both indoors and outdoors compared to the urban centers of Sherwood Park (indoor: 1.4 µg/m³; outdoor: 9.9 µg/m³). This was explained as a result of increased vehicular activities and industrial emissions in the urban area in Sherwood Park (Kindziarski and Sembaluk, 2001).

Monitoring of Sulphur Dioxide

SO₂ is monitored continuously by pulsed fluorescence. In this method, air is drawn through a sample chamber where it is irradiated with pulses of ultra-violet light. Any SO₂ 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 SO₂ concentration (CASA, 2005).

2.3.3 Nitrogen Oxides

All fossil fuel burning processes produce NO_x. The principle oxides formed are nitric oxide (NO), which represents 90%-95% of NO_x formed; and nitrogen dioxide (NO₂), which represents most of the remaining nitrogen oxides. NO_x is formed primarily in a high temperature zone of a combustion process – where sufficient concentrations of nitrogen and oxygen are present. Fuel nitrogen and nitrogen contained in 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 combustion processes as a result of the reaction of N₂ and O₂ at very high temperatures. Nitrogen dioxide is formed in the ambient air through the oxidation of nitric oxide.

NO₂ is a strong oxidant and is a photochemically active species in a polluted atmosphere. It is essential ingredient in the formation of smog through photochemical reactions with volatile organic compounds. Nitrogen dioxide and nitric oxide are commonly classified together as NO_x, because of their inter-conversion during smog formation reactions.

Sources of Nitrogen Oxides

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 (Mauzerall et al., 2005; US EPA, 2001). Automobile exhaust acts as the major contributor among anthropogenic sources of NO_x in the atmosphere. Stationary fuel combustion and various industrial processes also have significant contributions. Indoor combustion sources of NO₂ include gas and wood stoves; and unvented propane, natural gas, and kerosene heaters.

Global production of NO_x is considered more significant from natural sources than anthropogenic sources, mainly as a result of activity of nitrogen consuming microorganisms in soil (Jin et al., 2005). Besides, 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 abiological processes in soil, and stratospheric intrusion (Cho and Peirce, 2005; Sawyer et al., 2003).

Monitoring Methods for Nitrogen Oxides

NO_x are measured continuously based on the principle of chemiluminescence (CASA, 2005). In this method, an air sample is split into two pathways – one to measure NO, and the other to measure total NO_x. In the first pathway, sample air goes directly to an analysis chamber, gets mixed with O₃ 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 sample air to NO₂. The sample then goes on to the analysis chamber. The measurement in this pathway is the sum of NO₂ and NO, expressed as NO_x. In the end the difference of the readings between the two pathways is determined electronically and gives the NO₂ concentration (CASA, 2005).

2.3.4 Particulate Matter

Particulate matter (PM) is the general term used for a mix of solid particles and liquid droplets found in air. According to Seinfeld and Padis (1997), PM 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. PM includes both fine and coarse particles. The former refers to particles less than or equal to 2.5 μm (PM_{2.5}) while the latter refers to particles that are greater than 2.5, but less than or equal to 10 μm in diameter (PM₁₀) (Cheng et al., 2000; Tucker, 2000; US EPA, 1997; Vassilaskos et al., 2005).

An additional peculiarity of PM 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; US EPA, 1997). Any source that emits these substances therefore contributes to their formation.

Atmospheric PM is a complex mixture of nitrate, sulphate, 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 fine particulate matter is characterized by its density and small size. It has 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 process of formation usually influences its 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).

Sources of Particulate Matter

PM may arise from a wide variety of natural or man-made sources. Natural sources include pollens, fungal spores, or re-suspended 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); and 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 PM in ambient air (Putaud et al., 2004). Combustion of fossil fuels is still an important source of SO₂ emission in many countries. A number of investigations on the impact of power plant plumes and on 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, SO₂ oxidation results in formation of new particles in the PM range <1 µm (Jaecker-Voirol and Mirabel, 1989; Korhonen et al., 1999). Again, in poor NH₃ and rich mineral dust environments, H₂SO₄ may react with mineral dust resulting in formation of CaSO₄ or Na₂SO₄, which is in the coarse PM range (Moreno et al., 2003; Pio and Lopes, 1998; Querol et al., 1998).

In Canada, transportation, industrial activities, forest fires, and non-industrial fuel combustion, were reported as 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) reported characteristics of PM and demonstrated that PM_{2.5} loadings are higher during winter. It was also demonstrated that a higher amount of soil-derived particles was found in coarse fraction PM (55% to 65%) than in fine fraction PM (7% to 8%). For rural areas, Sandhu (1998) reported that the background concentration for PM_{2.5} in Alberta was low (3 to 6 µg/m³), whereas that for PM₁₀ was within 10 to 24 µg/m³. The ratio of PM_{2.5} to PM₁₀ was reported about 0.3. Measurements made near significant local sources indicated that local and regional sources can have considerable impacts on PM_{2.5} and PM₁₀ concentrations (Sandhu, 1998).

Monitoring Methods for Particulate Matter

In Alberta, particulate matter is monitored on a continuous (hourly) and as well as intermittent (every sixth day) basis. PM_{2.5} and PM₁₀ 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 PM is aerodynamically separated 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 PM₁₀ are also monitored on an intermittent basis using dichotomous samplers (Brook et al., 1997; CASA, 2005). Like the TEOM, the sampler aerodynamically separates PM into two size fractions, fine (i.e., $\leq 2.5 \mu\text{m}$ and $\leq 10 \mu\text{m}$). These particles are collected by drawing a known volume of air through individual pre-weighed filters for a period of 24-hours and the total particulate concentration is calculated for the 24-hour period.

2.4 Dispersion of Pollutants in the Atmosphere

Air pollutants – when released into a moving, fluctuating atmosphere – are transported in complex ways (Stern et al., 1973). They tend to be most concentrated at the point of release (source). If there were no vertical or horizontal mixing of the atmosphere, a slug of air concentrated with a pollutant would stay in one place. However, random atmospheric motions impact turbulence and results in mixing and dilution of air and dilution of the pollutant in a downwind direction. Even during relatively stable atmospheric conditions, known as inversions, some mixing that takes place. The combination of winds and tendency of warm air to rise to higher elevations will do two things to a pollutant released to the atmosphere (Godish, 2004; Colls, 1997):

- dilution (spreading out of the pollutant as mixes it with a larger volume of air)
- transport 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)

The primary meteorological factors affecting the concentration of air pollutants are wind, temperature, atmospheric stability, mixing height, precipitation/humidity, and topography.

2.4.1 Wind

One of the primary factors affecting the transport and dispersion of pollutants in the atmosphere is wind. Wind is the natural horizontal motion of the atmosphere; it is caused by differences in pressure and temperature in the atmosphere. Differences in pressure cause air to move from high-pressure areas to low pressure areas, resulting in wind (Wark and Warner, 1981). Wind direction indicates the trajectory or path of air pollutants from the source to the receptor. Wind speed determines the distance from the source to the receptor and the time the ambient pollutants will take to reach the receptor (Myrick, 1995). Wind speed near the earth's surface is low due to the frictional effects proportional to the surface roughness; however, wind speed is greater further away from the earth's surface (Wark and Warner, 1981).

Wind speed can affect pollutant concentrations in a local area. Wind speed determines the extent to which pollutants are initially diluted in ambient air at the point of release. This effect is treated as an inverse relationship between wind speed and concentration of pollutants: the higher the wind speed, the lower the pollutant concentration. Wind dilutes pollutants and rapidly disperses them throughout the immediate area. According to Bronnimann et al. (2002), there is a negative relationship between wind speed and anthropogenic ozone concentration under fair

weather conditions and a positive relationship under poor weather conditions for natural ozone. Chaloulakou et al. (2003) studied the relationship between PM₁₀ and PM_{2.5} concentration and meteorological variables including wind speed, wind direction, and temperature and found a non-linear relationship.

2.4.2 Temperature

Temperature has an important influence on the existence of pollutants in the atmosphere (Jandali and Hrebnyk, 1985). Rate of change of temperature with altitude has a substantial effect on mixing of air pollutants in the atmosphere. Diurnal and seasonal solar cycles essentially control temperature profiles of the lower atmosphere. During the day, temperature in the lower atmosphere typically increases due to energy absorbed from the sun. As evening approaches, there is a decrease in solar heating that causes the lower atmosphere to cool. This heat loss from the earth's surface at night results in a temperature inversion which limits the rise of a plume from pollution sources, resulting in the pollutants staying longer in the atmosphere (Myrick, 1995).

Such temperature inversions are common in winter when heat from the sun is minimal. Persistence of temperature inversions over long periods of time may lead to increased concentration of air pollutants in the lower atmosphere. Most chemical reactions in the atmosphere that result in ozone and particulate matter formation proceed faster at higher temperatures (US EPA 2004a; 2004b).

2.4.3 Atmospheric Stability

Atmospheric stability is tendency of the atmosphere to resist vertical mixing or motion (Wark and Warner, 1981). Vertical mixing in the lower atmosphere is primarily dependent upon temperature gradient and mechanical turbulence. This tendency directly influences the ability of the atmosphere to disperse pollutants emitted into it. A stable atmosphere does not exhibit much vertical mixing or motion, and pollutants emitted near the earth's surface remain there. When the stability is low, vertical motion is not suppressed, and pollutants are able to disperse higher from the surface. Stability is measured by variation of ambient air temperature with respect to the height above ground.

2.4.4 Mixing Height

Mixing height is the thickness of the layer of air in which pollutants are well-mixed (Holzworth, 1967). It is the space between the Earth's surface and the lowest level in the atmosphere at which the ground surface no longer influences meteorological variables through turbulent transfer of mass. The greater the vertical extent, the larger the volume of atmosphere available to dilute pollutants. Thermal buoyancy effects determine depth of the convective mixing layer, which is taken as the maximum mixing depth (MMD) (Wark and Warner, 1981).

In unstable air, MMD is higher, and in stable air, MMD is lower. There is also a seasonal variation in mixing depth. During summer daylight hours, MMD can be a few thousand feet, whereas in winter, it can be a few hundred feet. Mixing depth also varies over the course of a day, being lowest at night and higher during the day. A measure of both MMD and wind speed with respect to height can give a good idea of the amount of pollutant dispersion in the atmosphere.

2.4.5 Precipitation/Humidity

In meteorology, precipitation is any kind of water that falls from the sky as part of the weather, including snow, rain, sleet, freezing rain, and hail, whereas humidity is the amount of moisture in the air. Precipitation and humidity sometimes have a beneficial effect on the environment by washing pollutant particles from the air; however, precipitation can also act on pollutants in the air to create more dangerous secondary pollutants, such as the substances responsible for acid rain (Elsom, 1992).

Small water droplets in clouds or fog can increase particle formation rates. For example, sulphur dioxide is converted to sulphate much more quickly under foggy conditions, leaving higher particle concentrations in air after the fog has evaporated. Kim et al. (1997) found a strong inverse relationship between relative humidity and lead levels in air; however, a weak positive and negative correlation was found for particulate matter in air.

2.4.6 Topography

Land orientation and the structure of terrain also influences air motion and mechanical turbulence in the lower atmosphere. Terrain factors such as mountains, hills, and valleys have a significant effect on pollutant dispersion as they largely control wind speed and wind direction (Myrick, 1995). Large mountains and hills may divert wind and channel it through valleys. Highly variable terrain features of an area may also affect diurnal variations of wind.

2.5 Air Quality Trend Techniques

Responding to public perceptions and concerns about air quality remains a challenge and requires sound assessment. It is of great interest to know whether changes in air quality have occurred over time where continuous air monitoring is conducted. Assessment of short-term trends offers a credible scientific approach for responding to public perceptions and concerns about air quality and establishing whether or not change are occurring.

There are two basic types of trends that can be statistically analyzed: step trends and monotonic trends (Oregon DEQ, 2003). Step trends include either a sudden increase or decrease in concentration resulting from sudden change. Monotonic trends are generally gradual changes

that are either increasing or decreasing with no reversal of direction. Statistical tests for trends in environmental data can be classified into two categories: parametric and nonparametric. Parametric tests involve an independent student's t-test between two means, ANOVA, linear regression, or polynomial regression with the least square method, or autocorrelation tests (McLeod and Hipel, 1991). Nonparametric tests include the Mann-Kendall test, Seasonal Mann-Kendall test, Spearman's Rho test, Kruskai-Wallis test, and Spearman Partial Rank Correlation test (McLeod and Hipel, 1991).

Parametric tests require making assumptions about normality of data and homogeneity of variance of data. At the very least the Central Limit Theorem should apply, i.e. sample size should be sufficiently large (usually greater than 30) to lead to approximate normality and variances of the different samples should be approximately equal. Nonparametric tests, e.g. Mann-Kendall test and Sen's test, do not require these assumptions. Parametric tests are generally more powerful than nonparametric tests and they have an ability to quantify the magnitude of a trend. Most nonparametric tests cannot quantify the magnitude of a trend but can only detect presence/absence of a trend (change) without the requirement of a normal distribution (McLeod and Hipel, 1991).

According to Blanchard (1999), the usefulness of trend analysis depends on the magnitude of emissions of interest, quality, and length of record of monitoring data, and relative magnitudes of emissions-and-weather driven variations in ambient concentrations. Other studies have reported that estimation of emission-related trends require statistical models that account for sources of variability underlying the pollutants, such as seasonal changes and meteorology (Porter et al., 2001; Lynch et al., 2000; Holland et al., 1999).

Weatherhead et al. (1998) discussed statistical criteria for detecting linear trends in environmental data and reported that precision of trend estimates is strongly influenced by variability and autocorrelation of the underlying noise process. According to Weatherhead et al. (1998), detectability of a trend can be summarized in two common ways:

- Precision of a trend estimate as measured by its standard deviation.
- Number of years of data required to detect a trend of a given magnitude using the trend estimate.

Weatherhead et al. (1998) concluded that it takes several decades of high-quality data to detect trends likely to occur in nature. The practical implication is that detection of trends over shorter time periods (less than a decade) does not represent long-term trends. Three widely used methods discussed here for detecting trends in air quality are: Linear Regression, Seasonal Mann Kendall test, and t-test adjusted with seasonality.

2.5.1 Linear Regression

Regression analysis is a popular statistical tool for illustrating trends. Linear regression attempts to model the relationship between two variables by fitting a linear equation to the observed data (Freund and Wilson, 2003). One variable is considered to be an explanatory variable, and the other is considered to be a dependent variable. Linear regression is useful for exploring the relationship of an independent variable that marks the passage of time with a dependent variable when the relationship is linear, i.e., when there is an obvious downward or upward trend in the data over time (Gilbert, 1987).

Linear regression, however, fails to capture seasonal, cyclical, and counter-cyclical trends in time series data. Neither does it capture the effects of changes in the direction of time series data, nor changes in the rate of change over time. For time series regression, it is important to obtain a plot of the data over time and inspect it for possible non-linear trends. There is also a problem of auto-correlation in the time series data, if the values at one point in a time series are determined or strongly influenced by values at a previous time. Auto-correlation occurs when values of the dependent variable over time are not randomly distributed. This problem can more likely be satisfied by using yearly average as response variables (Hess et al., 2001).

2.5.2 Seasonal Mann Kendall test

The Seasonal Mann Kendall test is an extension of the Mann Kendall test that accounts seasonality in the data (Hess et al, 2001). It is a distribution-free, nonparametric test that compares relative ranks of data values from the same season. For example, January (seasonal) values are compared to January (seasonal) values; February (seasonal) values are compared to February (seasonal) values, and so forth. No comparisons are made across seasonal boundaries. The test assumes that data are independent and from the same statistical distribution.

The Seasonal Mann Kendall test statistic is the summation of the Mann-Kendall test results from all the seasons. A Mann-Kendall test statistic (S) and variance (VAR) are calculated separately for each season with the data collected over the year. These seasonal statistics are then summed and a Z statistics is calculated (Gilbert, 1987). The trend test statistic (Z) is used as a measure of trend magnitude or of its significance. The null hypothesis can be accepted or rejected for the presence of trend by comparing the Z statistics with the Z_{α} or $Z_{\alpha/2}$, where α is the chosen significance level. The Seasonal Kendall slope estimator is computed as the median slope of all the pair-wise comparisons from all of the seasons expressed as rate of change per year (Gilbert, 1987).

The Seasonal Mann Kendall test is a rank-based procedure and is suitable for non-normally distributed data. It can also capture outliers and non-linear trends, which can cause a disproportionate influence on the estimate of slope calculated by linear regression. One of the limitations of the Seasonal Mann Kendall test is that it is restricted to monotonic trends, which provides a limited insight in comparison to other statistical methods (Gilbert, 1987).

2.5.3 t-test Adjusted with Seasonality

One of the simplest approaches to detect a trend is by assessing a statistically significant difference between the theoretical means (μ) using a two-sample t-test. The t-test helps to determine if the true slope is not different from zero (Snedecor and Cochran, 1980).

Unfortunately, the t-test can be misleading if there are seasonal cycles in data, data are not normally distributed, or data are serially correlated (Gilbert, 1987). Hirsch et al. (1982) found that in these situations, the t-test may indicate a significant slope when the true slope is zero.

The seasonal effect can be incorporated into a t-test by using a linear model that includes seasons and year as factors, with an assumption that both season and year effects are considered fixed. According to Hess et al. (2001), if Y_{ijk} is the (k^{th}) observation from season (j) of year (i), with the assumption that these values are independent with constant variance, then the following model can be obtained:

$$Y_{ijk} = \mu + T_i - M_j - e_{ijk} \quad [1]$$

Where (T_i) is the effect for the year (i), (M_j) is the effect for season (j), and (e_{ijk}) is the error which is independently and identically normally distributed with mean 0 and variance σ^2_e .

3 Methodology

3.1 Monitoring Data

Pollutants and measurement techniques varied between the two air monitoring stations (Tomahawk and Carrot Creek) along with observation periods. Data for meteorological parameters were not available in this study, though this does not limit the underlying purpose of trend analysis (Sandhu, 1999). Table 2 lists 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, is presented in Appendix A.

Table 2 Stations, measurement instruments, and observation period for trend analysis (after www.wcas.ca).

Station	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 Matter (PM _{2.5} , PM ₁₀)	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, 2005). These electronic data were obtained in temporal order of year, month, day, and hour. Initially 8 years of historical data – 1997 to 2004 – were considered for O₃, SO₂, and NO₂; and 5 years – 2000 to 2004 – were considered for PM_{2.5} and PM₁₀. Carrot Creek commenced data collection for O₃, SO₂, and NO₂ from 1998 and this station does not monitor for PM_{2.5} and PM₁₀.

AMD (1989) suggests that 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. However, for this study an arbitrary cut-off of 80% completeness was used to determine whether to include an annual dataset in trend analysis. This criterion represents 7,008 hourly values for an annual dataset and was judged sufficient for purposes of this study. Although this criterion is not consistent with the AMD (1989), it is similar to that used by others (i.e. 85% as used by Jo et al., 2000).

The 1999 dataset for Tomahawk had to be eliminated for O₃ and SO₂. Similarly, datasets for the years 1998 and 1999 for Tomahawk had to be eliminated for NO₂, and 2000 for PM_{2.5}. PM₁₀ 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 carried out 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; US EPA, 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 to assist in understanding of trend analysis results.

Diurnal, weekly, and seasonal (monthly) patterns were examined using the entire data set for each pollutant. For example, for diurnal patterns, average ozone concentrations for the Tomahawk station at 8:00 was calculated as the average of all 8:00 hour readings in the data period (1997 to 2004), regardless of day of week or season. Yearly averages and number of hours in which average hourly concentrations exceeded the maximum one-hour concentration Alberta Ambient Air Quality Objective were also counted for each pollutant.

3.2 Temporal Trend Analysis Using Regression

Most air quality trend analyses are based upon tracking annual mean or maximum concentrations or frequency of exceedences of maximum concentrations above air quality criteria (e.g., Carslaw, 2005; Gunes, 2005; Gehrig and Buchmann, 2003; Ontario MOE, 2002; Jo et al., 2000). In areas where air quality is good most of the time – as is the case for Tomahawk and Carrot Creek – changes to annual mean concentrations and/or exceedences of maximum concentrations above air quality criteria are rare.

In the case of concentration maxima, this is not unexpected as such exceedences tend to be associated with rare meteorological (e.g., weather inversions) or emission events (e.g., upsets, start ups, forest fires). Thus evaluating observed air quality against air quality criteria would not be sensitive enough to detect gradual changes to air quality. Other approaches are required to accomplish this. Two benchmark approaches were used here, described further below.

Initially, the datasets were transformed into an ascending concentration-based order and were ranked (cumulatively) and assigned a percentile frequency. A plot of concentration values versus percentile frequency was used to show the cumulative frequency distribution of a respective pollutant for a year. This procedure was used to select and examine changes (trends) in various hourly concentrations at different percentiles of a distribution.

Using an assumption that ambient air concentrations display a temporal trend with time, two benchmark methods were used to examine trends:

- A concentration-based benchmark (based on concentrations of various pollutants at the 50th, 65th, 80th, 90th, 95th, and 98th percentiles for each year). These benchmarks were concentrations of a pollutant corresponding to the respective percentiles on a cumulative frequency distribution plot.
- A frequency-based benchmark (based on frequencies or number of hours in which the concentration of various pollutants exceeded benchmark concentrations established at the starting year). Frequency-based benchmarks were determined by selecting concentrations corresponding to 50th, 65th, 80th, 90th, 95th, and 98th percentiles on a cumulative frequency distribution plot for a starting year (first year of data for trend analysis). For example, if a 50th percentile concentration for CO in the starting year was 0.2 ppm, then the 50th percentile frequency for subsequent years was determined as the number of hours exceeding 0.2 ppm each year. This approach is analogous to tracking frequency of exceedences of maximum concentrations above an air quality criterion each year.

Both of these approaches are more sensitive than just tracking frequency of exceedences of maximum concentrations above an air quality criterion in that they should be able to identify gradual changes over time. A parametric statistical approach (linear regression) was applied to analyze trends in concentrations (concentration-based approach) and exceedence frequency hours (frequency-based approach). These summary statistics were assumed to be linear in time and were analyzed using simple linear regression.

Linear regression is a powerful tool used to find the best-fit line by minimizing the sum of squared errors (Harnett, 1982). Hypothesis testing using the Student's t-test and ANOVA was conducted to examine whether slopes of best-fit lines were greater or less than zero at a significance level of $\alpha=0.05$. Since only selective values from cumulative frequency distribution curves were analyzed for testing trends, influences of seasonality and autocorrelation data can be ignored.

3.2.1 Regression Procedure

Microsoft Excel® was used for regression analysis with the following assumptions:

- The concentration/frequency variable was assumed normally distributed.
- Summary statistics were assumed to be linear in time to enable regression analysis.

Data in the form of concentrations (concentration-based approach) and hourly frequencies (frequency-based approach) for various years were plotted. Such plots help to visually determine whether a straight-line approximation to the data appeared reasonable, and to make rough

estimates of the intercept (a) and slope (b). A model with a least squared regression line was obtained for every plot of the various percentiles using the “add trend line” function in Excel. The regression model used the following equation:

$$\hat{y} = bx_i + a \quad [2]$$

Where a is the intercept, b is the slope, x_i is the concentration/frequency, and \hat{y} is the estimated y . The terms a and b can also be calculated mathematically by the following formula (Harnett, 1982):

$$a = \bar{y} - b\bar{x} \quad [4]$$

$$b = \frac{\frac{1}{n-1} \sum_{i=1}^n (y_i - \bar{y})(x_i - \bar{x})}{\frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2} \quad [3]$$

The slope, b , for each best-fit line determined using regression analysis was tested with a t-test and ANOVA at a significance level $\alpha=0.05$ to establish whether it was different from 0.

3.2.2 t-test

Hypotheses made for the t-test were:

H_0 : Slope = 0

H_1 : Slope \neq 0

The formulas used for the t- test consisted of (Harnett, 1982):

$$t_{(\text{statistic})} = \frac{\text{Statistic hypothesized value}}{\text{Estimated standard error of the statistic}} \quad [5]$$

or

$$t_{(n-2)} = \frac{b - b_0}{S_b} \quad [6]$$

where $b_0 = 0$ and $b =$ slope and

$$S_b = \frac{S_e}{\sqrt{SSX}} \quad [7]$$

where SSX is the Standard Error of the Estimate:

$$SSX = \sum (X - \bar{X})^2 \quad [8]$$

$$S_e = \sqrt{\frac{SSE}{(n-2)}} \quad [9]$$

where SSE is the Sum of Squared Error

$$SSE = \sum (Y - \hat{Y})^2 \quad [10]$$

such that if $t_{(calculated)} > t_{(tabulated)}$, then reject H_0 and the slope $\neq 0$.

This type of outcome represents a trend (increasing if a positive slope and decreasing if a negative slope).

3.2.3 ANOVA (F - test)

The hypotheses made for the ANOVA test were

H_0 : Slope = 0

H_1 : Slope $\neq 0$

Formulas used for the ANOVA (F-test) consisted of (Harnett, 1982):

$$F_{(Statistics)} = F_{(1, n-2)} = \frac{MSR}{MSE} \quad [11]$$

$$MSE_{(Mean\ Square\ Error)} = \frac{SSE}{(n-2)} \quad [12]$$

$$MSR_{(Mean\ Square\ Regression)} = \frac{SSR}{1} \quad [13]$$

such that if $F_{(calculated)} > F_{(tabulated)}$ then reject H_0 and the slope $\neq 0$.

This type of outcome represents a trend (increasing if positive slope and decreasing if negative slope).

Results of regression analysis, t-tests and F-tests were further confirmed using the “Data Analysis – Regression” function of the program Excel in Microsoft Office®.

4 Results

4.1 Diurnal, Weekly, and Seasonal Patterns

Short-term (daily, weekly, and monthly) variations were examined for pollutants listed in Table 2 at Tomahawk and Carrot Creek. Only O₃ and PM_{2.5} (and NO₂ to some extent) showed variation for these short time frames. These results are presented in the following sections.

4.1.1 Tomahawk

At Tomahawk, O₃ and PM_{2.5} showed significant diurnal and seasonal patterns. Some variation was observed in seasonal trends for NO₂. These results are discussed below.

Ozone (O₃)

Hourly Variation

Figure 2 shows the variation of O₃ concentrations with hour of day. Concentrations were averaged through out 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- $\mu\text{g}/\text{m}^3$) difference between the minimum average – which occurs after sunrise, and the maximum average – which occurs in the late afternoon. The distinct relationship with hour of day signifies the effect of photochemical reactions for 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. Overall ground-level O₃ concentrations at Tomahawk were found to be well below the AAQG value of 82 ppb/hour (164 $\mu\text{g}/\text{m}^3$) for the study period, with an average hourly concentration close to 30 ppb (60 $\mu\text{g}/\text{m}^3$).

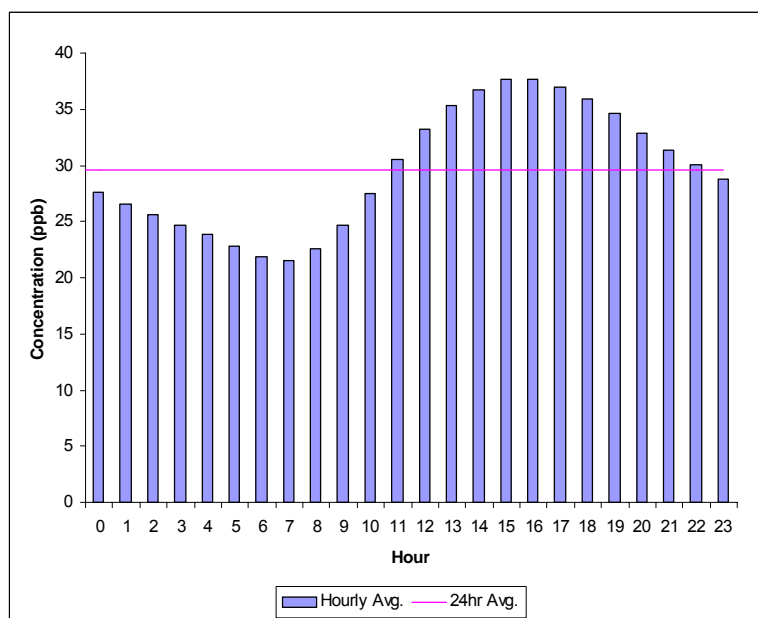


Figure 2 Tomahawk 1997-2004 diurnal hourly average concentration trend for O₃.

Weekly Variation

Very little variation was observed in the weekly average concentration pattern for O₃ for all the years analyzed. These plots are presented in Appendix B. Maximum hourly O₃ values on the weekend did not show a discernible pattern, with only 2002 data showing marginally higher values as the week progressed (with Saturday being the highest).

Monthly Variation

There was well-defined seasonal variation in both the composite mean and maximum hourly O₃ concentrations at Tomahawk. The monthly trend of hourly O₃ concentrations increased during late winter and reached a peak in April (Figure 3). O₃ concentrations diminished steadily as the summer season progressed, reaching minimum O₃ concentrations between September and December of a calendar year.

Monthly patterns for maximum hourly O₃ concentrations showed a different trend. Here concentrations gradually increased from January and reached peak in July, and then decreased as winter approached (Figure 4). Two exceedences of the AAQG occurred – one in July and one in June.

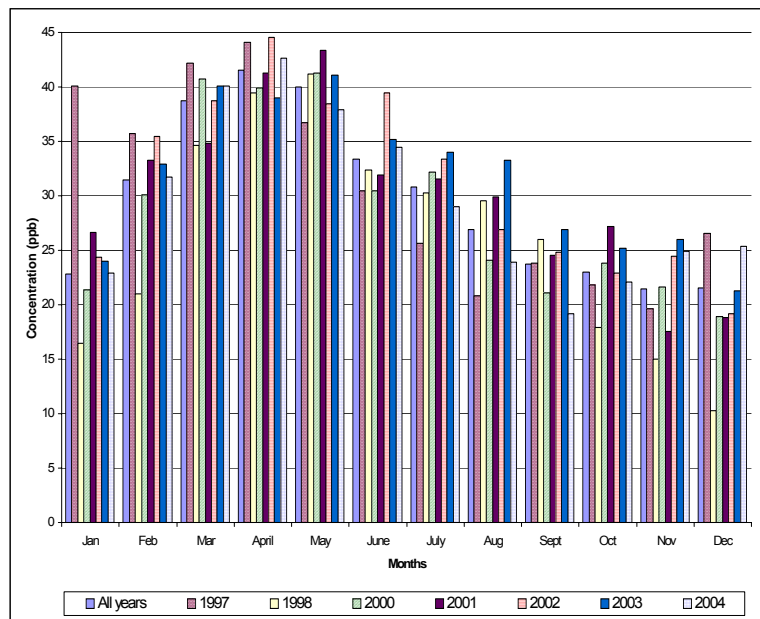


Figure 3 Tomahawk 1997-2004 seasonal (monthly) trend for O₃ based on average hourly concentrations for the month.

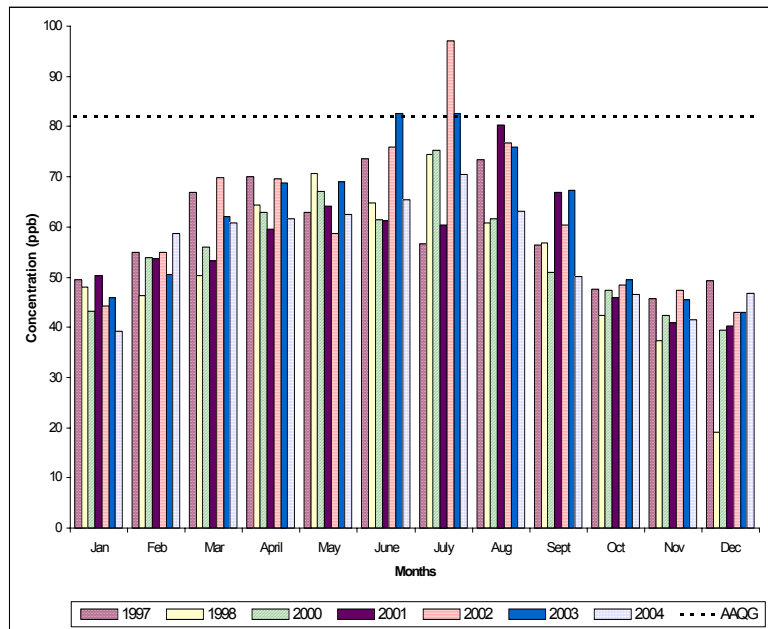


Figure 4 Tomahawk 1997-2004 seasonal (monthly) trend for O₃ based on maximum hourly concentrations for the month.

Fine Particulate Matter (PM_{2.5})

Hourly Variation

Hourly average values of PM_{2.5} concentrations were computed from the average of each hour of the whole study period. The 24-hour rolling average was close to 4 μg/m³, which is considerably lower than the Canada-Wide Standard 2010 target value of 30 μg/m³. It is also well below the US Environmental Protection Agency (US EPA) daily PM_{2.5} standard, which is 65 μg/m³ (established in 1997) (Vassilakos et al., 2005). Very little variation was observed in hourly average PM_{2.5} concentrations over the study period (Figure 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 time or season (DeGaetano and Doherty, 2004). However, the data for Tomahawk did not seem to relate to the day of the week (Appendix B).

Monthly Variation

No clear seasonal trend was apparent in the data for Tomahawk, despite the fact that on a number of occasions hourly PM_{2.5} concentrations proved to exhibit strong seasonal trends in previous studies (Hien et al., 2002; Laakso et al., 2003) (Figure 6). Sandhu (1998) reported that typical behaviour of PM_{2.5} levels in Alberta shows higher 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 6).

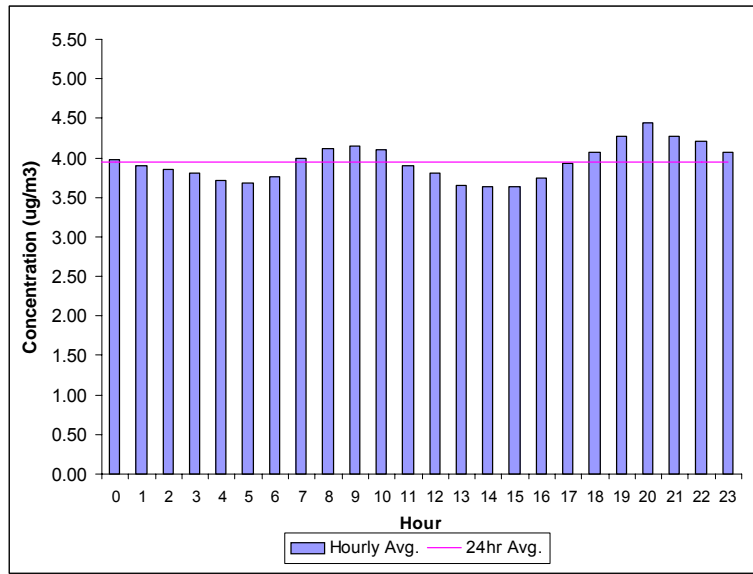


Figure 5 Tomahawk 2001-2004 diurnal hourly average concentration trend for PM_{2.5}.

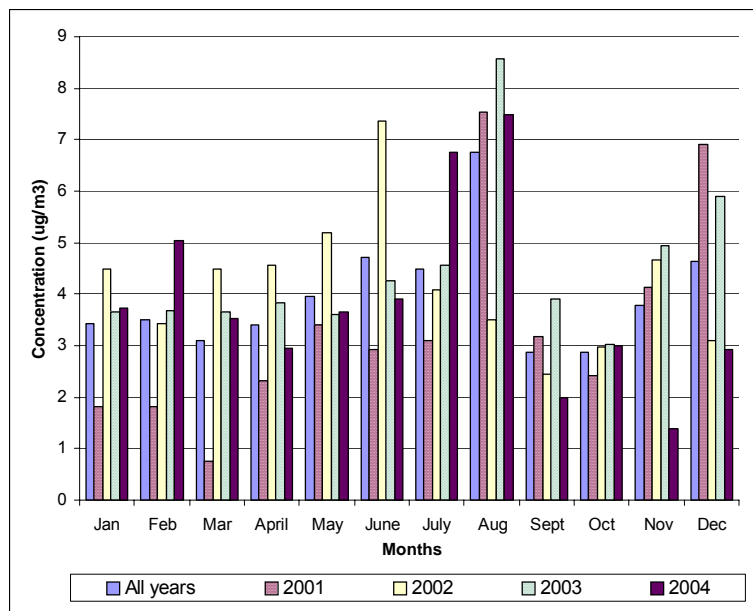


Figure 6 Tomahawk 2001-2004 seasonal (monthly) trend for PM_{2.5} based on average hourly concentrations for the month.

Maximum hourly concentrations did not show any seasonal trend (Figure 7a) at Tomahawk. Similarly, no trend was visible for maximum 24-hour average concentrations (Figure 7b).

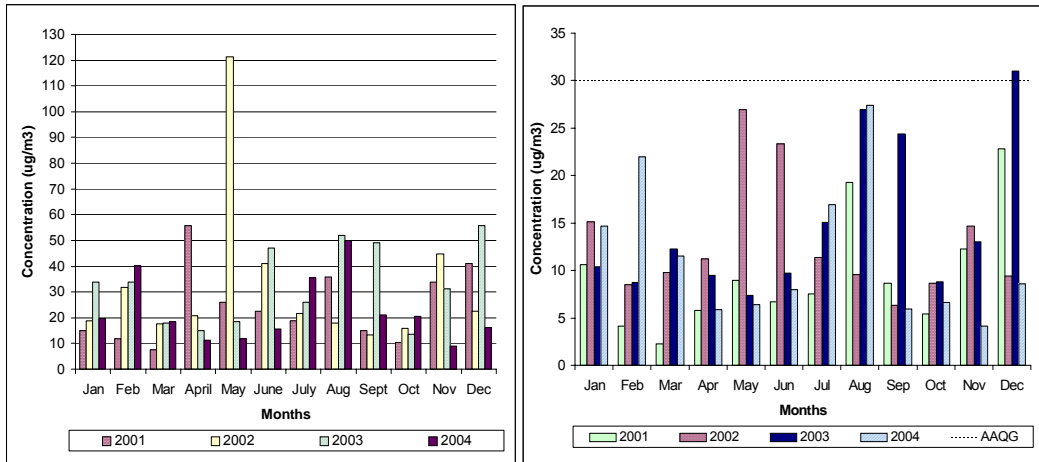


Figure 7 Tomahawk 2001-2004 seasonal (monthly) trend for PM_{2.5} based on (a) maximum hourly concentrations and (b) maximum 24-hr average concentrations.

Nitrogen Dioxide (NO₂)

Average hourly concentrations for NO₂ did not show any distinct diurnal patterns with concentrations very low ranging from 3 to 6 ppb (6 to 11 µg/m³) (Appendix B). With respect to weekly variations, no weekday/weekend effect was observed for NO₂ concentrations (Appendix B). Both of these trends tend to suggest that the Tomahawk station represents a truly rural location.

Hourly NO₂ levels showed clear monthly variation (Figure 8). NO₂ average hourly values were highest during winter, and then gradually decreased reaching a minimum during summer. The maximum hourly average was recorded in December 2001 as 13 ppb (25 µg/m³). The monthly variation in maximum hourly concentrations did not show any discernible pattern (Appendix B).

4.1.2 Carrot Creek

At Carrot Creek, variation was observed in the diurnal and monthly trend of O₃ and in the monthly trend of NO₂. PM_{2.5} is not measured at the station. These results are discussed below.

Ozone (O₃)

Hourly Variation

The hourly average ground-level ozone concentrations in Carrot Creek were largely below the AAQG value of 82 ppb for the study period, with an average hourly concentration of 28 ppb (56 µg/m³) and a 95th percentile value of 39 ppb (78 µg/m³). The relationship between hourly O₃ concentration and hour of day for Carrot Creek (Figure 9) appeared very similar to that for the Tomahawk station (Figure 2). An O₃ maximum occurred between 15:00 and 16:00.

A daily ozone minimum occurred at 7:00. During early morning hours O₃ concentration values remained quite low (Figure 9) compared to Tomahawk with no variation as opposed to a gradual decrease with increasing hours observed at Tomahawk (Figure 2). Also the maximum during daytime was higher at Carrot Creek than at Tomahawk.

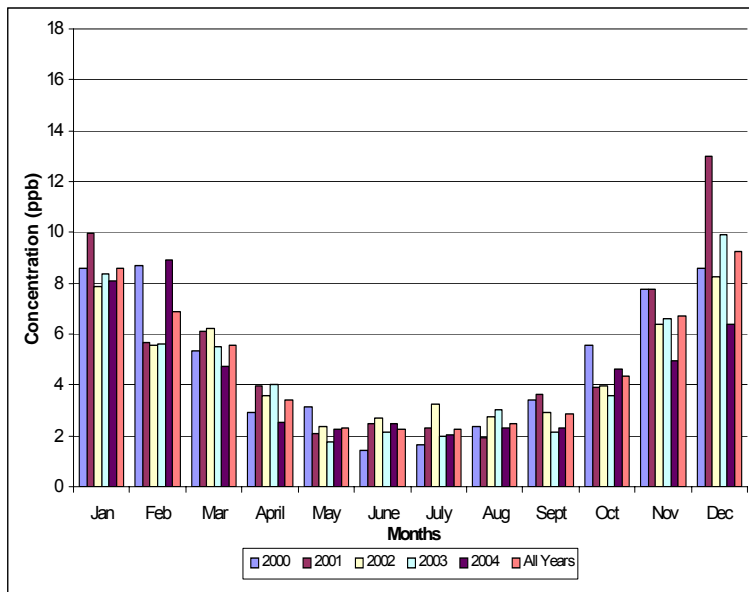


Figure 8 Tomahawk 2000-2004 monthly average concentration trend for NO₂.

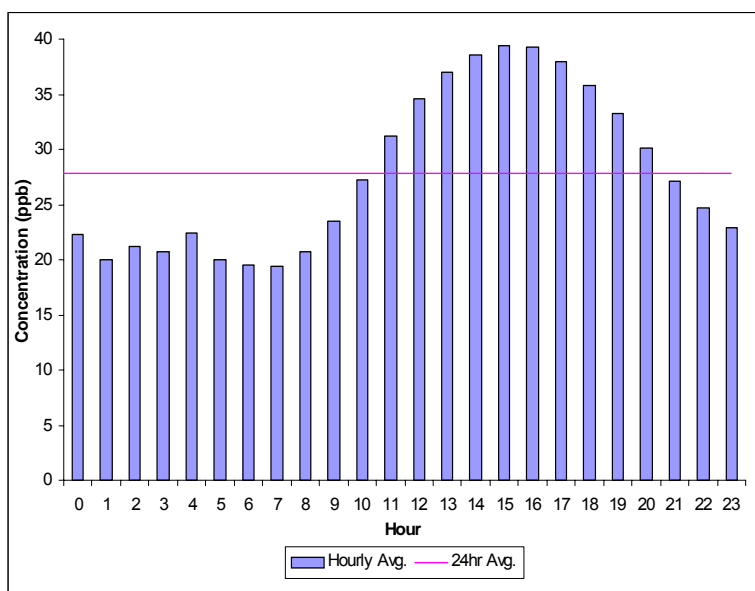


Figure 9 Carrot Creek 2000-2004 diurnal hourly average concentration trend for O₃.

Weekly Variation

Very little variation was observed in weekly average concentration patterns for O₃ for all the years analyzed. These plots are presented in Appendix C. Maximum hourly O₃ values on the weekend did not show a discernible pattern compared to weekday.

Monthly Variation

Once again, O₃ average concentrations at Carrot Creek (Figure 10) exhibited similar monthly variation compared to Tomahawk (Figure 3). The monthly trend of average hourly concentrations slowly increased during late winter, with their peak between April and May (Figure 3). The values then diminished gradually with the minimum concentrations being recorded at December.

Similar to Tomahawk, monthly patterns for maximum hourly O₃ concentrations showed a different trend (Figure 11). Here concentrations gradually increased from January and reached peak in July, and then decreased as winter approached. Only one exceedence of the AAQG occurred (in July 2002).

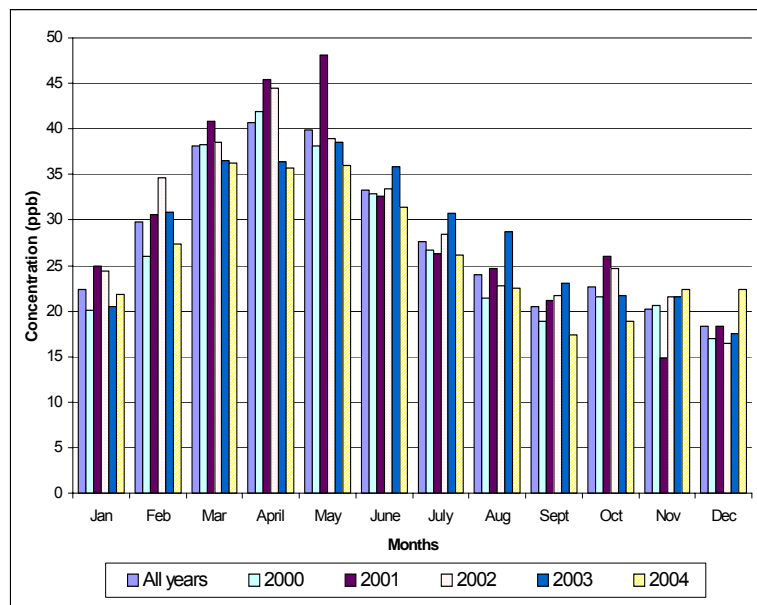


Figure 10 Carrot Creek 2000-2004 seasonal (monthly) trend for O₃ based on average hourly concentrations for the month.

Nitrogen Dioxide (NO₂)

Average hourly concentrations for NO₂ at Carrot Creek (Figure 12) reflected a more-defined diurnal trend than what was observed at Tomahawk. Two peaks were observed – the first one at around 9:00 followed by a second higher peak at midnight (10 ppb ≈ 20 μg/m³). Minimum

hourly average NO₂ concentrations were observed at 15:00 to 16:00 hours, directly corresponding to maximum hourly average O₃ concentrations (Figure 9).

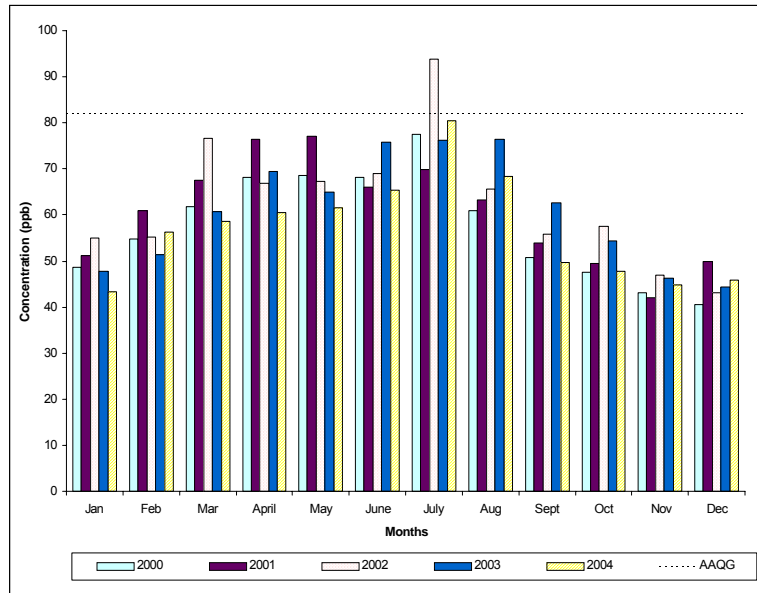


Figure 11 Carrot Creek 2000-2004 seasonal (monthly) trend for O₃ based on maximum hourly concentrations for the month.

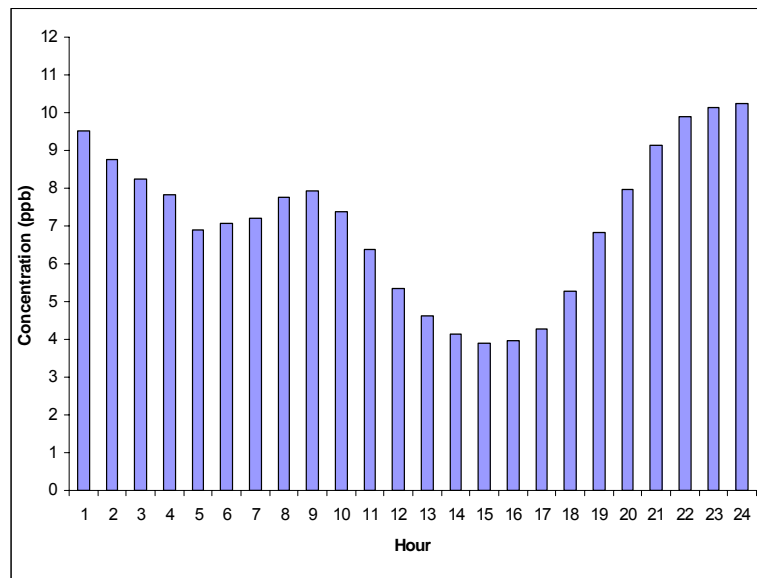


Figure 12 Carrot Creek 1998-2004 diurnal hourly average concentration trend for NO₂.

No weekday/weekend effect was observed at Carrot Creek, which was expected for a rural area. However, as in the case of Tomahawk, hourly NO₂ concentrations showed seasonal variation (Figure 13). NO₂ average hourly values were highest during late winter or spring, followed by a gradual decrease towards minimum summer concentrations. The maximum hourly average was around 16 ppb (31 µg/m³), recorded in February 2003. NO₂ maximum hourly values for each month did not show any trend.

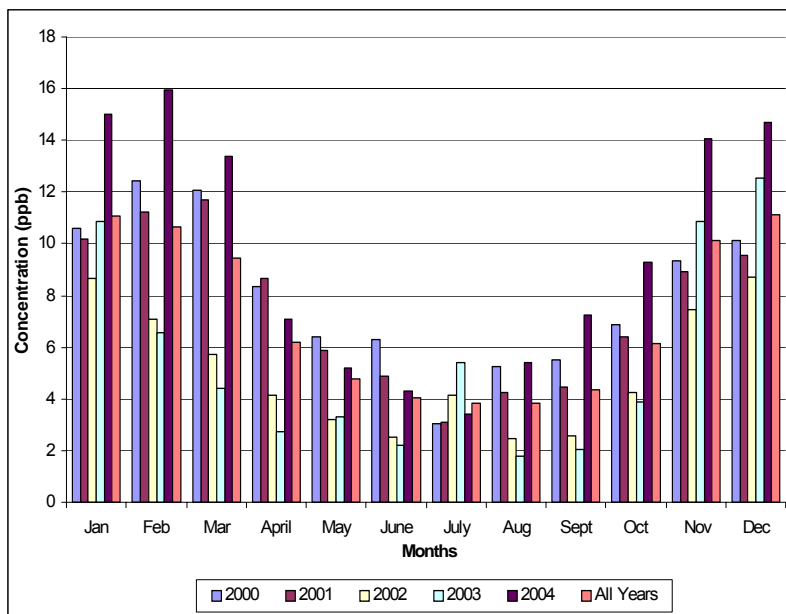


Figure 13 Carrot Creek 2000-2004 monthly average concentration trend for NO₂.

4.2 Temporal Trends

4.2.1 Tomahawk

Trends were observed over a period of seven to eight years at Tomahawk and Carrot Creek for all pollutants listed in Table 2. Results are presented in the following sections.

Ozone (O₃)

Cumulative Frequency Distribution

Hourly concentrations for O₃ for each year were sorted in ascending order to obtain a cumulative frequency distribution. From cumulative frequency distributions for 1997, 1998, 2000, 2001, 2002, 2003, and 2004. A typical cumulative frequency distribution is presented in Figure 14. In almost all cases, 90% of hourly values fell within 50 ppb (100 µg/m³). In general, concentrations were ≥70 ppb (137 µg/m³) 5% or less of the time. The 50th, 65th, 80th, 90th, 95th, and 98th percentile values of the distribution were selected to represent benchmark concentrations for trend analysis.

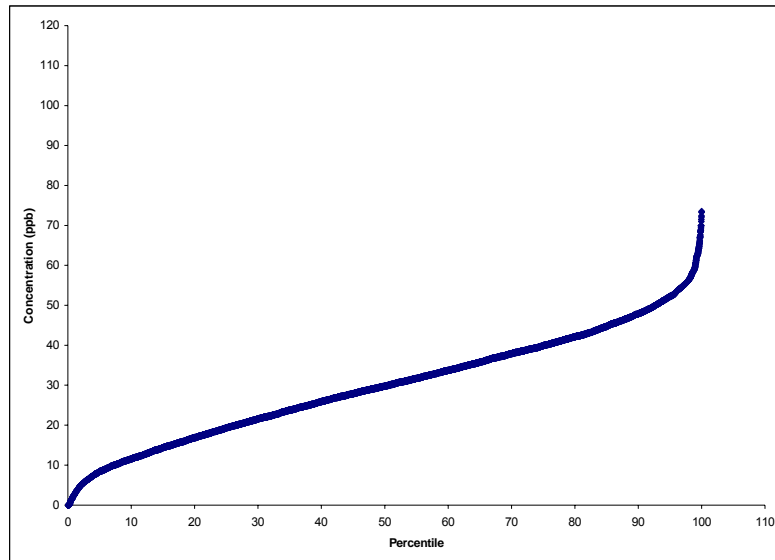


Figure 14 Cumulative frequency distribution for O₃ – 1997 Tomahawk.

Temporal Trends

At Tomahawk, the maximum one-hour average O₃ concentration observed for the study period was 97 ppb (190 µg/m³). Median O₃ concentration over the years ranged from 27 to 32 ppb (54 to 64 µg/m³). Lower median O₃ 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) were analyzed (Figure 15). Minor increasing trends were visually apparent at all percentiles (Figure 15), however none of the six trend lines proved statistically significant at $\alpha=0.05$. Frequency of exceedences was higher at the 50th percentile and gradually decreased as percentile values increased. Trend results observed using the frequency of exceedence approach are presented in Appendix D. This approach provided identical results as Figure 15. Although minor increasing trends were visually apparent at all percentiles shown in Appendix D for O₃, none of the trends proved to be statistically significant. Together these results indicate that that no significant change has taken place in O₃ concentrations during the study period.

Sulphur Dioxide (SO₂)

Cumulative Frequency Distribution

Hourly concentrations for SO₂ for each year were sorted in ascending to obtain cumulative frequency distributions. The distributions lay very close to 0 ppb at least up to 40th percentile for most of the years. For all years a small but gradual increase was apparent after the 40th percentile. In general, 90% of the hourly values fell within a very small concentration (2 ppb or 5 µg/m³).

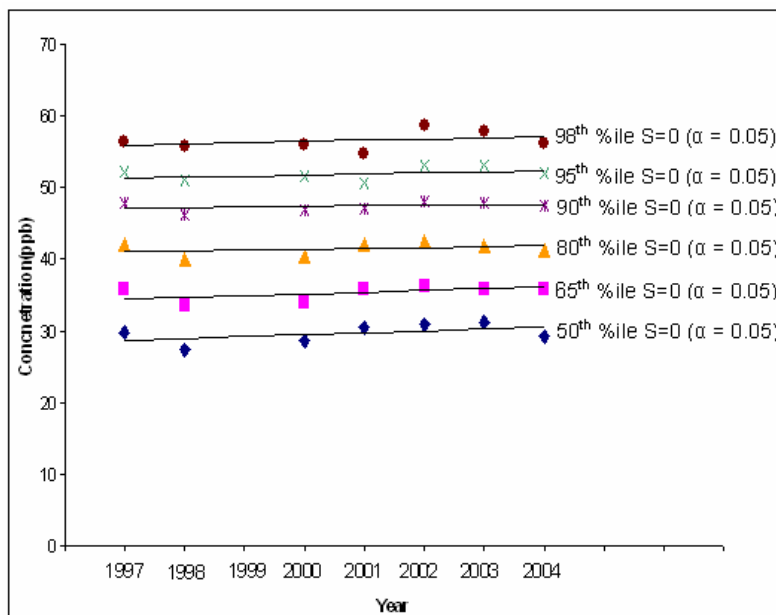


Figure 15 Tomahawk hourly average concentration trends for O₃.

Temporal Trends

Concentrations trends (best-fit lines) are shown in Figure 16 for SO₂. These decreasing trends were observed to be statistically significant at the 65th, 80th, and 90th percentiles ($\alpha=0.05$). Trend results observed using the frequency of exceedence approach are presented in Appendix D for SO₂. This approach provided almost the same results as Figure 16 (i.e. SO₂ showed statistically significant decreasing trends at all percentiles except for the 50th percentile ($\alpha = 0.05$)).

Nitrogen Dioxide (NO₂)

Cumulative Frequency Distribution

Hourly concentrations for NO₂ for each year were sorted in ascending to obtain cumulative frequency distributions. A general pattern of distributions was evident for NO₂ for the years 2000, 2001, 2002, 2003, and 2004. In most cases, 60% of the hourly concentrations fell within the range of 5 ppb (10 $\mu\text{g}/\text{m}^3$), and 90% fell within 10 ppb (19 $\mu\text{g}/\text{m}^3$). Only 5% of the hourly concentrations were above 15 ppb (29 $\mu\text{g}/\text{m}^3$).

Temporal Trends

Concentrations trends (best-fit lines) are shown in Figure 17 for NO₂. Decreasing visual trends were observed at all percentiles, among which the 65th, 80th, and 90th percentiles were statistically significant ($\alpha=0.05$). Trend results observed using the frequency of exceedence approach are presented in Appendix D for NO₂. Once again, this approach produced the exact same results. Decreasing trends were observed at all percentiles, among which 65th, 80th, and 90th percentiles were statistically significant ($\alpha=0.05$) (Appendix D).

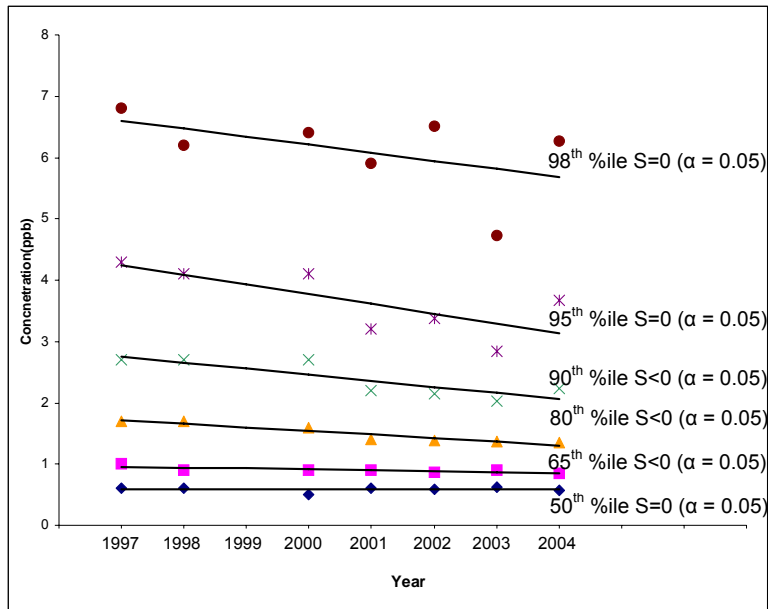


Figure 16 Tomahawk hourly average concentration trends for SO₂.

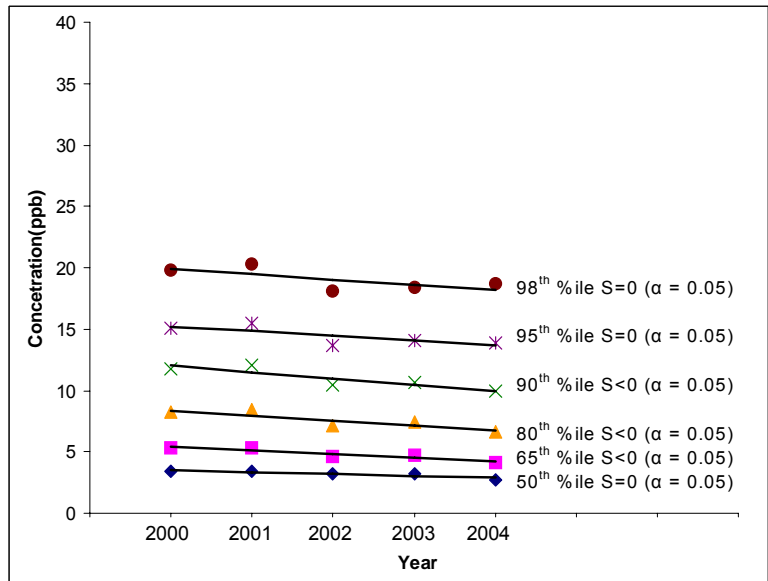


Figure 17 Tomahawk hourly average concentration trends for NO₂.

Fine Particulate Matter (PM_{2.5})

Cumulative Frequency Distribution

Hourly concentrations for PM_{2.5} for each year were sorted in ascending to obtain cumulative frequency distributions. In most of these cases, hourly concentrations were less than 10 µg/m³ (~90% of the time).

Temporal Trends

Concentrations trends (best-fit lines) are shown in Figure 18 for PM_{2.5}. Increasing visual trends were apparent, especially at higher percentiles (90th to 98th). However, none of the trends proved statistically significant ($\alpha=0.05$). Trend results observed using the frequency of exceedence approach are presented in Appendix D for PM_{2.5}. All percentiles showed visually increasing trends, however none of the trends proved statistically significant ($\alpha=0.05$) (Appendix D). Together these results indicate that that no significant change has taken place in PM_{2.5} concentrations during the study period.

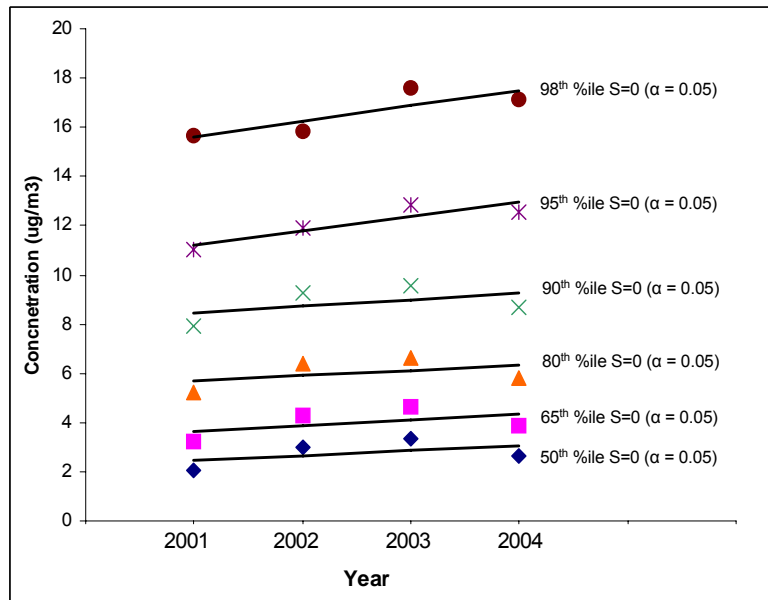


Figure 18 Tomahawk hourly average concentration trends for PM_{2.5}.

4.2.2 Carrot Creek

Ozone (O₃)

Cumulative Frequency Distribution

Hourly concentrations for O₃ for each year were sorted in ascending to obtain cumulative frequency distributions. These distributions indicated that hourly values were less than 50 ppb (100 µg/m³) almost 90% of the time. In addition, hourly values tended to only go above 52 ppb

about 5% of the time and above 55 ppb ($110 \mu\text{g}/\text{m}^3$) about 2% of the time. Hourly median O_3 concentrations ranged from 24 ppb to 30 ppb (48 to $60 \mu\text{g}/\text{m}^3$) year-to-year. Lower median hourly O_3 concentrations were mostly observed from midnight to early morning hours and higher median levels in the afternoon.

Temporal Trends

Concentrations trends (best-fit lines) are shown in Figure 19 for O_3 . Minor decreasing trends were visually apparent at all percentiles (Figure 19), however none of the six trend lines proved statistically significant at $\alpha=0.05$. Trend results observed using the frequency of exceedence approach are presented in Appendix E. This approach provided identical results as Figure 19. Although minor decreasing trends were visually apparent at all percentiles shown in Appendix E for O_3 , none of the trends proved to be statistically significant. Together these results indicate that that no significant change has taken place in O_3 concentrations during the study period.

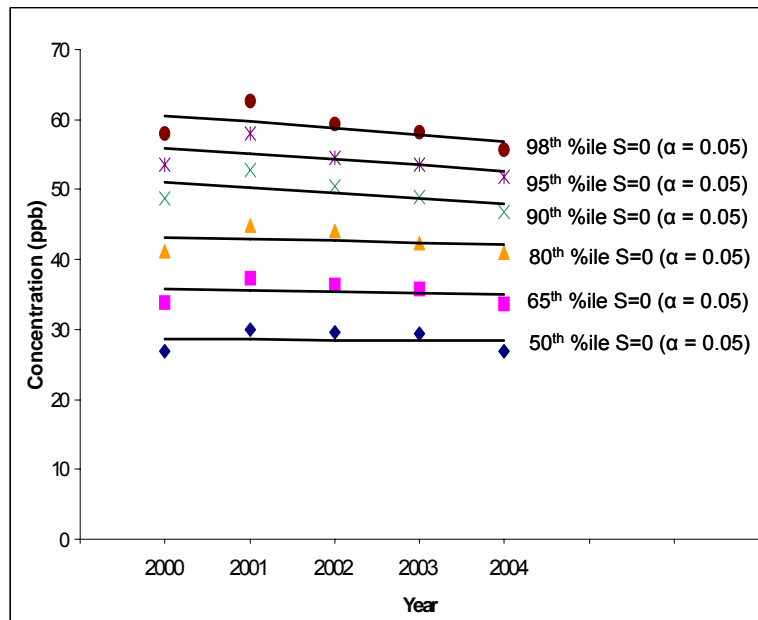


Figure 19 Carrot Creek hourly average concentration trends for O_3 .

Sulphur Dioxide (SO_2)

Cumulative Frequency Distribution

Hourly concentrations for SO_2 for each year were sorted in ascending to obtain cumulative frequency distributions. These distributions indicated that 20% of all hourly concentrations lay very closely to 0 ppb and 80% of hourly concentrations were below 2 ppb ($5 \mu\text{g}/\text{m}^3$). A maximum one-hour concentration of 54 ppb ($144 \mu\text{g}/\text{m}^3$) was observed.

Temporal Trends

Concentrations trends (best-fit lines) are shown in Figure 20 for SO₂. Decreasing trends were observed to be statistically significant at 50th, 65th, 80th, and 90th percentiles ($\alpha=0.05$). Trend results observed using the frequency of exceedence approach are presented in Appendix E for SO₂. Trend detection using this approach provided identical results (i.e. statistically significant decreasing trends at 50th, 65th, 80th, and 90th percentiles ($\alpha=0.05$)).

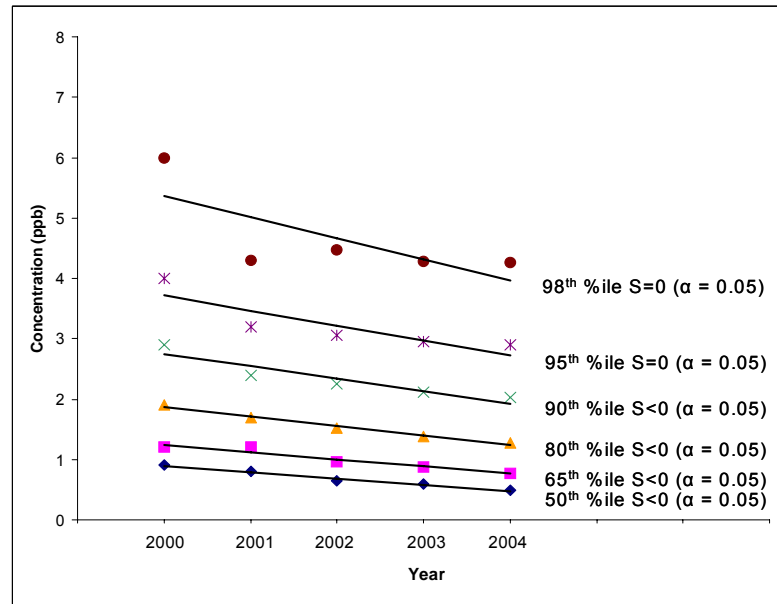


Figure 20 Carrot Creek hourly average concentration trends for SO₂.

Nitrogen Dioxide (NO₂)

Cumulative Frequency Distribution

Hourly concentrations for NO₂ for each year were sorted in ascending to obtain cumulative frequency distributions. For all years 90% of hourly concentrations was less than 17 ppb (33 $\mu\text{g}/\text{m}^3$).

Temporal Trends

Concentrations trends (best-fit lines) are shown in Figure 21 for NO₂. No obvious visual trends were observed at all percentiles. Further, none of the trends proved to be statistically significant ($\alpha=0.05$). Trend results observed using the frequency of exceedence approach are presented in Appendix E for NO₂. Once again, this approach produced the exact same results. None of the trends proved to be statistically significant, leading to the conclusion that no significant change has been taking place over the study period of 5 years with respect to hourly concentrations of NO₂.

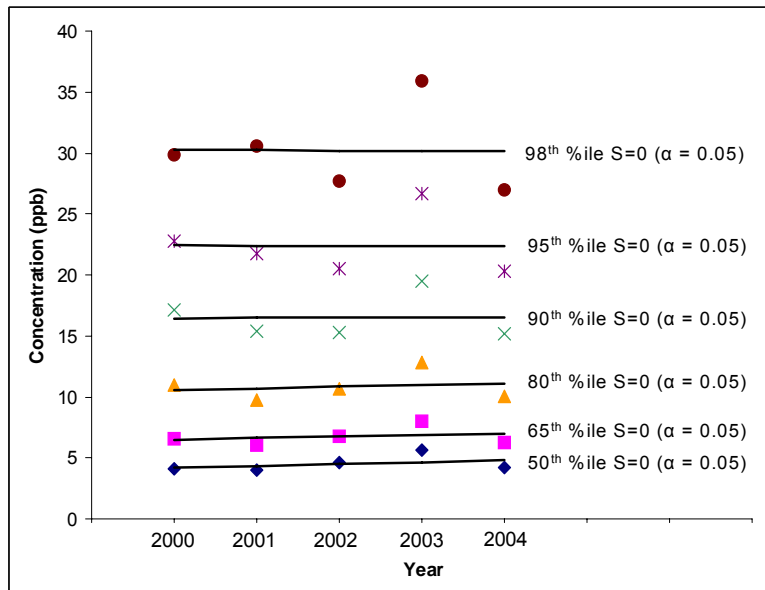


Figure 21 Carrot Creek hourly average concentration trends for NO₂.

A summary of hourly average concentrations trends observed for the different pollutants at Tomahawk and Carrot Creek are presented in Table 3.

Table 3 Summary of hourly average concentrations trends observed for the different pollutants at Tomahawk and Carrot Creek.

Station:	Tomahawk		Carrot Creek	
Statistical test:	t-test	F-test	t-test	F-test
Pollutant				
O ₃	Θ	Θ	Θ	Θ
SO ₂	65 th %ile (↓)	65 th %ile (↓)	50 th %ile (↓)	50 th %ile (↓)
	80 th %ile (↓)	80 th %ile (↓)	65 th %ile (↓)	65 th %ile (↓)
	90 th %ile (↓)	90 th %ile (↓)	80 th %ile (↓)	80 th %ile (↓)
NO ₂	90 th %ile (↓)	90 th %ile (↓)	90 th %ile (↓)	90 th %ile (↓)
	65 th %ile (↓)	65 th %ile (↓)	Θ	Θ
	80 th %ile (↓)	80 th %ile (↓)	Θ	Θ
PM _{2.5}	Θ	Θ	Θ	Θ

Note : %ile = percentile

Θ = no significant trend at all percentiles (50th, 65th, 80th, 90th, 95th, and 98th)

(↓) = statistically significant decreasing trend at indicated percentile only, no significant trend at all other percentiles (α=0.05)

4.3 Discussion

Ozone (O₃)

The diurnal behaviour of O₃ at both Tomahawk and Carrot Creek station (Figures 2 and 9) closely corresponded to that of turbulent mixing layer and conformed to the general behaviour of ground-level O₃ in rural areas – where it is strongly influenced by the interaction of source and sink mechanisms (Angle and Sandhu, 1986). These characteristic diurnal O₃ 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 this mixing during night time and early morning hours (He et al., 2005).

During day time vertical convective mixing, O₃ is being brought down from upper layers of the atmosphere, which leads to the highest O₃ concentrations at ground level between 3:00 pm to 5:00 pm (He et al., 2005). This time period corresponds to the steady period of maximum mixing height. During this period ground-level O₃ concentrations may approach levels in the tropospheric reservoir in air (Angle and Sandhu, 1986).

After this period, the mixing layer ceases to grow and it collapses at sunset. Angle and Sandhu (1986) further stated that generally at night, an inversion prevents downward transport of O₃ and facilitates surface O₃ destruction to progress. Destruction of O₃ from physical contact with surface vegetation accumulates during early hours of the next morning and achieves a decrease in the ambient concentrations at ground level. About three hours after sunrise this nocturnal inversion is replaced by a mixing layer which again transports air, containing O₃, to the surface.

Negligible “weekday versus weekend” differences were expected at stations like Tomahawk or Carrot Creek. These are largely rural areas where variation of activities between weekdays and weekends is not great. The “weekend effect” of ozone reported in literature is mostly observed at urban areas or urban-influenced areas, and can be attributed to different emission patterns between weekends and weekdays (Altshuiler et al., 1987; Qin et al., 2004). Both NO_x and VOCs emission sources tend reduced on the weekend in urban areas. However, it is likely that the weekend effect of O₃ becomes weak with distance from urban areas or areas with greater anthropogenic emissions (Qin et al., 2004).

Seasonal monthly average and monthly maximum patterns at Tomahawk (Figures 3 and 4) and Carrot Creek (Figures 10 and 11) appear to reflect the contribution of photochemically-generated O₃ from sunshine and anthropogenic and natural precursors (Jo et al., 2000; Su et al., 2005). Elevated O₃ concentrations during summer season at these stations (Figures 4 and 11) could be the result of a combination of locally formed O₃ and long-distance O₃ transport (Fuentes and Dann, 1994). During summer, especially around July, hourly O₃ concentrations show much greater variability than that of late winter or around March. This is illustrated in hourly O₃ concentration standard deviations being higher in July than in April. Therefore, despite maximum hourly concentrations occurring in July (Figures 4 and 11), overall variability of the data lowers the hourly average for this month (Figures 3 and 10).

Fuentes and Dann (1994) observed a similar trend at rural locations in Eastern Canada and suggested that higher O₃ concentrations recorded during spring at these eastern locations might reflect the impact of O₃ transport from the upper atmosphere. In the northern hemisphere there is increased transport of stratospheric O₃ into the free troposphere during spring (Fuentes and Dann, 1994). Fuentes and Dann (1994) further stated that because of the longer lifetime of O₃ during winter, accumulation of anthropogenically-produced O₃ may contribute to spring O₃ maxima recorded in the lower troposphere of the northern hemisphere. Similar seasonal patterns were also found over much of United States and Europe (Logan, 1985; Feister and Balzer, 1991).

Results of the short-term trend analysis (Table 3) showed that – at both Tomahawk and Carrot Creek stations – air quality remained unchanged with respect to O₃ as none of the trends exhibited any statistically significant change. This is not unexpected at rural sites, where the influence of local and regional sources of anthropogenic pollutant is not high compared to cities. The majority of ground-level O₃ at rural locations in west central Alberta likely results from natural processes (He et al., 2005). These processes include transport from the “ozone-rich” upper atmosphere and reactions of precursor organic compounds (from vegetation) with NO_x in presence of sunlight (CASA, 2003).

CASA (2003) also reports that 8-hour average O₃ concentrations approaching or exceeding the Canada-Wide Standard (CWS) in several areas in the province – including Hightower Ridge, Violet Grove, and Carrot Creek in the WCAS zone – were the case only if the higher O₃ concentrations were determined to be caused by natural sources or sources outside of Alberta. Sandhu (1999) stated that O₃ formation is relatively suppressed in Alberta as the meteorology is not favourable for it. Sandhu (1999) further stated that high temperatures and shallow mixing depths necessary for O₃ formation do not exist. Peake and Fong (1990) stated that under climatological and meteorological conditions existing in Alberta, O₃ concentration exceedences are more likely in remote areas than in cities or in areas under the direct influence of urban and industrial emissions.

Results of short-term trend analysis in this study are consistent with that observed by others. Wolff et al. (2001) reviewed O₃ concentration trends over North America and reported that in Ontario, Alberta, and British Columbia, mean daily maximum one-hour O₃ 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.

Sulphur Dioxide (SO₂)

Background concentrations of SO₂ in North America are reported to range from 0.3 to 0.7 ppb (0.8 to 1.6 µg/m³) (Miller and Flores, 1992). While hourly SO₂ concentrations are considered low at the two WCAS stations, it was clearly observed that they are decreasing (e.g., refer to Table 3 and Figures 16 and 20 for Tomahawk and Carrot Creek, respectively). In investigating possible causes for this change, Environment Canada (2004) estimated that 51% of SO₂ emissions in Alberta are produced by upstream oil and gas industries, while power plants and oil sands produce about 25% and 18% of SO₂ emissions, respectively. Other reported sources include gas plant flares, oil refineries, pulp and paper mill, and fertilizer plants.

Flaring and venting of unprocessed natural gas (solution gas) is commonly associated with oil and gas extraction and processing activities. Flaring is controlled burning of natural gas waste that is unable to be processed. Flaring is sometimes required for processing of sour gas (natural gas containing hydrogen sulphide) and sweet gas (natural gas that does not contain hydrogen sulphide). When natural gas is flared, it primarily produces carbon dioxide, water vapour, and small amounts of unburned fuel and other gases. SO₂ is produced during combustion of hydrogen sulphide in sour gas. Venting is the direct release of solution gas to the atmosphere through an oil well casing vent. Venting from heavy oil production has been traditionally used to relieve gas pressure from heavy oil wells if there are insufficient volumes or pressures to support continuous combustion in a flare (Lye, 2001).

The Alberta Energy and Utilities Board (EUB) has been activity working with the oil and gas industry in Alberta to reduce solution gas flaring and venting. The EUB has been documenting annual volumes of solution gas flared and vented in Alberta since 1999 broken down by field centres (Figure 22) (Alberta EUB, 2006). Table 4 summarizes total reported amounts of solution gas flared and vented in the Drayton Valley field centre (after Alberta EUB, 2006). The Drayton Valley field centre (Figure 22) closely overlaps with WCAS zone shown in Figure 1. Table 4 demonstrates continuously reduced flared and vented solution gas volumes in the Drayton Valley field centre during the period 1999 to 2004. These data offer a reasonable explanation for decreasing hourly SO₂ concentration trends observed over a similar time period at the Tomahawk and Carrot Creek stations, which are located within the Drayton Valley field centre.

Table 4 Reported annual total solution gas flared and vented volumes in the Drayton Valley field centre (after Alberta EUB, 2006).

Year	Volume [10^3 m^3]
1999	86,109.6
2000	74,497.9
2001	58,423.5
2002	49,357.2
2003	40,902.1
2004	37,971.1

Nitrogen Dioxide (NO₂)

Seasonal variation of average monthly NO₂ concentrations (Figures 8 and 13) showed an expected approximate inverse relationship to seasonal variation of average monthly O₃ concentrations (Figures 3 and 10). Specifically, maximum monthly average NO₂ concentrations in November, December, and January corresponded to minimum monthly average O₃ concentrations. While NO₂ concentrations are much lower compared to O₃, scavenging reactions between these two gaseous pollutants and decreased reactivity of NO₂ in winter months are plausible explanations for seasonal variation of average monthly NO₂ concentrations.

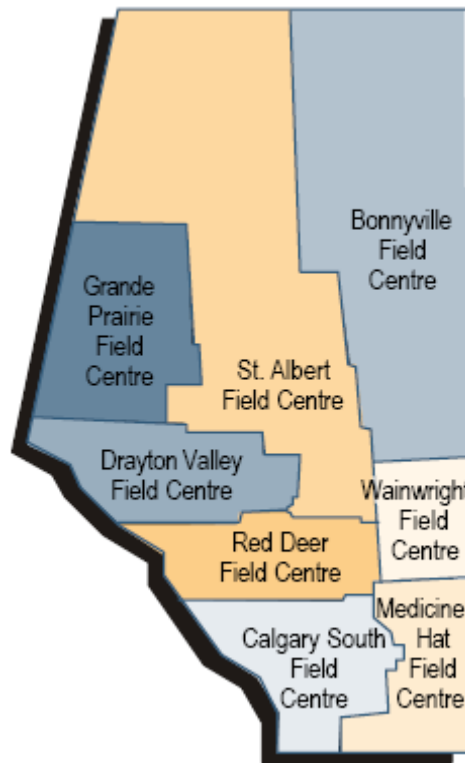


Figure 22 Alberta Energy and Utilities Board regional field centres in Alberta (after Alberta EUB, 2006).

While hourly NO₂ concentrations are considered low at the two WCAS stations, it was clearly observed that they decreased at Tomahawk (refer to Table 3 and Figures 17) and did not change at Carrot Creek (refer to Table 3 and Figures 21) during the period of study. In investigating possible causes for change at Tomahawk and no apparent change at Carrot Creek, both stations are located in rural areas.

The Tomahawk station is located in an agricultural area and is about 30 to 40 km from four coal-fired power plants. Emissions from these plants were largely unchanged during the period of study and therefore are unlikely to have been a dominant factor explaining decreased hourly NO₂ concentrations at Tomahawk. In addition, not enough information is known about whether any differences exist among NO_x source emissions in close proximity to the Tomahawk and Carrot Creek stations that might offer plausible explanations for the change (or lack thereof) over the period of study.

Fine 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 any substantive trend (Figure 5), which is consistent with the rural character of the site. The non-existence of a seasonal trend (Figures 6 and 7) or the lack of proper understanding of it

could be due to the short period of record (2000-2004). This short period is insufficient to exhibit any consistent underlying seasonal trend.

Winter time concentration maxima observed in Figures 6 and 7 could be a result of various factors, e.g., lower mixing heights during this period (Brook et al., 1997). Namdeo and Bell (2005) reported on a study at two rural locations in UK under the influence of anthropogenic activities. They made a clear observation that at both urban background and rural sites, the proportion of fine particles was greater in winter than in summer. Namdeo and Bell (2005) concluded that more efficient mixing of pollutants in the atmosphere in hotter months is likely the reason for lower concentrations of PM_{2.5} during summer.

The Tomahawk station is located in an agricultural area and major source of particulates at this monitoring location are likely agriculture dust and road dust from traffic traveling on roads adjacent to the station. The station is about 30 to 40 km from four coal-fired power plants. Sulphate- and nitrate-derived particles from emissions of SO₂ and NO_x may be additional sources. Results of trend analysis (Table 3) tend to suggest that the air monitoring station is influenced by mostly rural activities of low importance. Specifically, local anthropogenic sources influencing this station are relatively few in number and small in emissions. These 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 prevailing background conditions.

5 Findings

A statistical evaluation of ambient air trends was undertaken using hourly averaged data for an eight-year period (1997 to 2004) from two West Central Airshed Society monitoring stations. These stations are located in a rural area of west central Alberta with anthropogenic activities (oil and gas wells, gas processing plants, coal-fired power plants).

Ozone (O₃)

The diurnal behaviour of O₃ at both Tomahawk and Carrot Creek station closely corresponded to that of turbulent mixing layer and conformed to the general behaviour of ground-level O₃ in rural areas – where it is strongly influenced by the interaction of source and sink mechanisms. Seasonal monthly average and monthly maximum O₃ concentration patterns at Tomahawk and Carrot Creek appear to reflect the contribution of photochemically-generated O₃ from sunshine and anthropogenic and natural precursors.

Results of short-term trend analysis showed that – at both Tomahawk and Carrot Creek stations – air quality remained unchanged with respect to O₃. None of the trends exhibited any statistically significant change. This is not unexpected at rural sites, where the influence of local and regional sources of anthropogenic pollutant is not high compared to cities.

Sulphur Dioxide (SO₂)

Hourly SO₂ concentrations are considered low at the two WCAS stations and trend analysis clearly indicated that they are decreasing. In investigating possible causes for this change, the Alberta Energy and Utilities Board (EUB) has been actively working with the oil and gas industry in Alberta to reduce solution gas flaring and venting and documenting annual volumes of solution gas flared and vented since 1999. These data show continuously reduced flared and vented solution gas volumes in the WCAS zone. These data offer a reasonable explanation for decreasing hourly SO₂ concentration trends observed at the Tomahawk and Carrot Creek stations.

Nitrogen Dioxide (NO₂)

Seasonal variation of average monthly NO₂ concentrations showed an expected approximate inverse relationship to seasonal variation of average monthly O₃ concentrations. Specifically, maximum monthly average NO₂ concentrations during November, December, and January corresponded to minimum monthly average O₃ concentrations. While NO₂ concentrations are much lower compared to O₃, scavenging reactions between O₃ and oxides of nitrogen and decreased reactivity of NO₂ in winter months offer plausible explanations for seasonal variation of average monthly NO₂ concentrations.

Trend analysis showed that hourly NO₂ concentrations decreased at Tomahawk and did not change at Carrot Creek during the period of study. Not enough information is known about

whether any differences exist among NO_x source emissions in close proximity to these stations that might offer plausible explanations for the change (or lack thereof) observed.

Fine Particulate Matter (PM_{2.5})

At Tomahawk, the diurnal pattern of PM_{2.5} concentrations did not show any substantive trend, consistent with the rural character of the site. Lack of a temporal trend suggests that the air monitoring station is influenced by mostly rural activities of low importance.

The period of study over which trends were observed is acknowledged to be short (less than a decade). Changes or lack of changes observed do not necessarily provide an indication of what may happen over the long term. Results of this study are indicating that air quality is unchanged for O₃ and PM_{2.5} and improving in the case of SO₂. The former condition would be expected for rural areas with little or no strong source emission influences. The latter condition is consistent with reduced solution gas flaring and venting in the region of study.

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Appendix A Summary Statistics

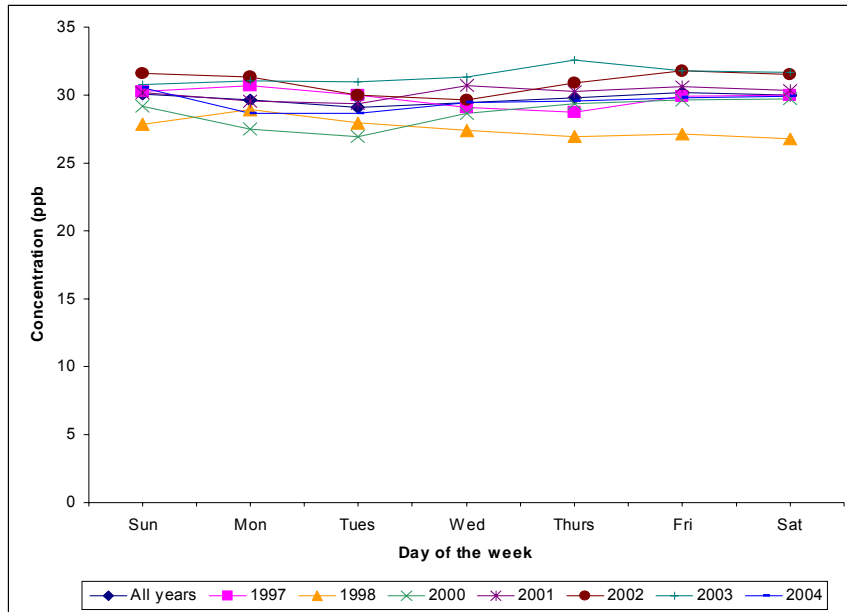
Table A.1 Detection limits and statistics of monitoring data for pollutants at Tomahawk.

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 µg/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 µg/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	

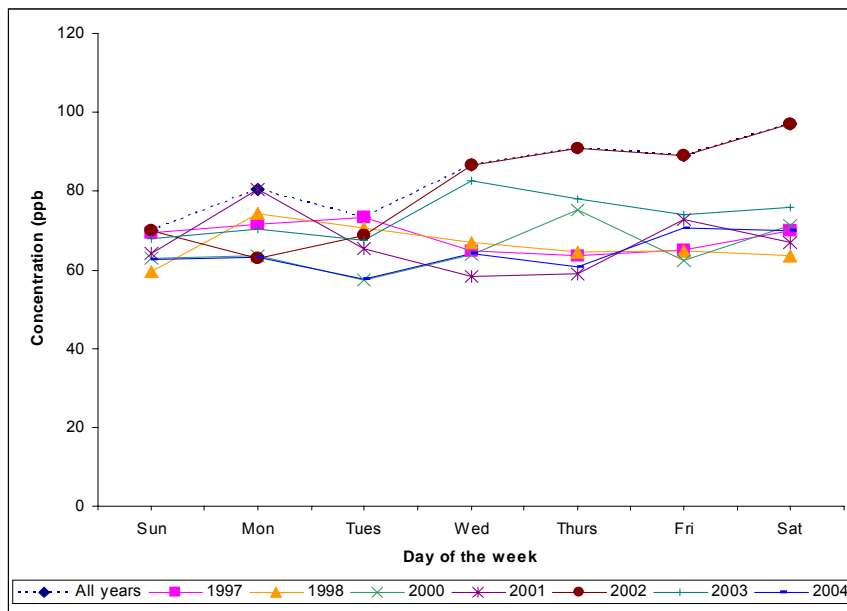
Table A.2 Detection limits and statistics of monitoring data for pollutants at Carrot Creek.

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

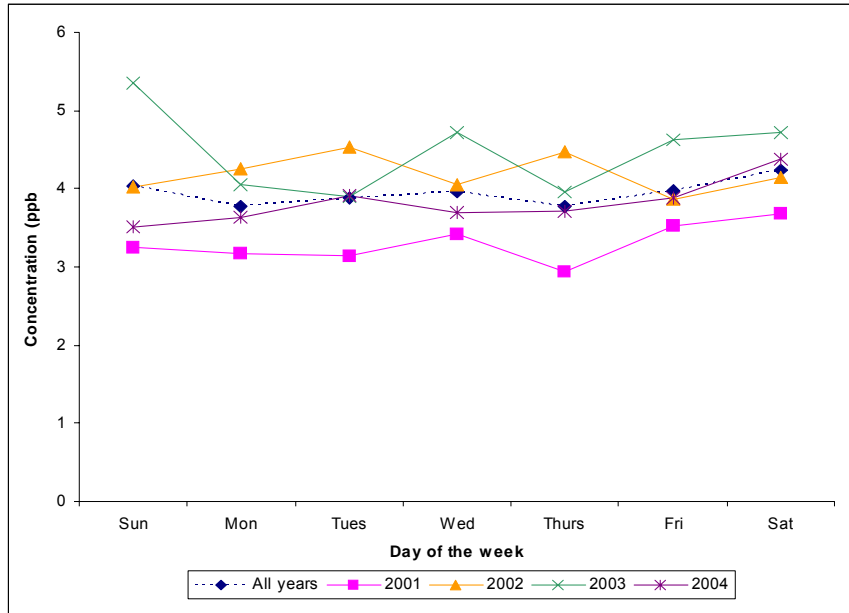
Appendix B Selected Concentration Patterns for Tomahawk



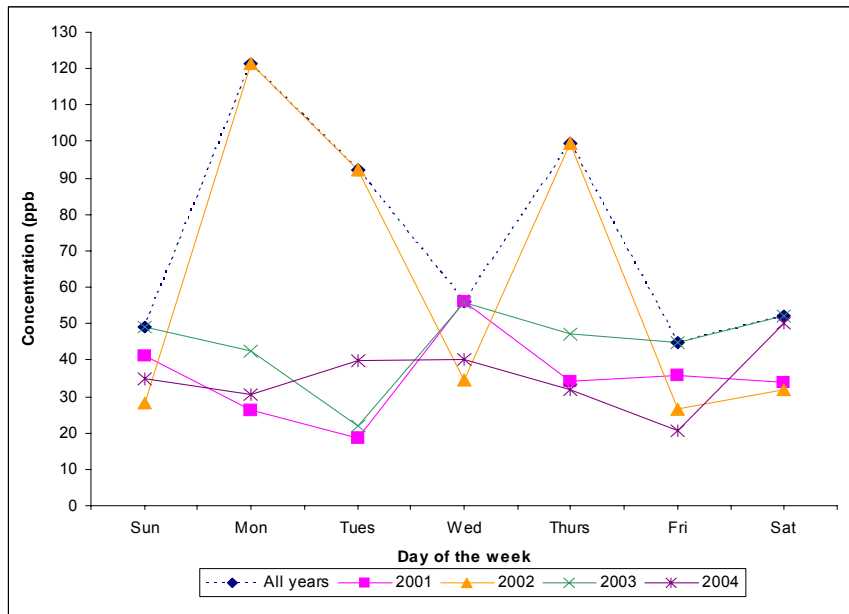
Tomahawk 1997-2004 day of the week trends for O₃ (daily average concentration for year).



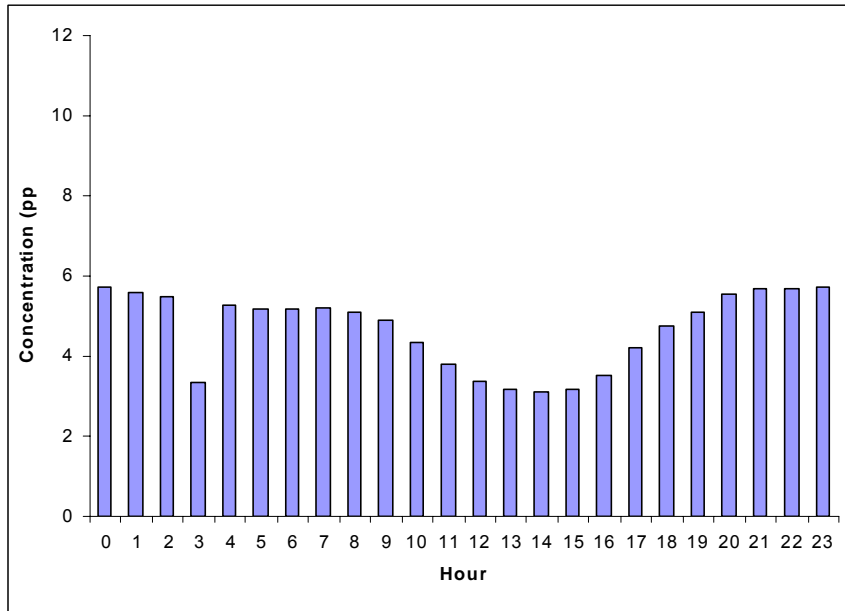
Tomahawk 1997-2004 day of the week trends for O₃ (daily maximum 1-hr concentration for year).



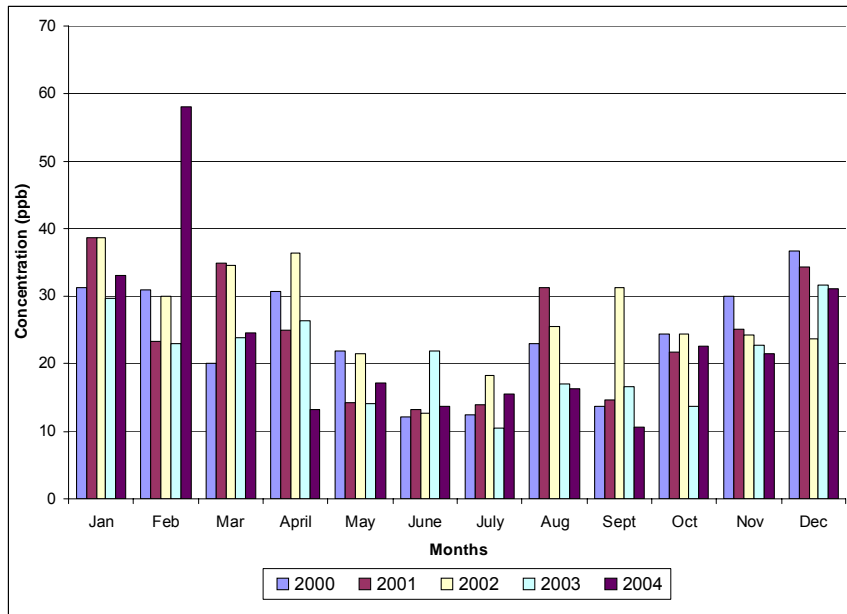
Tomahawk 2001-2004 day of the week trends for PM_{2.5} (daily average concentration for year).



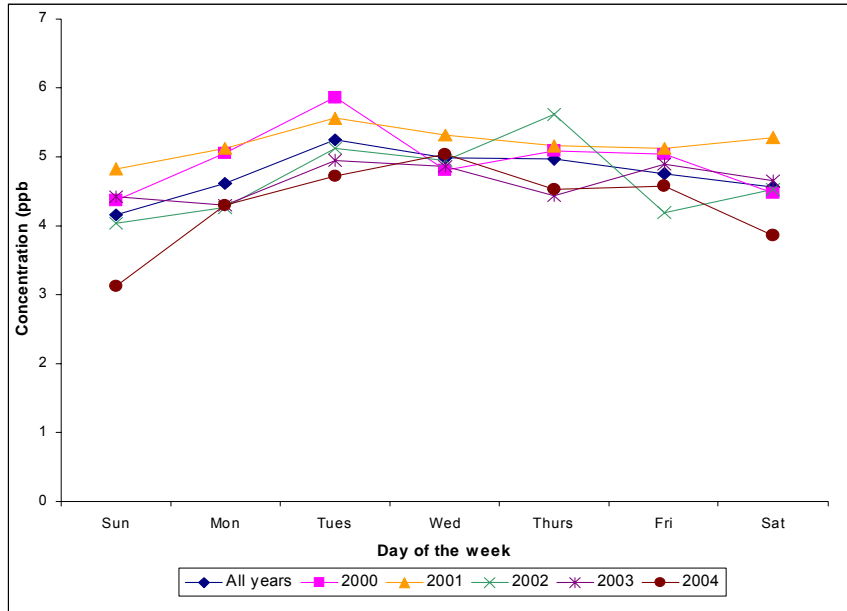
Tomahawk 2001-2004 day of the week trends for PM_{2.5} (daily maximum 1-hr concentration for year).



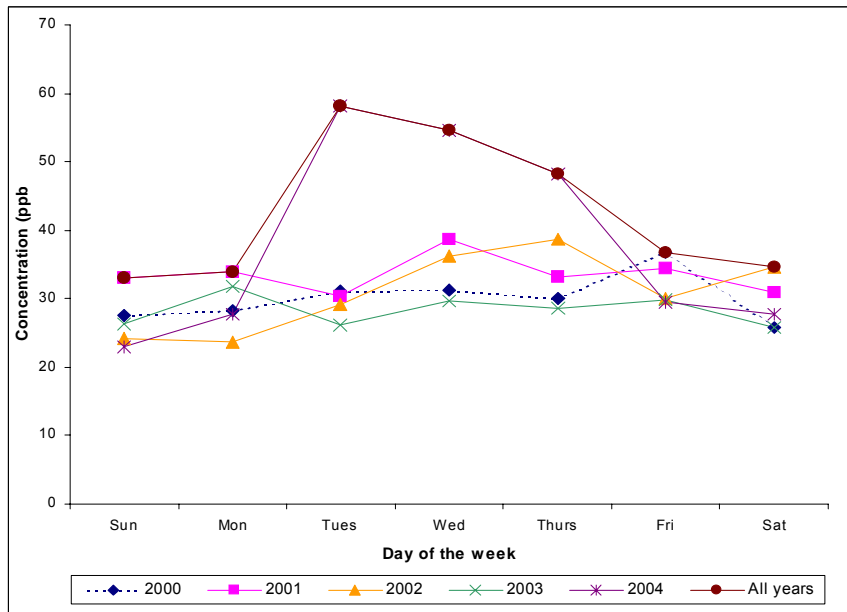
Tomahawk 1998-2004 diurnal hourly average concentration trend for NO₂.



Tomahawk 2000-2004 seasonal trend for NO₂ (monthly 1-hr maximum concentrations).

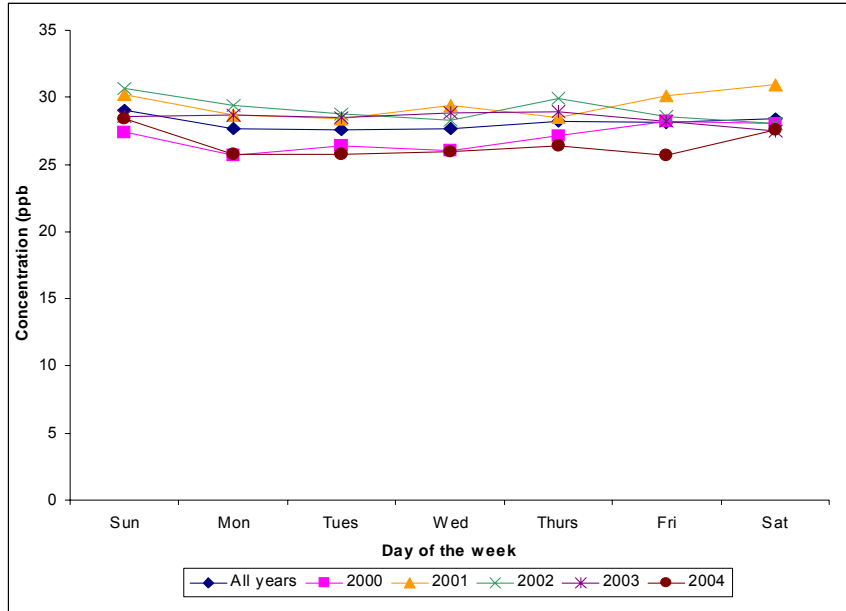


Tomahawk 2000-2004 day of the week trend for NO₂ (daily average concentration for year).

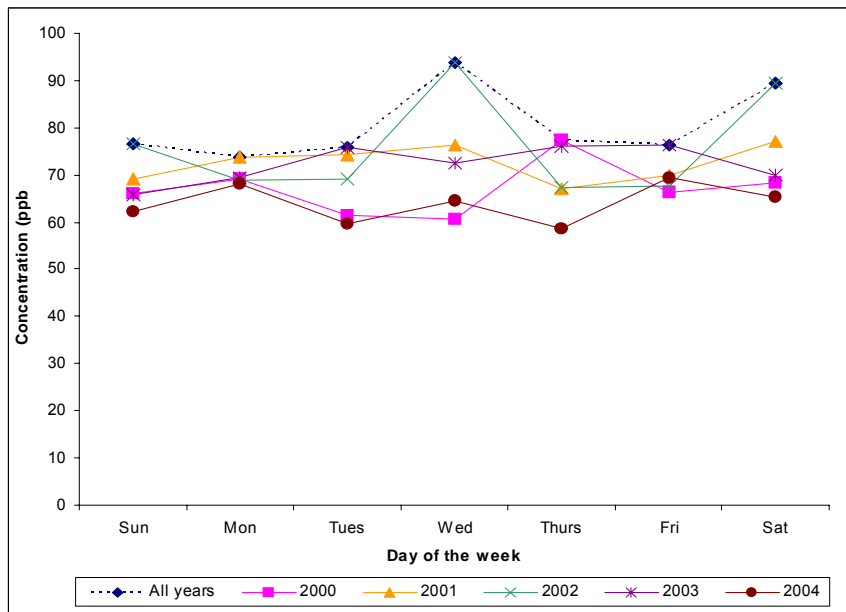


Tomahawk 2000-2004 day of the week trend for NO₂ (daily 1-hr maximum concentration for year).

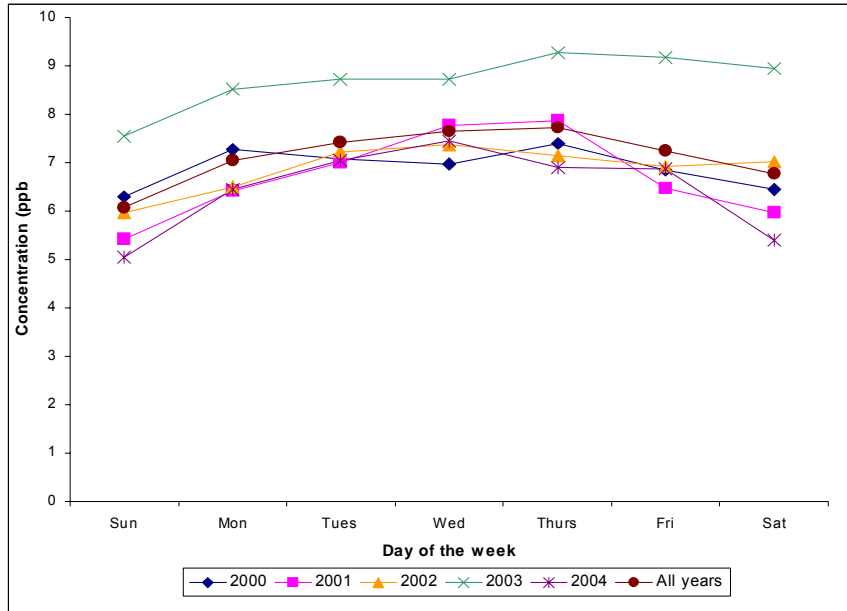
Appendix C Selected Concentration Patterns for Carrot Creek



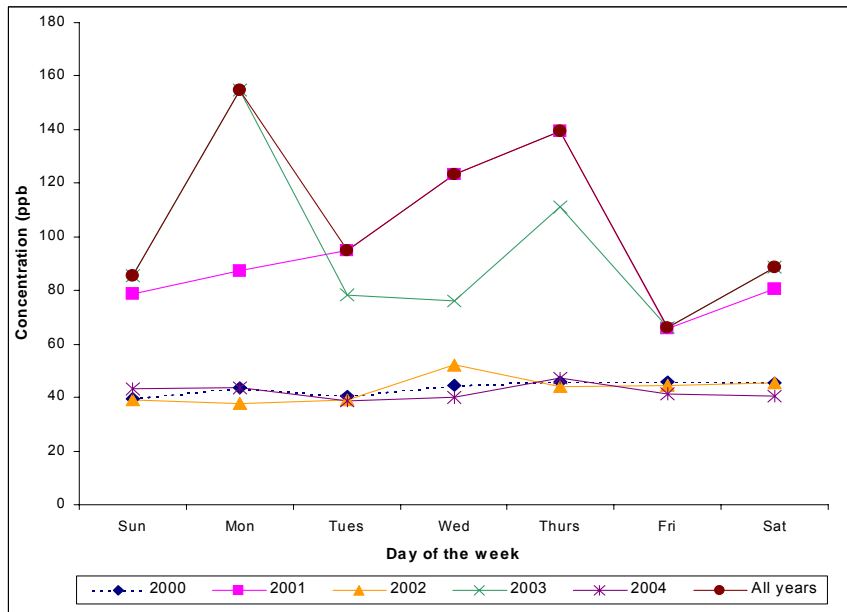
Carrot Creek 2000-2004 day of the week trends for O₃ (daily average concentration for year).



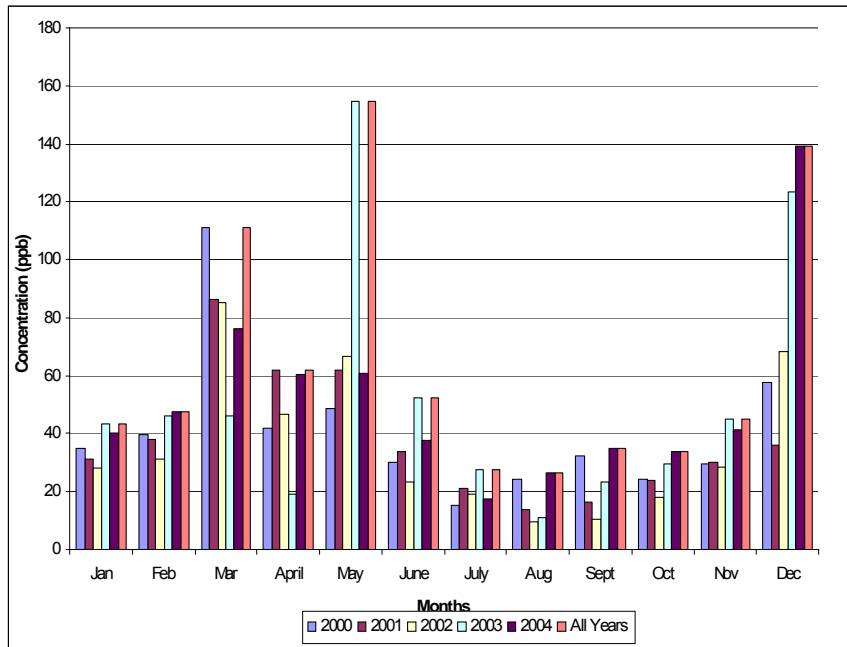
Carrot Creek 2000-2004 day of the week trends for O₃ (daily 1-hr maximum concentration for year).



Carrot Creek 2000-2004 day of the week trend for NO₂ (daily average concentration for year).

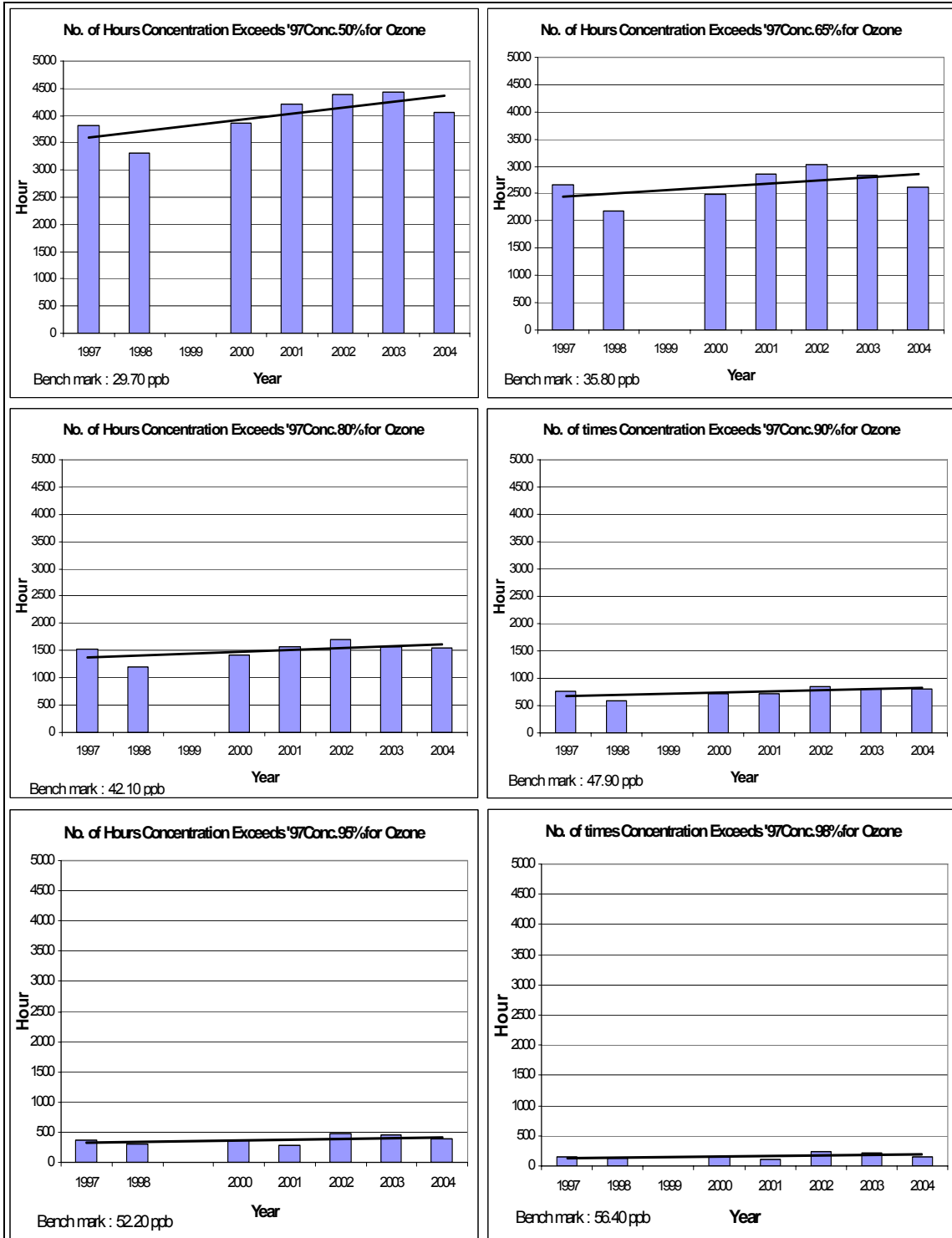


Carrot Creek 2000-2004 day of the week trend for NO₂ (daily 1-hr maximum concentration for year).

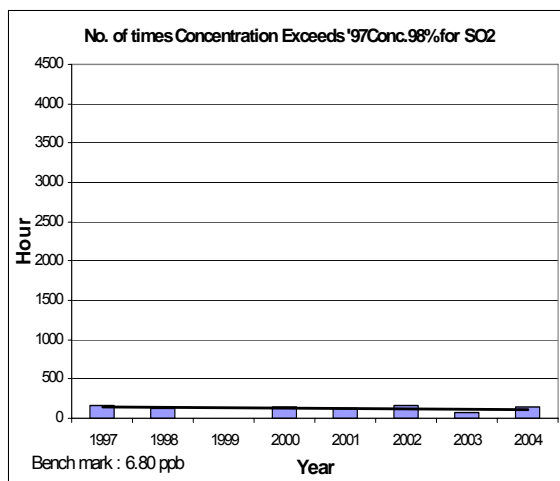
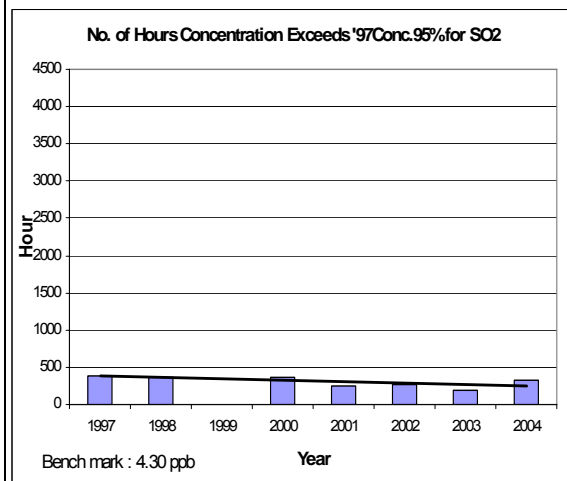
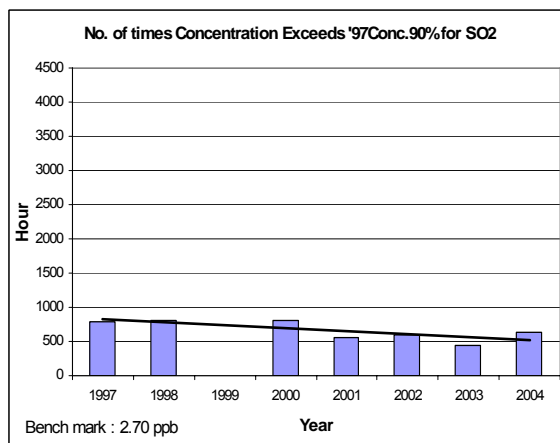
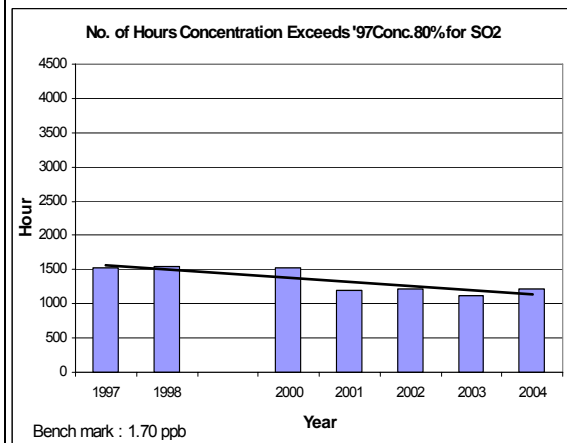
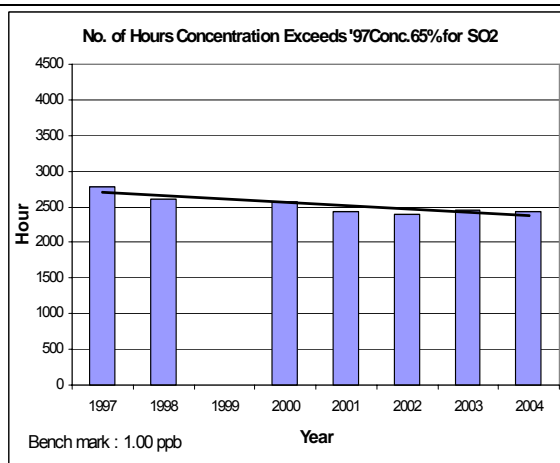
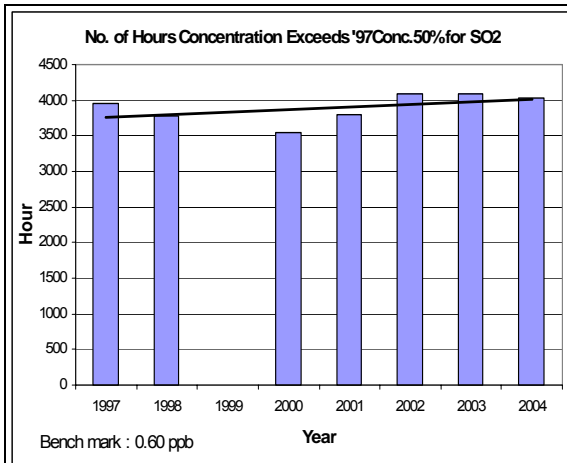


Carrot Creek 2000-2004 seasonal trend for NO₂ (monthly 1-hr maximum concentrations).

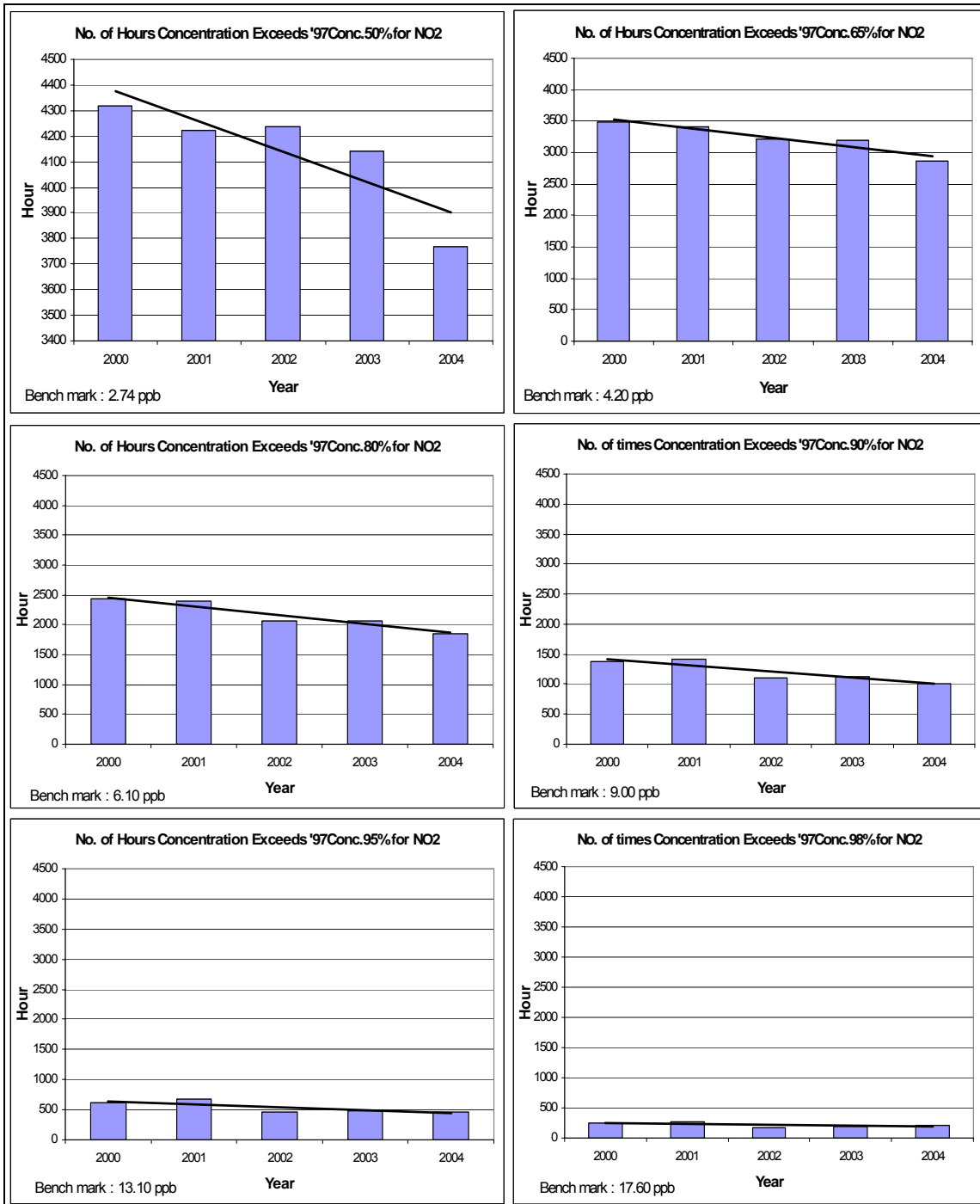
Appendix D Benchmark Exceedence Frequencies for Tomahawk



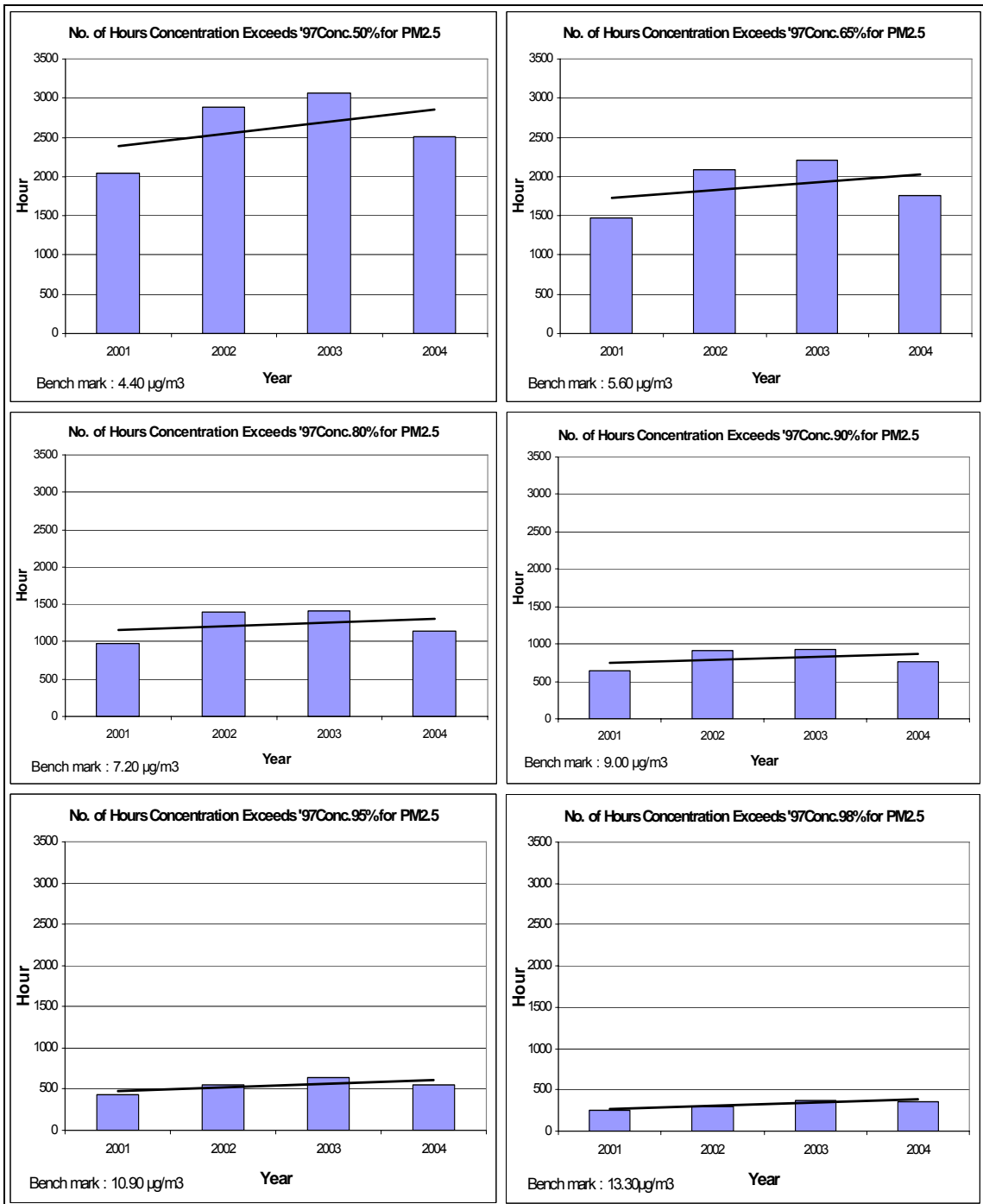
Tomahawk – O₃



Tomahawk – SO₂

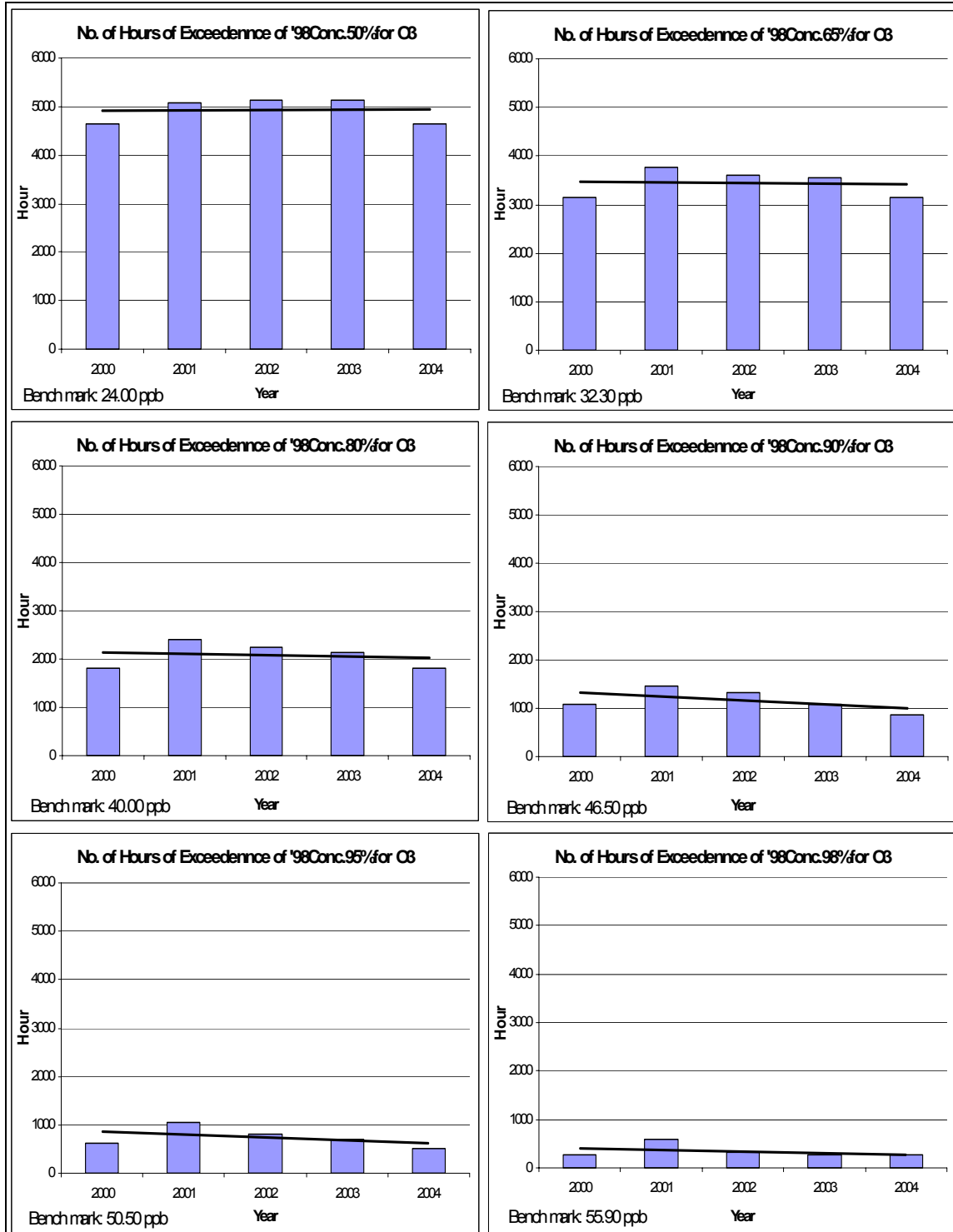


Tomahawk – NO₂

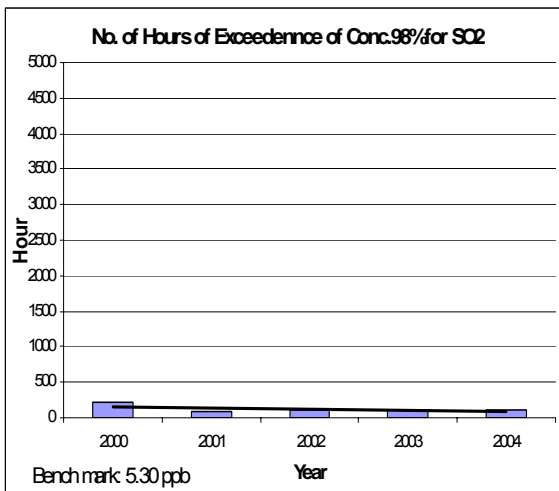
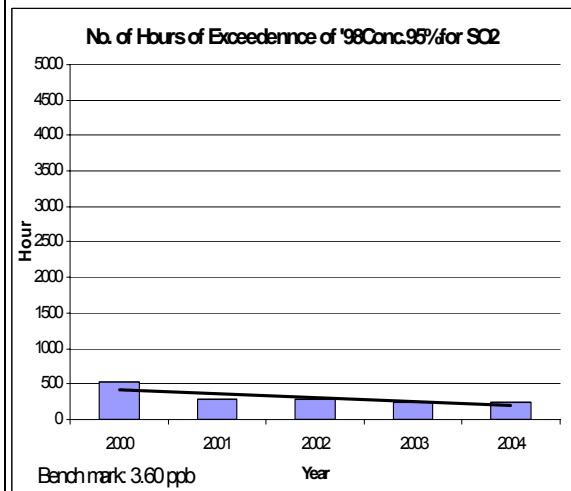
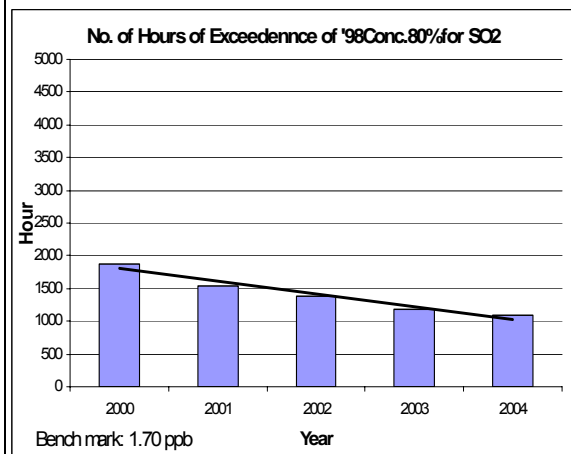
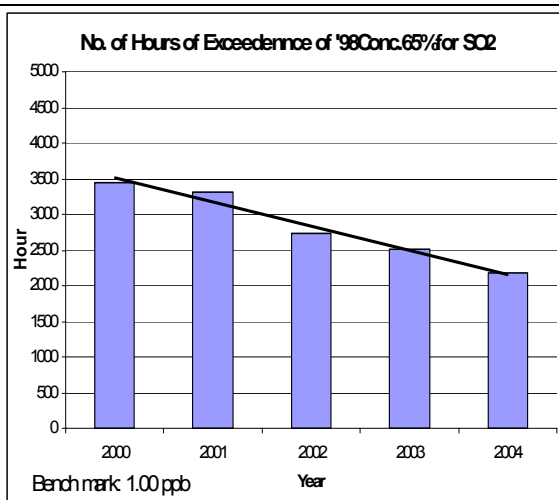
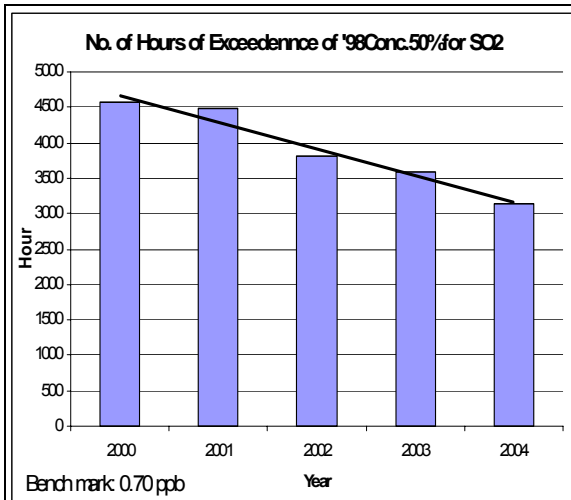


Tomahawk – PM_{2.5}

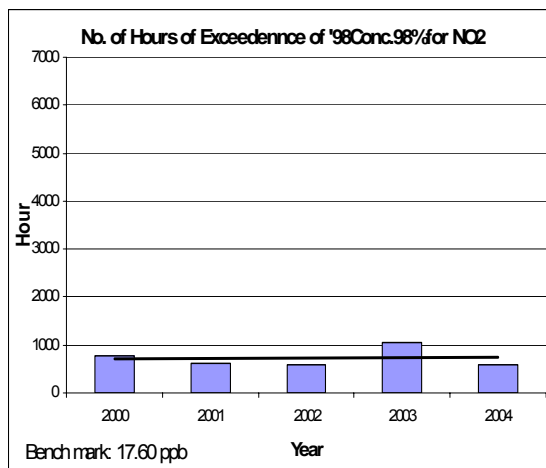
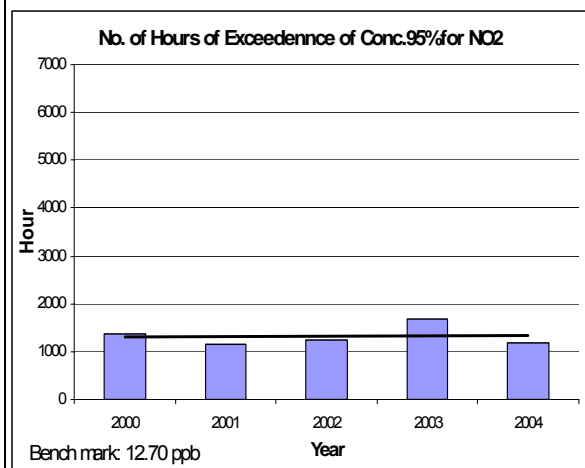
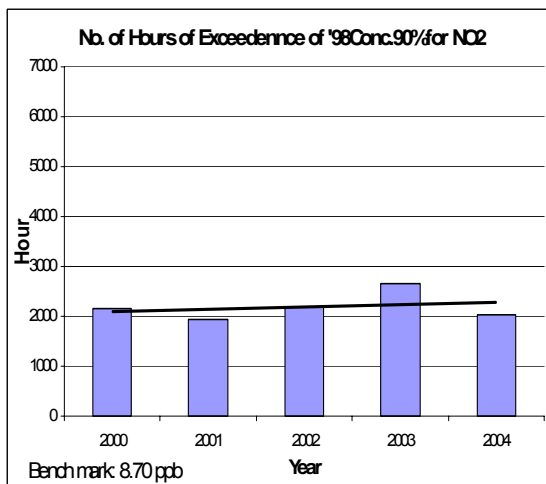
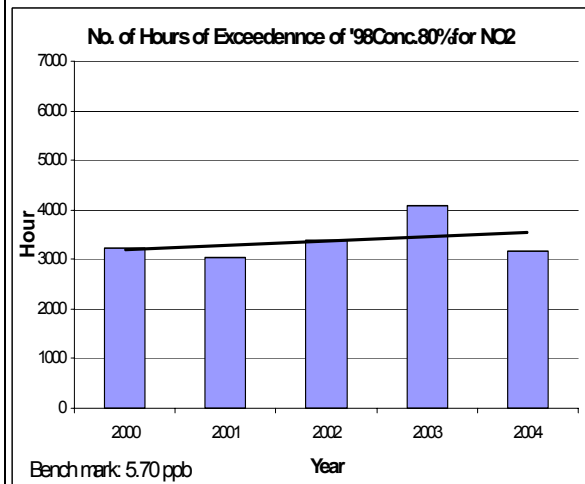
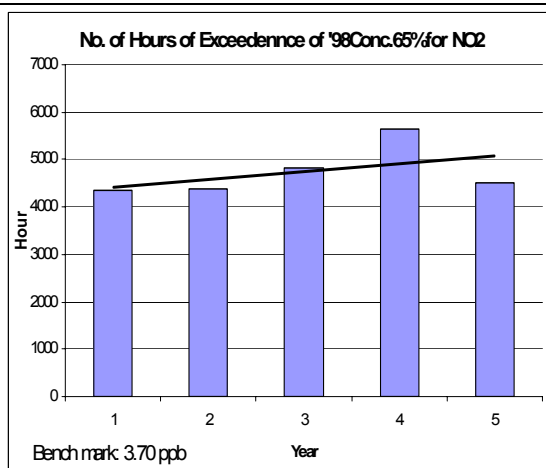
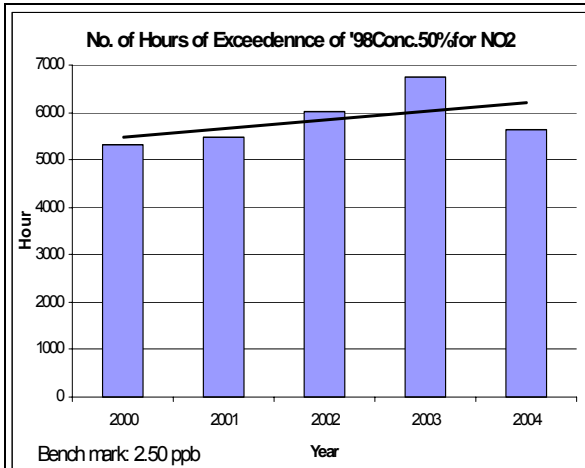
Appendix E Benchmark Exceedence Frequencies for Carrot Creek



Carrot Creek – O₃



Carrot Creek - SO₂



Carrot Creek – NO₂