University of Alberta

Non-Parametric Statistical Analysis of Air Quality Data in Alberta

by

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ABSTRACT

In order to address state and trends of air quality, and to understand impacts of urbanization and industrialization on ambient air quality, two non-parametric methods – the Mann-Kendall test and Sen's test were used for trend analyses of ambient air monitoring data in Alberta. Pollutant concentrations and hourly exceedance frequencies corresponding to cumulative frequency values of the 50th, 65th, 75th, 80th, 90th, 95th, and 98th percentiles for each year were examined as indices in the analysis. In Edmonton, statistically significant decrease trends were observed for indices of SO_2, CO, and $PM_{2.5}$, while no trends were observed for indices of NO_2, O_3, and total hydrocarbons (THCs) over 1997 to 2004. In Fort MacKay, no statistically significant trends were observed for most indices of NO_2, O_3, $PM_{2.5}$, THCs, and SO_2 over 1999 to 2004, except that NO_2 concentration and $PM_{2.5}$ concentration corresponding to the 98% cumulative frequency value exhibited a significant increase trend.

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To my parents, Renfeng Xu, and Chunxing Wang

To my grandmother, Suying Yu

To my wife Huixin Lu, and my daughter Helen Xu

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List of Symbols, Nomenclature and Abbreviations

hrs/yr	hours per year
$\mu g/m^3$	micrograms per cubic meter
μm	micrometer (a millionth of a meter)
AWMA	Air & Waste Management Association
CAA	Clean Air Act
CAAA	Clean Air Act Amendments
CACs	criteria air contaminants
CASA	Clean Air Strategic Alliance
CNN	cloud condensation nuclei
CO	carbon monoxide
CO_2	carbon dioxide
EIA	environmental impact assessment
GHG	greenhouse gas
H_2S	sulfureted hydrogen (hydrogen sulphide)
M_e	metal ion
M_m	any molecule
M_r	passive reaction site
NAAQS	National Ambient Air Quality Standards
NMHC	non-methane hydrocarbons
NO	nitric oxide
NO_2	nitrogen dioxide
NO_3	nitrate
NO_x	nitrogen oxides
NPRI	National Pollutant Release Inventory
O_3	ozone
PM	particulate matter
PM_{10}	fine particles with aerodynamic diameters less than 10μm
$PM_{2.5}$	fine particles with aerodynamic diameters less than 2.5μm
ppb	parts per billion
ppm	parts per million

R	organic radical
RO	organic alkoxy radical
RO_2	organic peroxy radical
SO_2	sulphur dioxide
SO_4	sulphate
SO_x	sulphur oxide
TEOM	Tapered Element Oscillating Microbalance
THCs	total hydrocarbons
US EPA	United States Environmental Protection Agency
WBEA	Wood Buffalo Environmental Association
WMO	World Meteorological Organization

1.0 INTRODUCTION

1.1 Theme and Scope

The province of Alberta has better air quality than many areas in Canada. A region encompassing the Fort McKay oil sands area and the urban area of Edmonton are representative airsheds of interest in the province with respect to possible changes in air quality due to economic and industrial growth during the last ten years. This research provides an assessment of air quality in these two areas.

The Fort McKay air monitoring station of Wood Buffalo Environmental Association (WBEA) has been in operation since 1999 continuously measuring sulfur dioxide (SO_2), total hydrocarbons (THCs), ozone (O_3), nitrogen dioxide (NO_2), and particulate matter ($PM_{2.5}$). All of these pollutants are produced by the petroleum production and processing industry and other sources.

Edmonton is a major city in central Alberta with a regional population of about one million. Combustion of fossil fuels such as coal, oil products, and natural gas, is currently a major source of air pollution in large cities. Transportation activities (road, sea, rail, and air), commercial operations, and industries such as power stations and refineries contribute to air pollution through burning of fossil fuels. In particular, automobile exhaust is a major source of air pollutant emissions in the urban areas, mainly contributing nitrogen oxides (NO_x), total hydrocarbons (THCs), sulfur dioxide (SO_2), carbon monoxide (CO) and particulate matter (PM). Urban areas may also have high concentrations of ground level ozone (O_3 formed from its precursors NO_x and THCs), and H_2S from natural sources, wastewater treatment and landfills.

This study analyzed the extent to which concentrations of ambient air quality parameters changed, trends, at an air monitoring station in Fort McKay and at two stations in Edmonton during a nine-year period (1997 to 2005).This research attempted to explore potential changes in air quality occurring over time in the Regional Municipality of Wood Buffalo due to the current and proposed oil sand extraction and production activities within the WBEA air shed. The same analysis was undertaken for the Edmonton area.

1.2 General Problem Statement

Ambient air quality depends on a number of factors including types and amounts of pollutants released in a given area (source strength), meteorological conditions dispersing these pollutants, and other atmospheric and topographical factors affecting removal of pollutants from the atmosphere.

The public often recognizes air quality as having the potential to negatively affect health. It is important to collect and evaluate the monitoring data of ambient air quality in order to define and understand the state of air quality and how it may relate to health. Nevertheless, this information alone is not sufficient for understanding changes in air quality over time. Trend analysis of ambient air quality is another critical aspect for understanding the state of air quality (Kindzierski and Scotten, 2003). Analysis of trends also provides an indication as to whether air quality is changing for better or worse.

This research conducted trend analysis of ambient air data at two Alberta monitoring locations: 1) Edmonton – a major city in central Alberta with a regional urban population of about 1,000,000 and 2) Fort

McKay – a small community of about 400 people situated among major oil sand extraction and production facilities in northern Alberta.

For each pollutant in this study, summary statistics were used to represent mid-concentration to upper concentration values derived from a cumulative frequency distribution during a calendar year. Concentration values occurring between the 50th and 98th percentiles of a cumulative frequency distribution were considered for evaluation. Statistical analysis was used to examine trends in two areas: 1) the mid to upper concentration values and 2) annual hours exceeding selected concentration benchmarks occurring between the 50th and 98th percentiles of the cumulative frequency distributions for the eight-year period (1997 to 2004). Monitored data were only available for a six-year period (1999 to 2004) for the Fort McKay station, whereas eight years (1997 to 2004) of monitoring data were available for Edmonton stations.

One of the difficulties encountered in the interpretation of environmental data is the quantification of trends by virtue of the calculation of slope and the demonstration that this slope is statistically different from zero. As a result of the assumption that ambient air concentrations display a long-term trend with time, two non-parametric test methods, the Mann-Kendall test and Sen's test, were used. Historical data for SO_2, NO_2, O_3, $PM_{2.5}$, and total hydrocarbons (THCs) were analyzed for Edmonton and Fort McKay over an eight year (1997 to 2004) and a six year period (1999 to 2004) respectively.

These two non-parametric methods do not require the assumptions regarding normality of the data and homogeneity of variance of data commonly required for statistical tests. These assumptions are usually not satisfied with environmental data. The Mann-Kendall test and Sen's test are also powerful enough to eliminate the effects of missing data, outliers and below detection limit data (Gilbert, 1987; Gibbons and Coleman, 2001).

2.0 BACKGROUND INFORMATION

2.1 Air Quality and Air Pollution

2.1.1 Petroleum and Petrochemical Industry

The definition of environmental pollution is 'the introduction by man into the environment of substances or energy liable to cause hazard, harm to living resources and ecological systems, damage to structure or amenity or interference with legitimate use of the environment.' Colls (1997) stated "Pollution can be classified into anthropogenic pollution from human activities and biogenic from animals or plants. The air pollution is the solid, liquid or gaseous material emitted into the air from stationary or mobile sources, moving subsequently through an aerial path and perhaps being involved in chemical or physical transformations before eventually being returned to the surface". He also stated that "the environmental impacts would occur after the interaction between these materials and the other molecules in the atmosphere (e.g., photochemical formation of ozone from hydrocarbons), electromagnetic radiation (e.g., by greenhouse gas molecules), liquid water (e.g., the formation of acid rain from sulfur dioxide), vegetation (e.g., the direct effect of ozone), mineral surfaces (e.g., soiling of buildings by particles) or animals (e.g., respiratory damage by acidified aerosol)".

Jones (1973) defined the oil industry (petroleum and petrochemical) as involving petroleum production, petroleum processing and marketing. He stated that the "petroleum production industry includes drilling oil fields, removing oil from the ground, pretreatment at the well site, and transporting crude oil to refinery. Petroleum processing includes oil refinery, upstream and downstream petroleum-chemical production. Marketing includes the distribution and sale of the finished petroleum and petrochemical products. All of the above may be sources of emissions for air pollution, some of which is not visible, and many of them are odorless" (Jones, 1973).

Jones also stated that although certain technological processes and pollution control measures have been implemented and improved in order to meet more and more stringent environmental standards and regulations, air pollution still exists and air contaminants could be released into the ambient environment from the various sources of operations and processes stated above. In industry, the contaminants may be released during routine production and equipment startups and shutdowns of the production, as well as unusual operation of the installation when problems are occurring with the operation. It should be noted that the pollution could be severe during unstable operation of the plants, or when sweeping (cleaning) instruments such as pipelines and vessels for heavy repairing (Jones, 1973). Resulting local scale or regional scale acidic rain and ozone smog can cause adverse impacts on public health and ecosystems particularly when the resident area is contiguous to the plant location (Lin et al., 2004).

Lin et al. also stated that the emission scale relevant to the oil industry depends upon the factors of crude oil processing capacity, the air pollution control measures that are in effect, the general level of maintenance and management, and the processing scheme employed. The important potentially emitted contaminants contributing to air pollution are hydrogen sulfide, sulfur oxides, nitrogen oxides, hydrocarbons, carbon monoxide, ozone and particulate matter (Lin et al., 2004).

Jones (1973) summarized that hydrogen sulfide is the precursor of sulfur oxides and can be produced during hydroprocessing (catalytic reforming, hydrotreating and hydrocracking), cracking (catalytic cracking, thermal cracking), and coking. Sulfur oxides and nitrogen oxides may result from the combustion of fuels containing sulfur and nitrogen compounds. Hydrocarbons can be vaporized during oil processing or from tanks containing light oil as gasoline or crude oil. Carbon monoxide is emitted as a by-product from the catalytic cracking process (Jones, 1973). Potential sources of specific emissions from oil refineries are presented in Table 1.

Jones also claimed that the extent of air pollution induced by the petroleum and petrochemical industry depends on the source emissions, the topography, and the meteorology. The strength of source emissions depends upon not only the processes, equipments and the age of the investigated target refinery, but also on the types of crude oil processed, the types of oil products, the scale of the production, the appropriate operation and maintenance of the equipment, and the management of the production (Jones, 1973).

Jones further claimed that the petroleum and petrochemical industry is an important source of hydrocarbons which can react photochemically in the atmosphere to produce characteristic photochemical smog (involving ozone) or other air pollution manifestations. These photochemical products can be enhanced by the simultaneous release of nitrogen oxides that are also pollutants from oil processing. Petroleum hydrocarbons involve a large group of various compounds from light, volatile compounds to heavy, nonvolatile oil residue. Unsaturated hydrocarbons are the most active ones in photochemical smog formation. Both oil refineries and automotive traffic share significant contribution to the atmospheric pollution in the vicinity of the industrial area as the two main sources of hydrocarbons and aromatic hydrocarbons (Lin, 2004).

Table1. Potential sources of specific emissions from oil refineries (after Jones, 1973)

Emission	Potential Sources
Sulfur Oxides	Boilers, process heaters, catalytic cracking unit regenerators, treating units, H_2S flares, decoking operations.
Hydrocarbons	Loading facilities, turnarounds, sampling, storage tanks, wastewater separators, blowdown systems, catalyst regenerators, pumps, valves, blind changing, cooling towers, vacuum jets, barometric condensers, air-blowing, high pressure equipment handling volatile hydrocarbons, process heaters, boilers, compressor engines.
Nitrogen Oxides	Process heaters, boilers, compressor engines, catalyst regenerators, flares.
Carbon Monoxide	Catalyst regeneration, decoking, compressor engines, incinerators
Particulate Matter	Catalyst regenerators, boilers, process heaters, decoking operations, incinerators
Ammonia, Aldehydes	Catalyst regenerators
Odors	Treating units (air-blowing, steam-blowing), drains, tank vents, barometric condenser sumps, wastewater separators.

Jones expanded on the potential emission sources in the oil processing industry. The barometric condenser on the vacuum distillation tower can release non-condensable compounds, including light hydrocarbons, which may be the major source of hydrocarbon emissions from oil refining. The pollutant emissions to the atmosphere mainly depend on the size, the feedstock type and the cooling water temperature of the plant units. Catalytic cracking using the controlled coke combustion process may be a significant source of discharged pollutants of catalyst fines, unburned hydrocarbons, sulfur oxides, carbon monoxide, ammonia, and nitrogen oxides. Valve stems and pump shafts in the high process pressures required in the conversion processes of alkylation, polymerization and isomerization can release significant amount of hydrocarbons and other pollutants because they are difficult to seal completely as a result of the high volatility of hydrocarbons. Processes handling liquid petroleum gas (LPG), gasoline or other highly volatile compounds can emit hydrocarbons at a higher rate than similar processes limited to producing lubricants, asphalts, fuel oils, or other heavier oil products having low vapor pressures (Jones, 1973).

The processes treating spent acid and acid sludge as well as the processes being employed for recovery or disposal of hydrogen sulfide are potential sources of sulfur oxides, hydrocarbons and visible plumes. The catalyst regeneration in catalytic cracking, air agitation in mixing tanks and other air-blowing operations in a refinery can be potential sources of SO_2, hydrocarbons and particulate matter. Numerous emission sources such as settling tank vents, surge tanks, water treatment units, wastewater treatment units, drains, valves and pump seals throughout the plant may be responsible for fugitive malodorous substances such as H_2S and mercaptans, which even in trace quantities are offensive to nearby residents (Jones, 1973).

2.1.2 Natural and Anthropogenic Emission Sources

1. Sulfur emissions

   The sources of natural sulfur emissions were recounted by Colls (1997) mainly as dimethyl sulphide (DMS) from marine phytoplankton, SO_2 from the oxidation of DMS in the atmosphere and volcanoes, hydrogen sulphide (H_2S) from decay processes in soil and vegetation, sulfur hot springs, sloughs, swamps and lakes, and sulfur trioxide (SO_3) from further oxidation of a small portion of SO_2.

It was also described by Colls that almost all the anthropogenic sulphur emissions are from the combustion of fossil fuels including coal, oil and oil byproducts, and natural gas. Various economic sectors including agriculture, transportation (road, sea, rail and air), commerce, and industry such as power stations, refineries and others use combustion in their activities. Industrial and agricultural emission sources of H_2S and TRS include fugitive emissions from oil refineries, tank farms for raw oil and unrefined petroleum products, natural gas plants, petrochemical plants, oil sands plants, sewage treatment facilities, pulp and paper plants using the Kraft pulping process, and animal feedlots (Colls, 1997) .

2. Nitrogen oxide emissions

With regards to nitrogen oxide emissions, Colls stated that nitrogen oxide (NO_x), reported as NO_2, has two principal forms: nitric oxide (NO) and nitrogen dioxide (NO_2). The source strengths are described as NO_2 equivalents because all NO can be potentially oxidized to NO_2 even though most direct emissions are NO. The natural and anthropogenic sources of nitrogen oxide NO_x are mainly lightening, nitrogen oxides from the stratosphere, NH_3 oxidation, biomass burning, and soil release. The significant transportation, commercial, and industrial NO_x sources are similar to those of sulfur emissions cited above. Nitric oxide and nitrogen dioxide directly participate in the photochemical reactions cycles that involve ozone, organic compounds and radicals.

According to Colls, the relevant reactions are as follows:

$$N_2 + O = NO + N \quad (1)$$

$$N + O_2 = NO + O \quad (2)$$

3. Volatile organic compounds (VOCs) and Total Hydrocarbons (THCs) Emissions

It was summarized by Colls that volatile organic compounds (VOCs) included methane, non-methane hydrocarbons (NMHC, including alkanes, alkenes and aromatics), halocarbons (such as trichloroethylene) and oxygenates (alcohols, aldehydes and ketones). Hydrocarbons (including chlorinated and oxygenated hydrocarbons) play an important role in photochemical reactions in the atmosphere due to their potential involvement in a series of reactions with NO_3, OH radicals or O_3, such that the hydrocarbons can be reversibly transformed into more stable or soluble compounds and particles. Industrial processes, solvents use, and transportation are the main contributors of the total global emission of VOCs or THCs which is at the annual level of over two million tons. This amount is similar to the amount of NO_x and SO_2 produced. As previously stated, VOCs and THCs are also related to ozone formation (Colls, 1997).

Colls claimed that the main anthropogenic emission sources of VOCs include road traffic and solvents use (paints, adhesives, aerosols, metal cleaning and printing). Substantial anthropogenic VOC emission sources include painting (evaporation of solvents), oil production (flaring and venting of gas), oil refining (flaring and fugitive emissions), and distribution of oil or refinery products (evaporation from storage, displacement release when venting tanks). Other sources include dry cleaning (final drying of clothes), use of aerosol sprays (both in the product and from the propellant), inefficient combustion of bituminous coal in domestic grates, production of alcoholic drinks (breweries and distilleries) and arable farming (crop growing, silage manufacture, sludge spreading). The naturally biogenic VOCs emissions from forests and other creatures have not been completely understood, but global emissions are estimated as high as about 400 Mt of carbon as both isoprene and monoterpene (Colls, 1997).

4. Ozone Formation

The natural ozone layer formed by the action of UV photons on oxygen molecules accounts for about 90% of the total ozone in the atmosphere and is found in the stratosphere at a height of 15 to 50 km. Some of this ozone can diffuse downwards from the stratosphere to the troposphere. There exists a background concentration of 10 to 20 ppb (Colls, 1997).

According to Colls, the photochemical reactions of UV photons on NO_x can produce ozone via the following reactions:

$NO_2 + h\nu = NO + O$ (NO_2 photolysis) (3)

(where the wavelength of the photons are 280-430 nm)

$O + O_2 + M_m = O_3 + M_m$ (O_3 formation) (4)

(where M_m is any molecule, such as N_2 or O_2)

$NO + O_3 = NO_2 + O_2$ (NO_2 formation) (5)

In an unpolluted atmosphere, the cycle and equilibrium of the above three reactions can result in a few ppb concentration contributing to the stable background concentration of ozone. According to Colls, additional ozone can be formed in the troposphere as a secondary pollutant by a series of photochemical reactions:

$O_2 + OH + RH = RO_2 + H_2O$ (6)

$RO_2 + NO = RO + NO_2$ (7)

$NO_2 + h\nu = NO + O$ (8)

$O + O_2 + M_m = O_3 + M_m$ (9)

(Where M_m *is any molecule,* R *is an organic radical,* RO *is an organic alkoxy radical, and* RO_2 *is an organic peroxy radical)*

As Colls concluded, NO_x and hydrocarbons are important precursors for secondary ozone formation. During the daytime, the production and photolysis of NO_2 and the formation of ozone occurs as shown in the above reaction scheme. In addition, two further secondary pollutants, formaldehyde (HCHO) and peroxyacyl nitrate (PAN), both of which are toxic irritants, can be formed at significant concentrations. During the nighttime, there are no UV photons present to produce NO by photolysis, rather NO is consumed by its reaction with O_3, reaction (5), leading to a decrease in concentrations of both NO and O_3, paired with an increase in the concentration of NO_2. Excessive NO_2 can react with organic molecules through various intermediates to produce nitric acid (HNO_3) after which HNO_3 can be transferred to water droplets in the atmosphere. Together with H_2SO_4 formed from SO_2 and SO_3 in the atmosphere, these HNO_3 water droplets contribute remarkably to the acidification of precipitation (Colls, 1997).

Colls also mentioned that the requirement of UV photons for the formation of O_3 and the short persistent time of O_3 molecules in the atmosphere results in a characteristic diurnal fluctuation of ozone concentration in the lower troposphere. Ozone can also be formed via more complex reaction cycles involving the oxidation of methane and/or carbon monoxide with nitrogen oxide acting as a catalyst, along with hydroxyl radicals playing an important role in removing pollutants in the atmosphere (Colls, 1997).

5. Particulate Matter Emission

Colls (1997) stated that particulate matter (PM) could be either a primary pollutant or a secondary pollutant, and either solid or liquid. The main sources of natural particulate matter are erosion of soil by wind, evaporation of sea water droplets (leaving small crystals of sea salt in the atmosphere), and other natural sources such as volcanoes, biomass combustion, spores, and pollen.

Colls (1997) also mentioned that anthropogenic sources of PM are mainly from the activities involving combustion, melting, grinding, crushing, plowing and spraying. Depending upon the initial size distribution of PM released during these activities, a portion of the particles can be sufficiently fine so as to remain suspended in the air for a period of time before sinking. Colls (1997) further pointed out that the major sources of secondary particulate matter are from the oxidation of SO_2 and succeeding hydration to form sulfuric acid droplets, and the similar procedure of NO_2 to nitric acid vapor. Both of them (sulfuric acid and nitric acid) can react with ammonia gas released from the degradation of animal urine and/or emissions from industry, to produce minicrystals of ammonium sulfate and ammonium nitrate salt. For industrial regions having intensive animal breeding or abundant stock raising, a characteristic smog of fine particles can appear in the open air (Colls, 1997).

2.1.3 Motor Vehicles

As Colls (1997) proposed, both of the number of vehicles in use and the annual traveling distance of each vehicle had been increasing steadily and greatly in most cities around the world. The result of those increases is that pollution from mobile sources has become the major threat to the atmospheric environment, replacing the static sources of fossil fuel combustion. Presently, automobile exhaust contributes more to air pollution than any other single human activity. Motor vehicles have become the dominant air pollution source impacting towns and cities. The population and vehicles are concentrated in urban areas resulting in those areas having the highest emission densities and the worst dispersion conditions. The main pollutants released from motor vehicles include CO, NO_x, THCs, SO_2 and particulate matter (PM) (Colls, 1997).

2.2 Criteria Pollutants and Their Sources and Sinks

The primary sources of air pollutants are motor vehicles, industry, and other human activities. A number of secondary air pollutants can be formed from the original pollutants. The original and secondary pollutants in the air are presented in Table 2 (Hao, 2002). The concentrations, and temporal and spatial concentration distributions of atmospheric pollutants depend upon source strengths of pollutant emissions, meteorological factors and geographical factors (Murray, 2003).

Table.2 Classification of air pollutants (after Hao, 2002)

Pollutant	Original Pollutant	Secondary Pollutant
S	SO_2, H_2S	SO_3, H_2SO_4, M_eSO_4
N	NO, NH_3	NO_2, HNO_3, M_eNO_3
C	CO_2, CO	
Organic	C_1--C_{10}	O_3, aldehyde , ketone, etc.
Halogen	HF, HCI	

Note: SO_4^{2-} is sulphate; NO_3^- is nitrate; M_e is a metal ion

2.2.1 Physical and Chemical Properties

The research group in Levelton Engineering Ltd. (2005) summarized the physical and chemical properties of the main associated pollutants in the atmosphere involving sulfur dioxide (SO_2), total reduced sulfur (TRS),total hydrocarbons (THCs), ozone (O_3), nitrogen dioxide (NO_2), carbon monoxide (CO) and particulate matter ($PM_{10}/PM_{2.5}$). Sulfur dioxide (SO_2) is a nonflammable, nonexplosive, and colorless gas that can be produced from the combustion of fossil fuels containing sulfur. SO_2 is a precursor to the formation of secondary particulate matter and is also an important contributor to acid rain. Total reduced sulfur (TRS) mainly includes hydrogen sulphide (H_2S) (a colorless gas with a rotten egg odor), mercaptans, dimethyl sulphide, dimethyl disulphide, and other reduced sulphur compounds.

Generally, total hydrocarbons (THCs) refers to a group of several hundred compounds composed of carbon and hydrogen, e.g., hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene.

Particularly reactive hydrocarbons, including non-methane hydrocarbons (NMHC), can participate in atmospheric photochemical reactions and are thereby important precursors of secondary particulate matter and ground-level ozone. Principally THCs are emitted from combustion processes, evaporation of materials such as petroleum products, paints and solvents, and naturally occurring sources (Levelton Engineering Ltd., 2005).

As the research group in Levelton Engineering Ltd. (2005) stated, nitrogen oxides (NO_x) include nitric oxide (NO) and nitrogen dioxide (NO_2), both of which are often combined and reported as equivalent NO_2. Nitric oxide (NO) is a colorless and odorless gas, most of which reacts with O_3 in the ambient air to produce nitrogen dioxide (NO_2). NO_2 is a reddish-brown gas with a pungent odor, and it is partially responsible for the "brown haze" that appears within and around large cities. NO_x can be produced in all combustion processes in which nitrogen oxides are formed from nitrogen in both the air and fuel. Similar to SO_2, NO_x plays an important role in the formation of ground-level ozone. NO_x can react with other contaminants such as ammonia to form secondary particulate matter, and contribute significantly to the formation of acid rain (Levelton Engineering Ltd., 2005).

Ozone (O_3) is a colorless gas. It is important to distinguish ground-level ozone from the stratospheric ozone layer. The stratospheric ozone layer helps to protect the organisms on the earth's surface from the adverse effects of the ultraviolet light in sunlight. It can also be depleted by reactions with emissions of some manufactured chemicals. Whereas ground-level ozone is a component of characteristic smog in cities, it has been associated with damage to human health, ambient environment and ecosystems. VOCs (including THCs) and nitrogen oxides are two important precursors for the formation of ozone, and they can be released by both natural and anthropogenic sources including biogenic emissions from vegetation, fuel combustion, and the use of paints and solvents. The formation reactions of secondary ozone from the precursors can be enhanced by higher ambient air temperature and stronger solar radiation with resulting elevation of the concentration of ground-level ozone (Levelton Engineering Ltd., 2005).

The research group in Levelton Engineering Ltd. (2005) also depicted the properties of carbon monoxide (CO) and particulate matter (PM). CO is a colorless, odorless, non-corrosive, and highly poisonous gas with a density similar to that of air. CO can be produced directly from the incomplete combustion of fuels. PM refers to microscopic particles of solids and liquids that remain suspended in the air over a certain time. Particles endue characteristic smog with its color and may cause reductions in visibility. Primary (direct) PM is mainly from fossil fuel combustion in industrial and non-industrial activities, especially traffic and wood-burning stoves or forest fires. Secondary (indirect) PM is formed by the physical transformation and actinic reactions of its precursors (NO_x, SO_x, VOCs and ammonia). PM can range in size, shape and chemical composition. In monitoring, PM is typically grouped into PM_{10} (inhalable, less than 10 microns in diameter), $PM_{2.5}$ (respirable, less than 2.5 microns in diameter) and ultrafine particles (less than 1.0 micron in diameter (Levelton Engineering Ltd., 2005).

The units used for air pollutant concentrations are usually $\mu g/m^3$, ppm, and ppb. As presented in Table 3, Colls (1997) summarized the conversion factors between volumetric and gravimetric units, by which values in units of $\mu g/m^3$ can be obtained expediently from values in ppb by multiplying by conversion factors corresponding to the homologous temperature in Table 3.

Table.3 Conversion factors from ppb to μg*m^{-3} (after Colls, 1997)

Pollutant	Molecular Weight(g/mol)	To convert			
		ppb to μg/m^3		μg/m^3 to ppb	
		0°C	20°C	0°C	20°C
SO_2	64	2.86	2.66	0.35	0.38
NO_2	46	2.05	1.91	0.49	0.52
NO	30	1.34	1.25	0.75	0.8
O_3	48	2.14	2	0.47	0.5
NH_3	17	0.76	0.71	1.32	1.43
CO	28	1.25	1.16	0.8	0.86

2.2.2 Dispersion, Transportation and Deposition of Pollutants

Onursal and Gautam (1997) proposed that concentrations of the ambient air pollutants were determined not only by the strengths of source emissions but also by the pathways in which primary pollutants were dispersed, were transported, and reacted with each other or other contaminants in the atmosphere to produce secondary pollutants. In addition, Colls (1997) stated that the release of pollutants from emission sources, and the dispersion, transportation and deposition of pollutants in the atmosphere were greatly related to the characteristics of the pollutants, meteorological factors, topography and the distribution of buildings in the urban areas (for city or town monitoring). Meteorology has the most important influence on dispersion, transportation, deposition of pollutants and hence on the concentrations and distributions of pollutants in the atmosphere. The important meteorological factors are wind speed, wind direction, atmospheric turbulence (atmospheric stability), temperature, the vertical gradient of temperature, humidity, etc. Among them, wind speed has the greatest effect because pollutant concentrations can be diluted in proportion to the wind speed past a source by the mechanical turbulence effect which results in increased mixing and dilution. In addition, a higher wind speed can 'bend over' a hotter or colder buoyant source of emitted pollutants more and keep it closer to its release height (Colls, 1997).

Specifically, Colls (1997) also stated that cloudy conditions, atmospheric pressure, together with wind speed, can affect the atmospheric vertical temperature gradient and consequently affect atmospheric stability. Specifically, during a cloudless daytime, solar radiation can warm the ground, then heat the lowest air layer and make lower air layers unstable. During a cloudless night, the ground can be cooled by net-upwards long-wave thermal radiation from the ground, and then a ground-level inversion is created because of the stability of the lower air layers. On the contrary, cloud cover can reduce daytime heating and nighttime cooling of the ground, thereby decreasing atmospheric turbulence during the daytime and relatively increasing it during the nighttime. Moreover, in a persistent high pressure region, a downward air movement at the center of the region often exists and creates an elevated inversion trapping pollutants near the ground (anticyclonic gloom) (Colls, 1997).

Lin (2004), and Onursal and Gautam (1997) provided further explanations. For example, dispersion of VOCs in the atmosphere is strongly influenced by meteorological parameters of temperature, relative humidity, solar radiation, wind direction and speed (Lin, 2004). Air pollutants are transported from one location to another by wind, and the trajectory of advection and the extent of dilution are greatly affected by wind direction and wind speed. Higher temperatures can accelerate the formation of secondary pollutants from primary pollutants in the atmosphere, and can also promote volatile pollutant emissions from vehicles and industrial sources. Solar radiation, the intensity of which is affected by the extent and degree of cloud cover, can enhance the formation of secondary pollutants such as ozone and PM. Therefore, urban areas with high traffic densities and warm and sunny climates tend to have high ozone levels because of more THCs and NO_X being emitted and ozone forming reactions being speeded up (Onursal and Gautam, 1997).

Onursal and Gautam (1997) also explained that mixing height (or ceiling height), representing the dispersion capacity of the atmosphere, was the height above the ground at which relatively vigorous vertical mixing occurred. Mixing height fluctuates diurnally and seasonally and can be affected by thermal inversions, which are of great concern especially when wind speeds are low. Under normal conditions with a normal vertical temperature gradient (air temperature decreases with altitude), hot pollutants rise upwards (by convection) to higher altitudes. But, under isothermal conditions, without a vertical temperature gradient, as usually occurred in winter or night, an inversion layer forming above the ground traps primary pollutants and enhances the formation of secondary pollutants. Besides the above factors, precipitation likewise affects concentrations of ambient air pollutants, particularly PM, by washing out contaminants from the air. Atmospheric humidity (reported as absolute or relative humidity) can intensify the corrosion of limestone buildings, sculptures and metallic structures caused by acidic air pollutants as well as influence the dry and wet deposition of air pollutants (Onursal and Gautam, 1997).

It was stated also by Onursal and Gautam (1997) that topography can also greatly influence the dispersion and transportation of the air pollutants. Urban areas with and surrounded by relatively flat topography can have better wind dispersion for air pollutants. Within the urban areas, buildings and other structures can greatly influence the dispersion of air pollutants, too. The "street canyon" effect often occurs as a pollution condition in which tall buildings prevent wind dispersion of ground-level pollutants. On the other hand, hills and mountains surrounding urban areas usually act as downwind barriers for pollutants' dispersion, which can limit air circulation and trap pollutants. Furthermore, the presence of an ocean coastline can lead to onshore and offshore diurnal wind patterns that help disperse pollutants (Onursal and Gautam, 1997).

Dobbins (1979) stated that dispersion of pollutants in the atmosphere could be described by the Gaussian plume model and the atmospheric dispersion equation (K theory). The Gaussian model has three assumptions: consistent steadiness (in time and space) of the boundary layer, chemical inertness, and constant magnitude and direction of wind profile in the boundary layer at all levels. The deficiency of excluding the vertical variation of wind speed in the Gaussian model limits its application to ground-level sources to some degree. Comparatively, an atmospheric dispersion model (K theory) can take into account and integrate all time-dependent meteorological parameters in detail, emission rates of possible unsteady (in time) source, and chemical reactions producing or depleting pollutants. More importantly, the atmospheric dispersion model (K theory) can predict a pollutant concentration at a specific location inside an air shed. Dispersion model can simulate the concentration fluctuation in time and space. Both of the Gaussian model and K theory have the equation solution or numerical solution of their modeling differential equations for point source, line source and area source. Usually road emission is considered as line source, residence emission from combustion for heating and cooking as area source, and industrial emission as point source (Dobbins, 1979).

Total deposition was described by Colls (1997) as the sum of dry deposition and wet deposition (rain, snow and droplets). Dry deposition of gas pollutants onto a surface is primarily determined by the concentration gradient between the atmosphere and surface. Dry deposition process starts with turbulent diffusion bringing the pollutants close to surface, followed by molecular diffusion moving the pollutants across the laminar boundary layer adjacent to the surface, and finally the air pollutants adhering to, dissolving in or reacting with the surface.

As Colls (1997) described, in wet deposition air pollutants are incorporated into cloud droplets, raindrops or snow flakes, and then deposited back to land or water bodies via precipitation. The wet deposition process involves complex reactions with O_3, H_2O_2, manganese and iron, and takes several days such that the pollutants may be deposited at a distance of thousands of kilometers from their source site. Many mechanisms in the process have not yet been fully understood. Ozone is photochemically formed from its precursors in the ambient air more commonly than being emitted directly. Sulfur and nitrogen pollutants are primarily released as gases which persist in the atmosphere for days and then sink to the ground as gases (dry deposition), acidified rain (wet deposition), or acidified cloud droplets (droplet deposition). Wet deposition involves dry reactions, wet reactions and cloud water deposition as follows (Colls, 1997):

- Dry reactions:

1. O_3 decomposition and OH radical generation:

$O_3+hv=O^*+O_2$ (10)

$O^*+H_2O=2OH$ (11)

2. Sulfate production:

$SO_2+OH+M_r=HSO_3+M_r$ (12)

$HSO_3+O_2=HO_2+SO_3$ (13)

$SO_3+H_2O=H_2SO_4$ (14)

(Where M_r *is a passive reaction site (e.g., a nitrogen molecule))*

3. Nitrate production:

During daytime by pathway of O_3 and OH radical consuming:

$NO+O_3=NO_2+O_2$ (15)

$NO_2+OH+M_r=HNO_3+M_r$ (16)

(Where M_r *is a passive reaction site)*

At night by pathway of O_3 and nitrate radical NO_3 consuming:

$NO_2+O_3=NO_3+O_2$ (17)

$NO_2+NO_3=N_2O_5$ (18)

$N_2O_5+H_2O=2HNO_3$ (19)

Colls pointed out (1997) that the H_2SO_4 and HNO_3 acid molecules might condense onto existing particles and/or self-nucleate to form pure acid droplets, both of which could absorb ammonia rapidly to form hygroscopic aerosol particles of ammonium sulfate or ammonium nitrate. The formed aerosol particles would then act as cloud condensation nuclei (CCN) and be returned to the ground in precipitation.

Cabral (1986) stated that H_2S could be oxidized into sulfur dioxide by oxygen and/or ozone in the atmosphere:

$2H_2S+3O_2=2H_2O+2SO_2$ (20)

$H_2S+O_3=H_2O+SO_2$ (21)

Then the formed SO_2 would participate the sulfate production reactions as stated above ((12), (13), and (14) equations).

- Wet reactions:

The rates of wet oxidation of nitric oxide and nitrogen dioxide are less significant and thus not important because of their low solubility. Nevertheless inside cloud droplets, wet oxidation of SO_2 into sulfuric acid is much faster than that in dry reactions (Colls, 1997):

$2SO_2+2H_2O=SO_3^-+HSO_3^-+3H^+$ (22)

Colls (1997) claimed that at low SO_2 concentration, in regions such as remote areas, the oxidant was basically H_2O_2:

$HSO_3^-+H_2O_2=HSO_4^-+H_2O$ (23)

In more polluted regions with higher SO_2 concentration, the oxidant was principally ozone. CO was also important in atmospheric photochemical reactions even at low concentration.

- Cloud water deposition:

Formation of cloud droplets starts from condensation of water vapor onto cloud condensation nuclei (CNN), which can be formed naturally or be formed from secondary aerosol particles such as ammonium nitrate or ammonium sulfate. Primary and secondary pollutants in the atmosphere, especially those easily dissolved, may congregate into cloud droplets, transfer with cloud layer movement, and then deposit onto the ground in precipitation (Colls, 1997).

2.3 Adverse Effects of Criteria Pollutants on Public Health and Ecosystems

2.3.1 NO_x

Murray and McGranaban (2003) stated that nitrogen dioxide (NO_2) was highly reactive and can affect the cellular and humoral immune system with impaired immune responses. Cases had been reported that NO_2 was one of the important in the pathogeny of bronchitis and pneumonia. NO_2 can increase the risk of respiratory illness for exposed children and it was reported to be related to mortality of children younger than 5 years old. Along with fine particulate matter (PM), NO_2 was also reported to induce considerable deficit of lung growth in children (Murray and McGranaban, 2003).

Between the two nitrogen oxides expressed as NO_x, Colls (1997) stated that NO_2 had much higher toxicity compared to NO. NO_2 has lower solubility than SO_2 and hence can penetrate into the deep lung tissue of an exposed person at a much higher proportion of the total exposure. Consequently, the respiratory system can be influenced severely by NO_2 through increased airway resistance, increased incidence of respiratory illness, and damage of the lung tissue. More severely, chronic exposure to high concentrations of NO_2 can also induce 'silo-filler's lung, while short-term exposure to NO_2 may increase the susceptibility of the respiratory system to other chemical and biological contaminants (Colls, 1997).

2.3.2 SO_2

Colls (1997) stated that SO_2 and particulate matter (PM) had combined effects with a tradeoff relationship in actions on human health. SO_2 is a gas with very high solubility and 95% of SO_2 exposure can be absorbed into the respiratory tract by the inhalation pathway with 1% penetrating the alveoli. The exposure of a lower concentration of SO_2 can induce bronchoconstriction and airway resistance of the respiratory tract. People having higher levels of physical exercises and daily activities and/or with respiratory disease should be more susceptible to this exposure (Colls, 1997).

Colls (1997) also stated that along with particles and water vapor, and with trace metals in the air as catalysts, SO_2 could be absorbed onto the particles and transformed into sulfuric acid. The formed fine particles can act as a media for transporting the sulfuric acid into the deep lung tissue via inhalation pathway. Consequently, the sensitive gas-exchange surfaces of the alveolus can be damaged resulting in the decrease of oxygen-exchange capacity of lung (Colls, 1997).

2.3.3 H_2S

The odor of H_2S can be detectable at levels as low as 130 ppb and is easily perceptible at a concentration of 770 ppb. It can be perceived as quite offensive at levels of 3000-5000 ppb by most people. The long term exposure to H_2S at low levels can induce a series of clinical symptoms, including eye irritation and cough, and central nervous system (CNS) symptoms such as fatigue, restlessness, depression, memory loss, decreased balance capacity, difficulty in sleeping, anxiety, lethargy, headache, dizziness, and deterioration in the senses. As for exposure to H_2S at higher levels, health effects may include eye and respiratory irritation, olfactory nerve fatigue, and pulmonary edema. In situations of extremely high concentration, H_2S can lead to respiratory failure, immediate unconsciousness, and death (Bates, 2002).

2.3.4 VOCs and THCs

It was described by Colls (1997) that VOCs were contained in raw oil, oil products such as gasoline, and chemical products such as resins. VOCs can also be produced from combustion and the production of petroleum products. VOCs involve a group of various compounds such as propane, benzene, ethanol, methane, methanol, ether, carbon tetrachloride and vinyl chloride. VOCs in ambient air are a concern not only because many of them are the precursors of ozone via atmospheric photochemical reactions, but also because some of them are carcinogenic and mutagenic. The health effect concern regarding VOCs is focused on benzene which is contained in gasoline up to 5% and with regard to which the present air quality standard is suggested 5ppb and targeted to 1ppb. It was reported that around 10% of the incidence of leukaemia in the UK might be caused by benzene and 1,3-butadiene exposure (Colls, 1997).

Murray and McGranaban (2003) stated that within the large family of the THCs, some reactive hydrocarbons had direct toxicity to humans, fauna (animals) and flora (vegetation), while some have perceptible odor. Indirectly, but more importantly, some THCs can react with other compounds in the atmosphere to form secondary ozone, which has adverse effects to public health when exceeding a certain ground level. In regards to impacts on public health, some of the THCs species can act on the human central nervous system, causing headaches and dizziness at high levels of ambient THCs concentrations in the air, and causing a nerve disorder called "peripheral neuropathy," having the symptom of numbness in the feet and legs. Other THCs species may have adverse effects on the blood, immune system, lungs, liver, kidney, skin, and eyes. Some THCs compounds have also been revealed to have influences on reproduction capability and fetus development in animal tests (Murray and McGranaban, 2003).

2.3.5 O_3

The main health concern about exposure to ozone focuses on its effects on the respiratory system, including the acute decrements in respiratory function, inflammatory responses and chronic lung impairment, and the sub-chronic plausibility of accelerated ageing of the lung (Colls, 1997).

Murray and McGranaban (2003) stated that acute exposures to ozone from 5 minutes to 6.6 hours had been reported with transient and apparently reversible effects, which involve changes in lung capacity, flow resistance, epithelial permeability and the reactivity to broncho-active challenges. These effects could be observed after a few hours of exposure, then persist for hours or days after the cessation of exposure, and would be exacerbated and prolonged by repetitive daily exposures over several days or weeks (Murray and McGranaban, 2003).

It was also reported by Murray and McGranaban (2003) that decreases in respiratory function and athletic performance, and increases in symptoms such as airway reactivity, neutrophil content in lung lavage and rate of mucociliary particle clearance were induced by the single exposure of healthy non-smoking young adults to ozone at 80 – 200 ppb concentration. The respiratory function decrease had also been observed for children at camps and for adults engaged in outdoor exercise exposed for only 30 minutes to a 100 ppb ozone microenvironment. The health effects of acute exposure to ozone had been documented as increases in emergency treatments and hospital admissions due to respiratory diseases, or increase in respiratory symptoms such as cough, throat dryness, eye and chest discomfort, thoracic pain and headache, and temporary lung function decrements. In addition, ozone exposure can exacerbate the symptoms in asthmatic subjects, and even lead to new diagnosis asthma for children having heavy exercise activities at high ozone concentration microenvironment (Murray and McGranaban, 2003).

Murray and McGranaban (2003) further described that clinically relevant changes representing the accumulation or progression of chronic lung damage such as symptoms, performance, reactivity, permeability and neutrophil counts, may occur with ozone exposure. Furthermore, sub-chronic or chronic human exposure to ozone in ambient air can lead to the accelerated ageing of the human lung as well as the accumulation of chronic lung damage, especially in the situations of having activity to some extent in the outdoors during warmer weather and/or being enhanced by other air contaminants in the ambient air (Murray and McGranaban, 2003).

2.3.6 CO

As Murray and McGranaban (2003) stated, carbon monoxide (CO), which enters the bloodstream via inhalation, forms and increases the concentration of carboxyhaemoglobin in blood, resulting in a decreased capacity of oxygen uptake and transport by the blood, and reduced oxygen delivery to body's organs, tissues, and cells. It had been observed that after successive short time exposures to carbon monoxide at lower levels of carboxyhaemoglobin of 3.2 to 4.2 percent, the detection of slight differences would be impaired and decreased. In particular, people with cardiovascular disease could be more susceptible to the adverse effects of CO exposure. In practice, carboxyhaemoglobin blood concentration is used as an indicator of CO exposure extent. Generally, higher carboxyhaemoglobin levels from 10 to 30 percent can lead to classic symptoms of CO poisoning such as headache and dizziness. Higher than about 30 percent can bring on symptoms such as severe headaches, cardiovascular symptoms and malaise. For levels above roughly 40 percent, there will be considerable risk of coma and death. According to investigated statistical results, there exists a significant positive correlation between the increase of hospitalizations and premature mortality from congestive heart failure and the higher level of CO concentration fluctuation (Murray and McGranaban, 2003).

2.3.7 PM

Onursal and Gautam (1997) stated that PM in ambient air had been associated with the increased mortality, morbidity and reduced lung function. The adverse health effects, including coughing and respiratory diseases such as pneumonia, asthma and bronchitis, had been reported among both adults and children exposed to PM. PM and SO_2 pollution often occur together in the ambient air and may have synergistic effects with other air contaminants. Although there may be differences in many other factors such as smoking habits and type of occupation, studies conducted in different parts of the world indicated relatively consistent correlation between the long-term exposures in residential communities polluted by PM and SO_2 and increased mortality rates. It had been reported by research in some cities that PM exposure should account for 4% increase in death rates from cardiovascular diseases (Onursal and Gautam, 1997).

Onursal and Gautam (1997) also stated that based on 24-hour exposure, PM at 250 $\mu g/m^3$ was associated with increased morbidity in acute respiratory diseases among adults, and PM_{10} at 110 $\mu g/m^3$ with decrease in lung functions among children. As for long-term exposure to PM at an annual mean of 100 $\mu g/m^3$, increased respiratory symptoms and decreased lung function or chronic respiratory diseases would be expected. Noticeably, health may be affected in exposure of PM even at lower concentrations. By nasal breathing pathway, PM in diameter greater than 10 μm can be deposited in the extra-thoracic part of respiratory tract; PM_{10} (2.5μm to 10 μm in diameter) is usually deposited near the fine tracts; whereas $PM_{2.5}$ (less than 2.5 μm in diameter) which is of a great health concern can evade the respiratory defense system and reach the lung tissue, where it can remain imbedded for years, or in the case of soluble particles, be absorbed into the bloodstream. Particle deposition in respiratory tract increases with mouth breathing (Onursal and Gautam, 1997).

2.3.8 Impacts of Air Pollutants on Ecosystems and Environment

Esmeralda (1986) stated that air pollutants such as sulfur dioxide, nitrogen oxides, THC, ozone (formed from the precursors as nitrogen oxides and various hydrocarbons), and PM (which had been released to the atmosphere), would eventually be returned to the earth via wet and/or dry deposition. There can be significant impacts of acidic deposition on ecological systems: on the soil, the water bodies, and the vegetation and forests. These impacts can be experienced at a place far away from the emission source sites. Onursal and Gautam (1997) stated that the impacts on the ecosystem and the environment also involved global climate changes resulting from greenhouse gases, acidification of soil and surface waters from sulfur and nitrogen emissions, adverse effects on flora and fauna in particular some plants including crops and animal species, and damage to buildings and structures.

Onursal and Gautam (1997) stated that sulfur dioxide (SO_2) impacted ecosystems and the environment directly or indirectly by acid deposition. For instance, it has caused the acidification of soils and lakes in Europe and North America, and has eroded marble structures and monuments by producing calcium sulfate (gypsum). Together with ozone and NO_x, SO_2 has damaged forests in Europe. Even at the concentration as low as 800 $\mu g/m^3$, SO_2 can harm crops such as wheat, oat, barley and cotton (Onursal and Gautam, 1997).

Onursal and Gautam (1997) also stated that CO could be oxidized into CO_2 in the atmosphere. As a result, an insulating blanket of CO_2 has been formed around the earth that prevents heat escape from the earth's aerosphere. Fifty percent of this greenhouse effect leading to global warming is contributed by CO_2 and the rest is contributed by the other greenhouse gases (GHG): methane, ground-level ozone, CFCs and nitrous oxide. It is expected that global warming will raise the global temperature by about 3°C by the end of the 21st century, and can cause changes in rainfall patterns, shifts in climatic zones, and a rise in sea levels (Onursal and Gautam, 1997).

Ozone can also damage the plants and vegetation. The degree of its damage is determined by ozone concentration, exposure extent, light intensity (solar radiation) and humidity. The ozone-sensitive plants include tobacco, beans, spinach, and clover that can be injured by exposure to ozone at an hourly concentration of 80 mg/m^3 or higher (tobacco), or 200 mg/m^3 concentration for several hours(beans, spinach, and clover). In addition, ozone is also a contributor to forest damage in the United States (e.g. the pines), Germany, and Europe (Onursal and Gautam, 1997).

PM can induce soiling and degradation of visibility. Depending on its settling characteristics and atmospheric conditions (especially wind), large-size PM quickly deposits onto the ground from the atmosphere. PM of a smaller size, such as PM emitted by motor vehicles as well as PM formed in the atmosphere as sulfate or nitrate aerosols, remains suspended in the air. PM in the atmosphere, even $PM_{2.5}$ can absorb and disperse light, hence reducing visibility, and deteriorating city landscape by darkening the color of the sky. Since $PM_{2.5}$ can be transported for long distances, the visibility reduction is also a larger regional problem (Onursal and Gautam, 1997).

Nitrogen oxides (NO_x) can produce nitrate and nitric acid, acidifying the soil and surface water bodies, and corroding buildings and other human and natural landscapes. In particular, N_2O contributes to global climate warming as a greenhouse gas by absorbing infrared radiation (Onursal and Gautam, 1997).

It was concluded by Cabral (1986) that both the water bodies and soils in most areas of Alberta had high buffering capacity against acidification except for in the northeast corner of the province. The extent of direct and indirect impacts of air pollutants on vegetation is determined by tree species. Coniferous trees, common in Alberta, can be more tolerant of acidic precipitation, but direct impacts of SO_2, NO_x, ozone and PM on coniferous trees may be significant and deserve attention (Cabral, 1986). Furthermore, it should be noted that meeting the Alberta Ambient Air Quality Standard or National Ambient Air Quality Standard does not guarantee that there will be no impact of an air pollutant on the environment and ecosystems (Cabral, 1986; Colls, 1997). Damage to building materials and other materials caused by air pollutants can occur even if there are no significant impacts directly on ecosystems (Cabral, 1986).

2.4 Legislation and Regulations

It was stated by Colls (1997) that generally three categories of philosophies had been used to constitute regulations or legislation by different organizations. Historically, emission standards had been established based on the assumption that targets of pollutant concentration in ambient air would be achieved as long as maximum emission concentrations were set appropriately. Afterwards, legislations in Europe and the USA have been framed in terms of air quality standards (AQS), which requires potential new releasers to prove that AQS will not be exceeded after their emissions. Currently, the most recent philosophy uses the critical load and level approach, in which the complex dispersion processes are modeled, and then the acceptable maximum emissions are calculated with the developed model to ensure that the critical loads and levels at a given receptor site will not be exceeded, and thus maximum deposition fluxes of gaseous and liquid contaminants and their impacts on local ecosystems are related.

Various terms such as standards, guidelines, limit values, and objectives are being used by different organizations that have independently evaluated the evidence on the pollutants and constituted somewhat different legislation and regulation of air pollutants. The World Health Organization (WHO), European Union (EU), United Nations Economic Commission for Europe and the United States Environmental Protection Agency (EPA) are the most influential organizations. Canada and the Canadian provinces usually follow the standards of the EPA. The objectives and guidelines of criteria air pollutants regulated by Alberta Environment (2005a), British Columbia Environment Protection (2005), and Environment Canada (2005) are presented in Table 4. In the United States, the National Ambient Air Quality Standards (NAAQS) along with control measures had been established and designed to achieve the goals of the Clean Air Act (CAA) which was passed in 1970 as an air quality-driven rather than emissions-driven regulations and the Clean Air Act Amendments (CAAA) which were passed in 1990. The NAAQS have two types of regulations: the primary, designed to protect public health, and the secondary, designed to protect everything else such as ecosystems and the environment. The secondary have the same or lower values as the primary. The CAA has the basic idea that the CAA is adaptable and that the NAAQS have to be reevaluated and modified regularly and continuously to reflect new scientific findings and understanding of impacts of air contaminants (Colls, 1997).

Colls (1997) also stated that standard-setting processes had three types: (1) direct observations of the short-term or long-term impacts of environmental pollutants, of actual incidents resulting in human morbidity or mortality, and of quantifiable damage to a receptor, and epidemiology studies of populations or other targets; (2) controlled experiments on laboratory animals and then extrapolation to humans, or the studies on a small number of plant species used to represent the whole domain of potential affected plants; and (3) development of computer models to simulate relationships between relevant interacting variables and then to determine the standards.

There exist other approaches, as stated by Colls (1997), for setting legislation. Standards can be set by an arbitrary safe factor multiplied by the threshold values based on the assumption that an organism is stressed by exposure to a pollutant and that the organism's natural repairing mechanism works well provided that the dose does not exceed a threshold value. Although this method is convenient for scientists and legislators, it should be determined in practice as to whether the responses of an exposed organism are economically and socially significant by comparing the risk from the pollutant itself with the other risks to which the population is being exposed. Because receptors such as people, animals, plants, and materials respond to pollutants in a very wide range between being sensitive and resistant, standards derived from this dose-response model are set to protect the most sensitive receptor.

Therefore, as Colls (1997) reported, it is often impossible to predict whether the short-term experimental responses will result in long-term actual effects. In addition, the responses depend not only on the concentration scale but also on the time period of exposure, so that statistical indicators such as the 98th percentile of daily means are used. Furthermore, in some cases, e.g. PM and SO_2 co-existing condition, there may be synergism operating among pollutants so that the standards of different contaminants should be considered together. There is no safe limit for carcinogenic or mutagenic material, since it is thought that just one molecule can initiate a cancer, and therefore standards should be expressed in terms of a risk of cancer formation per population per unit time at a given concentration.

Table.4 Objective and guideline of criteria pollutants (Alberta Environment, 2005a; Environment Canada, 2005; British Columbia Environment Protection, 2005)

Pollutant	Alberta Objectives		Canada Objective Maximum(µg/m³)			B.C. Objective/Guideline(µg/m³)		
	µg/m³	ppbv	desirable	acceptable	tolerable	level A	level B	level C
NO_2								
1-hour average	400	212		400	1000			
24-hour average	200	106		200	300			
Annual arithmetic mean	60	32	60	100				
SO_2								
1-hour average	450	172	450	900		450	900	900-1300
3-hour average						375	665	
24-hour average	150	57	150	300	800	160	260	360
Annual arithmetic mean	30	11	30	60		25	50	80
H_2S								
1-hour average	14	10	1	15		7.5-14	28-45	42-45
24-hour average	4	3		5		4	6-7.5	7.5-8
TRS								
1-hour average						7	28	
24-hour average						3	6	

Note: *Based on the annual 98th percentile value, averaged over 3 consecutive years (Established in 2000)

**Based on the 4th highest annual value, averaged over 3 consecutive years (Established in 2000)

Table.4 Objective and guideline of criteria pollutants (Alberta Environment, 2005a; Environment Canada, 2005; British Columbia Environment Protection, 2005) (Continued)

Pollutant	Alberta Objectives		Canada Objective Maximum(µg/m^3)			B.C. Objective/Guideline(µg/m^3)		
	µg/m^3	ppbv	desirable	acceptable	tolerable	level A	level B	level C
THCs								
O_3(ground level)								
1-hour average	160	82	100	160	300			
8-hour average				65**				
24-hour average			30	50				
Annual arithmetic mean				30				
$PM_{2.5}$								
24-hour average				30*				
PM_{10}								
24-hour average							50	
CO								
1-hour average	15000	13000				14300	28000	35000
8-hour average	6000	5000				5500	11000	14300

Note: *Based on the annual 98th percentile value, averaged over 3 consecutive years (Established in 2000)

**Based on the 4th highest annual value, averaged over 3 consecutive years (Established in 2000)

2.5 Monitoring Methods

2.5.1 Sampling

Colls stated that sampling methods for criteria air contaminants monitoring could be classified into three categories:

(1) Pumped systems sample air directly and continuously from ambient air, transfer it to the sample to the analyzer, and analyze it in real time.

(2) Pre-concentration method samples pollutants or their derivatives by absorption, adsorption or condensation capturing and then analyzes them later by standard methods.

(3) The grab sampling method which samples the air itself and is taken back to a laboratory for analysis.

2.5.2 Measurement

Measurement methods are often combined with sampling methods. The commonly used measurement methods for criteria air contaminants monitoring include the following (Colls, 1997):

(1) Wet chemical methods with real-time pumped systems and instruments directly convert physical or chemical effects into gas concentrations.

(2) Real-time remote systems detect optical properties of a gas by passing light through the air sample and then instantly translating the signals into recorded concentrations.

(3) Passive samplers sample using the pre-concentration technique and analyze it to obtain average concentrations over sampling period.

(4) Other methods include gas chromatography, liquid chromatography, and optical spectroscopy (such as atomic absorption spectrometry (AAS) and atomic emission spectroscopy (AES), etc.) (Colls, 1997).

2.5.3 Factors Determining the Measurement Methods Selection

For accurate measurement of a specific trace gas, it is critical to choose an appropriate measurement method. Specificity, sensitivity, reliability, stability, response time, precision and accuracy, and cost should be considered and balanced besides practical experience (Colls, 1997).

2.5.4 Quality Assurance and Quality Control (QA/QC)

A quality assurance and quality control (QA/QC) procedure for monitored and recorded raw data should include and combine blanks, duplicates and calibration at the least, and should involve further duplicates conducted by independent laboratories if necessary. The average of concentrations measured in the blanks should act as a baseline value and be subtracted from all actual measured values to eliminate systematic errors. The establishment of the baseline data should occupy at least 10 percent of the total measured samples. Calibration of instruments every several days is essential and important, because there may be drift of electronic components, contamination of the optical system, and/or fluctuation of operating temperature in monitoring instruments (Colls, 1997).

2.5.5 Measurement Principles for Specific Pollutants

Conor-Pacific Environmental Technologies Inc. (1997) summarized the primary measurement principles for determining concentrations of ambient criteria air pollutants. The main measurement methods for SO_2 include ultraviolet fluorescence, gas chromatographs with flame photometric detectors, colourimetry, infrared absorption and coulometry. The main measurement methods for nitrogen oxides (NO_2 and NO) include gas-phase chemiluminescence, liquid-phase chemiluminescence, colourimetry, and Fourier transform infrared absorption. For CO concentration measurement, the methods include non-dispersive infrared, gas filter correlation and Fourier transform infrared absorption. The measurement methods for THC include FID, photoionization detection (PID) and GC/FID analysis. For O_3 monitoring, the measurement methods include chemiluminescence, ultraviolet photometry, coulometry, and Fourier transform infrared absorption. The measurement methods for determining ambient PM concentrations involve beta ray absorption and optical absorption.

For the data tested in this research, CASA (2006a) described the specific measurement methods adapted at the ambient air monitoring stations in Fort McKay and Edmonton. Ozone is monitored by an ultraviolet (UV) light process, in which sampled air is exposed to UV light such that the amount of UV light absorbed by ozone is proportional to the amount of ozone in the sample (CASA, 2006b). Non-dispersive infrared photometry process or gas filter correlation is used to monitor CO. The absorption of infrared light by CO is quantified by the non-dispersive infrared photometry process. Gas filter correlation uses the same principle as non-dispersive infrared photometry but is more specific to CO by eliminating water vapor, CO_2 and other interferences (CASA, 2006c). A hydrogen flame ionization detector is used to monitor THC. Carbon hydrogen bonds are broken by high temperature to create ions conducting electric current. This current is measured by an electrometer to give a signal proportional to the number of ions (CASA, 2006d).

The principle of chemiluminescence is applied to measure NO_2 at the ambient air monitoring stations in Fort McKay and Edmonton. The air sample is split into two pathways: one to measure NO, and another to measure NO_x. In first pathway, the air sample goes directly to the analysis chamber, where it is mixed with ozone, and produces light in an amount that is proportional to the concentration of the NO. In the second pathway, all of the NO_2 in the sample is transformed to NO by a catalytic converter. Then, the sample enters the analysis chamber which measures the concentration of NO. The amount of light produced is proportional to the sum of the concentrations of NO_2 and NO and is expressed as NO_2 equivalents. The difference between the two pathways is the NO_2 concentration (CASA, 2006e).

The measurement methods of PM_{10} and $PM_{2.5}$ are classified into two categories: continuous monitoring and intermittent monitoring. Continuous monitoring uses Tapered Element Oscillating Microbalance (TEOM). Air sample is drawn through an inlet stream by TEOM, and the particles are separated aerodynamically according to specified diameter (2.5 or 10 μm). Then air sample passes through a filter and particles deposits onto the filter. This filter is attached to a tapered element vibrating at its natural frequency in the mass transducer. The oscillating frequency changes in proportion to the mass of particles deposited. Intermittent monitoring uses a dichotomous sampler that is a derivative of high volume sampler. Air sample of known volume is drawn through the sampler and two individual pre-weighed filters, and is separated aerodynamically and collected according to particle sizes: fine (<2.5 μm) and coarse (2.5 to 10 μm) for a period. The concentrations of two fractions of particles can be calculated for this period (CASA, 2006f).

Pulsed fluorescence is used for monitoring SO_2 and H_2S. An air sample is drawn through a sample chamber where it is irradiated with pulses of UV light. Fluorescence is released as SO_2 in the sample (which was excited to a higher energy level) returns to its original state. SO_2 concentration in a sample is proportional to amount of fluorescence measured (CASA, 2006g). Another sulfur compound H_2S is monitored by a similar method. Initially, all of the SO_2 is scrubbed from the air sample.

Then, all H_2S in sample is converted to SO_2 to be measured by the pulsed fluorescence method (CASA, 2006h).

2.6 Target Air Pollutants for this Research

The national framework for the petroleum refining industry focuses on the emission inventories of criteria air contaminants (CACs) including sulfur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOCs), particulate matter (PM_{10} and $PM_{2.5}$), carbon monoxide (CO), and benzene (Levelton Engineering Ltd., 2005). In response to the presence of the oil sand industry and available data from monitoring stations, target air pollutants for this research involves sulfur dioxide (SO_2), hydrogen sulphide (H_2S), total hydrocarbons (THCs), ozone (O_3), nitrogen dioxide (NO_2), carbon monoxide (CO) and $PM_{2.5}$.

2.7 Methods for Trend Analysis in Current Research

2.7.1 General Review

Detecting changes or trends in pollution levels over a certain period is one of the important aspects in environmental monitoring. The main purpose of trend analysis is to evaluate whether pollution levels have declined following pollution control measures and mitigation programs, or to check possible increased pollution resulting from development in agriculture, industry and other human activities (Gilbert, 1987). A significant trend of a pollutant indicates that a pollution problem exists and should be investigated completely before the establishment of a routine environmental monitoring program and mitigation measures (Gibbons, 2001).

Methods for detecting and estimating the trends of pollutants generally include graphical methods, regression methods (combined with t-test or ANOVA) and statistical test methods (Gilbert, 1987). The graphical method is a very useful tool for formal tests of trends. Usually in a graphical method, a figure plotting data versus time is constructed and then, a smoothing curve simulating the cycle and/or long-term trend is drawn by a suitable computational method or computer program. Another effective graphical method uses cumulative sum (CUSUM) charts, in which cumulative sums of deviations from a reference value or cumulative sums of residuals from a realistic stochastic model are calculated. Changes in the mean values can then be detected (Gilbert, 1987).

Statistical tests for trend analysis of environmental data in literature can be classified into two categories: parametric tests and nonparametric tests. Specifically, the parametric tests include an independent Student's t-test between two means, ANOVA, linear regression analysis, polynomial regression with the least squares method, and an autocorrelation test. The nonparametric tests include the Mann-Kendall test, the Seasonal Mann-Kendall test, Spearman's Rho test, the Kruskai-Wallis test, and the Spearman Partial Rank Correlation test (McLeod and Hipel, 1991).

In statistics, testing the null hypothesis and the alternative hypothesis at a 5% significance level (α=0.05) is customary (Montgomery, 2004). Byrne (1996) stated that there were two types of possible errors for statistical test results, that is, Type I error and Type II error. "Type I error is rejecting the null hypothesis when the null hypothesis is true, and Type II error is accepting the null hypothesis (more accurately, failing to reject the null hypothesis) when the null hypothesis is false." The maximum probability of making a Type I error equals to the significance level α. The significance level α is often referred to as a P-value, which is indeed the smallest significance level (α value) leading to the rejection of the null hypothesis, H_0, i.e., the smallest level of α at which the test results of the data are significant, since customarily the test statistic (of the raw data) is considered to be significant when the null hypothesis H_0 is rejected.

The probability of making a Type II error is expressed as β. Montgomery (2004) stated that the power of a statistical test (computed as $1-\beta$) was "the probability of rejecting the null hypothesis H_0 when the alternative hypothesis was true". Since power represents the probability of correctly rejecting a false null hypothesis, power is a very concise measure of the sensitivity, which refers to the ability of a statistical test to detect differences. If the power value is too small, either the significance level α value or the sample size n should be increased. Therefore, at 95% significance level (α=0.05), rejecting the null hypothesis indicates there is less than a 5% chance that the result violates the true situation; and just the opposite, not rejecting the null hypothesis means there is more than 5% chance that the result violates the true situation.

It should be emphasized that the conclusion of a statistical test must be understood and utilized correctly. The following key points according to statistical theory should be noted (Berthouex, 2002; Montgomery, 2004):

- Statistical test conclusions can provide the evidence which is not proof.
- Significant does not mean important, i.e. a significant change trend may be tested, but the size of the change (changing rate) may be too small to be important.
- If the null hypothesis for environmental data was rejected, the causation of the trend or change should be investigated.
- In typical statistical tests, the type I error probability α is controlled by the selection of a critical value. Customarily, rejecting the null hypothesis, H_0, is considered a strong conclusion, and not rejecting H_0 as a weak conclusion. Therefore, the terminology "fail to reject H_0" is preferred to "accept H_0".

- Failing to reject H_0 only implies that sufficient evidence for rejecting H_0 has not been found, and thus does not mean there is a higher probability that H_0 is true. More data may be required to reach a strong conclusion.

2.7.2 Preliminary Analysis of Air Quality Data

At an automatic monitoring station, air quality data are detected and recorded continuously or at an interval of seconds. There are generally three types of problems that need to be solved (Colls, 1997). Firstly, the monitored and recorded raw data are too abundant and detailed to provide direct conclusions and information about the air quality. Even after calculations of time-weighted averages, e.g., the original 1-minute value or 1-hour average value, the derived data can still show little information about air quality. If there is no missing data, there will be 8760 1-hour average concentrations for one pollutant each year and 70,080 1-hour average concentrations for one pollutant in 8 years. Secondly, there may be missing data creating incomplete datasets because of instrument or power failures, or routine calibration. Before further processing, the missing data should either be estimated or ignored (deleted from datasets) depending on the required accuracy, as well as on the permissible analysis method, and the certainty and representativeness of the data. Thirdly, outliers (that are not generally representative and that may bias the conclusion) may exist in the fluctuation of data. On the other hand, the impacts on the human health and ecosystems may occur in the short episodes of high concentration of pollutants (Colls, 1997). Therefore, preliminary analysis of raw data is a necessary and critical step in the complete data analysis procedure.

The arithmetic mean values (e.g. minutes of hour, hours of day, days of week, days of month, and months of year), and moving averages (e.g. rolling averages of 3 years) can help reduce the effects of occasional unrepresentative variations, and some special algorithms can further smooth the fluctuations of the time-series curves (Colls, 1997). The effects of averaging calculations can be estimated from the equation $C_{max,t}=C_{max,1hour} *t^q$, where $C_{max,1\ hour}$ is the maximum 1-hour concentration, $C_{max,t}$ is the maximum concentration over t time period, and q is an exponent for a specific gas with a typical value of -0.3 (Colls, 1997).

Arithmetic mean values from environmental data can be biased by high values because most environmental data usually have distributions that are skewed to the right as a result of the fact that, in environmental studies, most data values are low and only a few are high. For environmental data, the median value that divides the nonnormal data distribution into two equal halves is a more representative value than is the arithmetic mean (Alberta Environment, 2005b).

The data extracted from the frequency distribution and the cumulative frequency distribution of the raw data can be more representative than general average values (Colls, 1997). In the frequency calculations, hourly or daily average data are first sorted in ascending or descending order and the whole range of the data is divided into sub-ranges. The number of data falling in each sub-range is calculated and transformed into a percentile of the total number of data, i.e., the frequency expressed as percentiles of the data or percentiles of the time. It should be noted that air pollutant concentrations commonly fit a log-normal frequency distribution, that is, the logarithm of frequency values are normally distributed with different concentrations (Colls, 1997).

The cumulative frequency distribution can be derived by summing all the frequency values within the concentration sub-ranges that are less than a certain concentration, and then drawing a plot of the cumulative frequency versus the concentration sub-range. The plot derived is sigmoidal on linear coordinates but can be converted to a straight line with log-probability coordinates if the frequency distribution has a log-normal feature. This straight line can give the standard deviation value by its gradient, the total time period that any concentration is exceeded, and the concentrations corresponding to various cumulative frequencies that are exceeded. The parameters usually used for analysis are the monitored data corresponding to the frequency values between 50% (median) and 99%. For example, the European Union Directives on air quality use 98th percentile value of daily means, which is equivalent to the concentration that should not be exceeded more than 7 days in one year (Colls, 1997).

2.7.3 Autocorrelation, Seasonality and Nonnormality

The term autocorrelation refers to the existing tendency of similar characteristics or mutual bias for data of neighboring observations in time or space. Many environmental data are observed as temporal and /or spatial sequences. Serial correlation is defined as the autocorrelation in time series data (Berthouex and Brown, 2002).

The opposite aspect of autocorrelation is independence. Most statistical methods, such as confidence interval estimation and ordinary least squares regression, depend on the assumption of constant variance, and being normally distributed with errors being independent. Data independence is so critical that departure from independence can cause more serious errors in statistical conclusions than not having normality. Autocorrelation may or may not seriously affect parameter estimation; but, it can bias variance estimates and hence bias any statistics calculated from variances or statistical conclusions about hypothesis tests and probabilities like confidence intervals. Usual confidence intervals and statistical conclusions from t-tests and F-tests for data with positive autocorrelation are not strictly reliable because of distorted variance estimates (Berthouex and

Brown, 2002). Serial correlation of time series data can lead to the drifting of regression results and a conclusion of an unreal upward trend or downward trend over a short period of time. Opposite to that, autocorrelation can be reduced with randomization, data from measurements, or experiments without factors design, and randomization should be checked for autocorrelation before testing. The Durbin-Watson test can be used for checking autocorrelation (Berthouex and Brown, 2002).

It was reported by Ott (1995) that environmental quality data such as air quality data were time series data that had a sequential correlating relationship (autocorrelation) and were usually not normally distributed (nonnormality). Because of the autocorrelation of data, the distribution of the ambient air quality data often appears as right-skewed and lognormal curves even after a great number of average calculations for instantaneous measurements, and the resulting averages computed from these correlated time series will not obey the Central Limit Theorem and hence will not converge to a normal distribution as rapidly as the Central Limit Theorem predicts. On the contrary, in this situation, the Theory of Successive Random Dilutions, a special application of Kapteyn's Law, will apply, since a release process shares two common properties: (1) pollutants are emitted into a carrier medium at a relatively high concentration and are diluted by dispersion and/or convection; (2) the dilutions occur with considerable randomness (Ott, 1995).

It was argued that for autocorrelation environmental data whether the Mann-Kendall test should be modified to eliminate the influence of sequential correlation (autocorrelation) on statistical testing results (Yue and Wang, 2004a; Yue and Wang, 2004b; Yue and Wang, 2004c; Zhang and Zwiers, 2004). Autocorrelation can increase the probability of wrongly rejecting the null hypothesis when no trend actually exists (i.e.

probability of Type I error or its maximum value, significant level α) (Hamed and Rao, 1998). But for the air quality data extracted from annual cumulative frequency distribution curves of raw data, the autocorrelation can be ignored and the data can be considered as independent data. Furthermore, the seasonality of raw data can also be eliminated because of the power of using the cumulative frequency distribution within the time interval of a year (Serrano et al. 1999).

The normality of data can be estimated by checking whether the mean and median are equal and can be tested more accurately by using probability versus z-score plot. The mean and median are not equal for the skewed distribution, whereas the mean and median are equal in a normal distribution (Byrne, 1996). Bednorz and Kossowski (2004) investigated trend of snow depth changes by linear regression and the Mann-Kendall test. In their research, basic features of the data, such as mean, median, extreme value, and standard deviation were firstly calculated, and then trends were estimated by linear regression for normal distribution data and by the Mann-Kendall test for skewed distribution data. The distribution characteristics were determined according to whether mean and median were equal. They concluded that this method was effective because of the combination of advantages of the t-test and the Mann-Kendall test.

2.7.4 Comparison of Methods

The parametric tests, e.g. the t-test and the linear regression, require assumptions regarding the normality (normal distribution) of the data and the homogeneity of the variance of the data ("at the very least the Central Limit Theorem should apply, which means that 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, having the ability to quantify the magnitude of a trend, e.g., change rate expressed in the gradient of a trend. Most nonparametric tests, except the Sen's method cannot quantify the magnitude of a trend but can only detect the presence or the absence of a trend or change without the requirement of a normal distribution (McLeod and Hipel, 1991).

As Wheater and Cook (2000) indicated, since environmental data such as air quality data are likely to fail the normality criteria (the symmetrical distribution) and constant variance, transformation of the raw data set should be necessary before a parametric test is used. A square root transformation or logarithmic transformation is usually effective. In addition, it is also important to check normality of the transformed data before using a parametric test. A nonparametric test should be used for analyzing the trend of tested data if none of the transformations produce an approximately normal distribution.

McLeod and Hipel (1991) compared most of the parametric tests and nonparametric tests for time series environmental data in water quality. They divided the whole trend analysis procedure into two main stages of graphical trend studies and trend tests. Their research concluded that (1) the Kruskal-Wallis test can be used for testing seasonality (check and determine whether there exist seasonal characteristics in the raw data), (2) the Spearman Partial Rank Correlation test is more powerful for testing trends after removing seasonality for raw data, and (3) the Mann-Kendall test is much more powerful than the seasonal Mann-Kendall test if there is no seasonality in the raw data.

Domonkos and Tar (2003) analyzed the trend of observed temperature and precipitation data during 100 years. They analyzed long-term fluctuations of temperature and precipitation data by fitting polynomials with order values from 1 to 4, and selected the order of the polynomial according to the maximum F-test statistic value achieved with the polynomial regression method. In their research, a linear trend analysis was conducted by calculating mean systematic changes, and the t-test and the Mann-Kendall test were used to test statistical significance of the calculated linear trend values. It was concluded that the same and identical results should be mostly obtained by the t-test and the Mann-Kendall test. The t-test may be more powerful and its conclusion can usually be accepted in the case of huge tested data for significance test. In a situation where the raw data possesses extremely anomalous distribution (skewed distribution or nonnormal distribution), the results from the Mann-Kendall test should be accepted rather than the t-test.

Razak and Christensen (2001) analyzed and compared the changing trend of water quality parameter by the t-test and Mann-Kendall test in order to assess the impacts of deep tunnels for temporary storage of storm water and sewage on water quality. Through calculations checking the trend of annual average values of BOD, fecal coliforms, and zinc, it was concluded that the t-test and Mann-Kendall test should have consistent results for their research.

Wasmund and Uhlig (2003) applied the linear regression method and the Mann-Kendall test to investigate the long-term trends of phytoplankton concentration monitored by chlorophyll α concentration in the Baltic Ocean. They firstly conducted a logarithmic transformation for the arithmetic means of all samples during a season to eliminate the effects of anomalies, non-constant variance and seasonality. The Mann-Kendall test, the Theil slopes (the precursor of Sen's method) of the linear regression and the test based on a non-linear LOESS smoother were applied to the transformed data. It was found that the Mann-Kendall test could be used for non-normal monotonic trends to achieve a reliable result, and the test based on the LOESS smoother could lose power in case of non-normality but had a similar significance level (probability to reject the null hypothesis erroneously, i.e., Type I error probability α). Furthermore, the weighted LOESS smoother method might be suitable for situations in which the sampling frequency of tested data was extremely variable from year to year.

Hess et al. (2001) reviewed, evaluated, and compared existing statistical methods for trend analysis in environmental data. They simulated historical data of 11 years using S-Plus software for 6 commonly used methods for trend analysis. These applied methods involve the Spearman partial rank correlation (SPRC) test, the Seasonal Kendall (SK) test (with and without a serial dependence adjustment), regression on yearly averages (ordinary least squares (OLS) regression), generalized least squares (GLS) regression with autoregressive (AR) errors, Kolmogov-Zurbenko method, and t-test for difference between means. False rejection rate (Type I error rate) and power of the tests were used as the indicators of the test's performance. Besides emphasizing that the significance level α as the maximum probability value of a Type I error, they gave four useful and important definitions.

The power of a test was defined as "the probability that a test would reject the null hypothesis (no trend) when actually the alternative hypothesis (existing trend) was true". False rejection rate was defined as "the probability that a test would reject the null hypothesis (no trend) when actually the null hypothesis (no trend) was true". The null hypothesis H_0 was defined as "there being no significant trend present in the data, and the alternative hypothesis H_1 was that there is a linear increasing or decreasing trend present in the data" (Montgomery, 2004).

With a series of calculations and simulations, Hess et al. (2001) concluded that the t-test adjusted for seasonality (TAS) and the (ordinary) SK test could maintain their stated significant levels (α) and meanwhile have high power over indices of different trend functions compared to the other methods. In addition, the TAS method had a higher power than the SK test to determine whether or not there existed a step change trend. They further showed that although the assumption of independence and normality might not be met by environmental data, this assumption should more likely be satisfied if annual average was used as the response variable (index).

Feidas et al. (2004) analyzed the trends of annual and seasonal surface air temperature time-series data with the least squares method, Grenander's method for linear regression of autocorrelation data, and the Mann-Kendall test. From their research for the data of 46 years in 20 stations, they concluded that air temperature in Greece had no statistical significance trends (the overall trend of annual values was zero) without being consistent with the intense warming trends in the Northern Hemisphere. However, for satellite data of the recent 21 years, trends for mean annual data of air temperature in Greece were significant and consistent with the general situation in the Northern Hemisphere. Correlation relationships between temperature variability and atmospheric circulation (expressed in circulation indices) were also analyzed with the correlation analysis method. It should be noted that Grenander's method of linear regression does not demand the assumption of normality and independence for the raw data as does the least squares method, although there exists the defect that the estimated auto-covariances may be quite biased for the case of a large k value (the number of auto-covariances of the residuals) (Feidas et al., 2004).

2.7.5 Regression

Regression methods for trend testing focus on the linear regression technique. Montgomery et al. (2004) suggested that the concept of the linear regression model should refer to the linearity in parameters (regression coefficients of the equation) regardless of the shape of the surface generated by the model. Therefore, the simple linear regression model $Y=\beta_0+\beta_1X+\varepsilon$, and the polynomial regression model such as second-order model $Y=\beta_0+\beta_1X+\beta_2X^2+\varepsilon$, and the cubic model $Y=\beta_0+\beta_1X+\beta_2X^2+\beta_3X^3+\varepsilon$ should be classified into the category of linear regression model, and can be fitted with estimated coefficients by using the least squares method.

It was clarified by Gilbert (1987) that linear regression might be suitable for the situation where a set of time series data suggested a simple linear increasing or decreasing trend on a plot of data against time. The t-test or ANOVA is typically used to test whether the true slope of data is different from zero. However, in situations where seasonal cycles (seasonality) are present, the data are not normally distributed (non-normality), and/or the data are serially correlated (autocorrelation). Consequently, the t-test can give misleading results, that is, the t-test indicates a significant slope but indeed the truth of slope is actually zero. If only the seasonality was present but with normally distributed data and without serial correlation, the seasonal regression (data are deseasonalized and then applying the linear regression with t-test) will result more accurate and reliable conclusion. For the skewed, cyclic and/or serially correlated data, a seasonal Kendall test will perform better. For a long time sequence data of at least 50 and preferably 100 or more data collected at equal or approximately equal time intervals either without missing data or without data reported as trace or less-than values, the autoregressive integrated moving-average (ARIMA) time series models (Box and Jenkins,

1976) may give a more reliable result for detecting the trends or changes in the average level (Gilbert, 1987).

The linear regression methods involve simple linear regression, multiple linear regression, and high order linear regression (2nd order and 3rd order polynomial regression). Regression coefficients for fitting a regression model can be estimated by the least squares method, and can be computed by many software packages. The statistical tests for significant trends in simple linear regression and multiple linear regression can be calculated by the t-test or the analysis of variance (ANOVA) (Montgomery, 2004).

The calculation procedures of several regression methods are provided in Appendix 3-A3.1.

2.7.6 Mann-Kendall Test

Although the World Meteorological Organization (WMO) suggested the Mann-Kendall method for assessing the trend of environmental time-series data (Paulo and Silva, 2004), there exist few reports on the application of Mann-Kendall test or seasonal Mann-Kendall test to the research in air quality. The existing applications to environmental time-series data focus mainly on water quality, wastewater quality, hydrology, and meteorology.

Zhou et al. (2004) applied the Mann-Kendall test, the Seasonal Mann-Kendall test, and Sen's test to research on the sediment flux of rivers. The monthly and extreme daily sediment flux data for 32 years from two hydrological stations were studied. Trends of annual sediment yield, annual maximum monthly sediment flux, and annual maximum daily sediment flux were analyzed with the Mann-Kendall test. Trends of monthly sediment flux were analyzed with the Seasonal Mann-Kendall test because of the seasonality of monthly data. The corresponding slopes of the significant trends were calculated using Sen's test. In addition, 5-year moving average sediment fluxes of the two stations were also compared to check spatial variability. In their research, the Mann-Kendall test and Sen's test were found to be effective for determining the significance and slopes of changing trends in environmental data.

Although detection efficiency may decrease compared to parametric statistical methods, the Mann-Kendall test is a particularly useful nonparametric statistical test for trend detection. It is especially suited for trend analysis of environmental data because any specific distribution of these data is not required and missing values are also permitted in this test (Gilbert, 1987). If it is acceptable in the context of the population being sampled, the Mann-Kendall test can assign the data reported as trace level or data less than the detection limit a common value smaller than the smallest measured value in the data set, and hence use them for statistical testing. All of these above advantages are derived from the fact that the Mann-Kendall test investigates only relative magnitudes of data rather than their actual measured values (Gilbert, 1987). Hollander and Wolfe (1973) demonstrated that for time series data the Mann-Kendall test could be deemed as a nonparametric test of the linear regression with a zero slope (Gilbert, 1987).

The calculation procedure of the Mann-Kendall test is provided in Appendix 3-A3.2.

2.7.7 Sen's Test

Sen (1968), as cited by Gilbert (1987), developed the Sen's test for estimating the true slope of historical data at a sampling and monitoring station by a nonparametric calculation. Sen's method is an extension of the

Theil test proposed by Theil (1950), and Sen's method itself was illustrated by Hollander and Wolfe (1973).

Although linear regression with the least squares method can compute a slope (change per unit time) apparently accurately, the slope computed with the least squares method may indeed deviate greatly from the true slope of data change trend, especially, if there were gross data errors or outliers in the tested data. On the other hand, Sen's test is not considerably biased by gross data errors or outliers, and is suitable for data sets with partial data missing. The Sen's test has an intimately mutual relationship and is closely interconnected with the Mann-Kendall test (Gilbert, 1987):

The calculation procedure of the Sen's test is provided in Appendix 3-A3.3.

3.0 RESEARCH OBJECTIVES

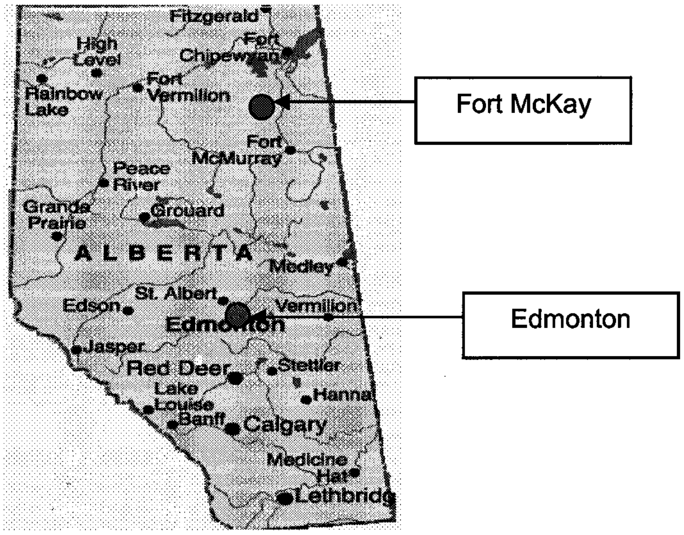
The objective of this study was to investigate the use of non-parametric methods for analyzing trends in ambient air quality in Fort McKay and Edmonton city.

In this study, non-parameter statistical analyses were used to identify mid-concentration to upper-concentration values derived from annual cumulative frequency distributions for each pollutant. Concentration values and annual hours exceeding a certain concentration occurring between the 50th and 98th percentiles of a cumulative frequency distribution were analyzed for trends.

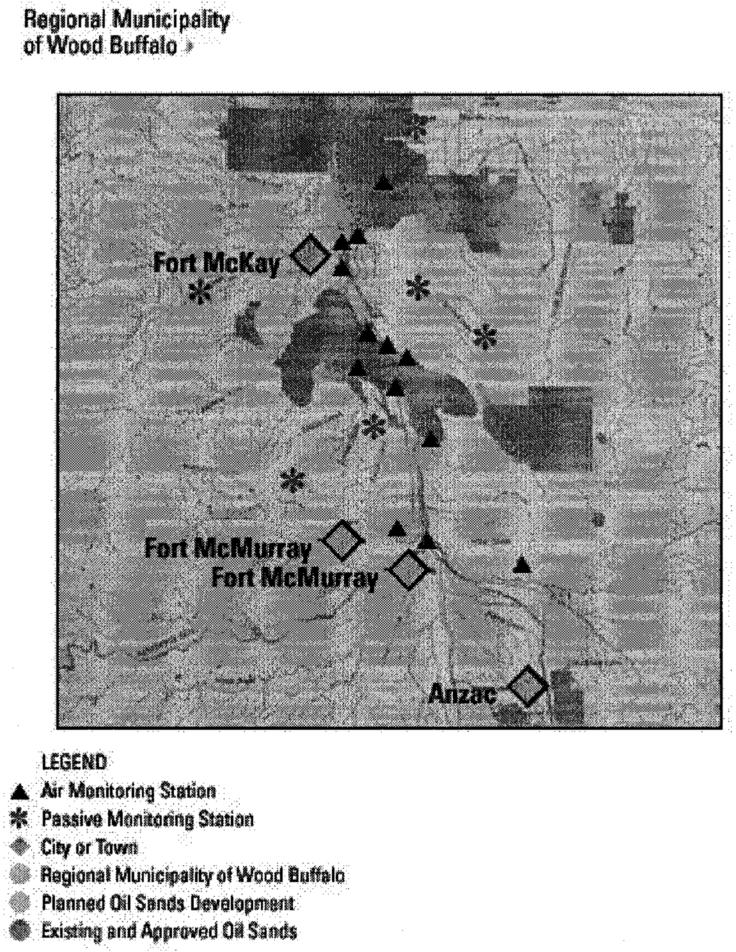
4.0 DESCRIPTION OF STUDY AREA

Fort McKay is a small community with less than 400 people and it is located in the northeast Alberta (Map 1). It is situated among three large oil sand extraction and refining facilities with several more planned in the next five to ten years (Alberta Energy, 2006). Prior to 2002, two of these facilities produced in excess of 500,000 barrels per day of synthetic oil. The third facility was commissioned in 2003. These industrial sources contribute to the emissions of most of the criteria air pollutants, especially NO_2, O_3, PM, sulfur compounds and total hydrocarbons (THCs). The pollutants are released during routine production and equipment startups and shutdowns, as well as during abnormal operating conditions. The proximity of these facilities has raised concerns among residents regarding community air quality. The Fort McKay air monitoring station (Map 2) is operated by Wood Buffalo Environmental Association and located at the northwest corner of the community (WBEA, 2005).

Map 1: Map of Alberta showing the location of Fort McKay and Edmonton.



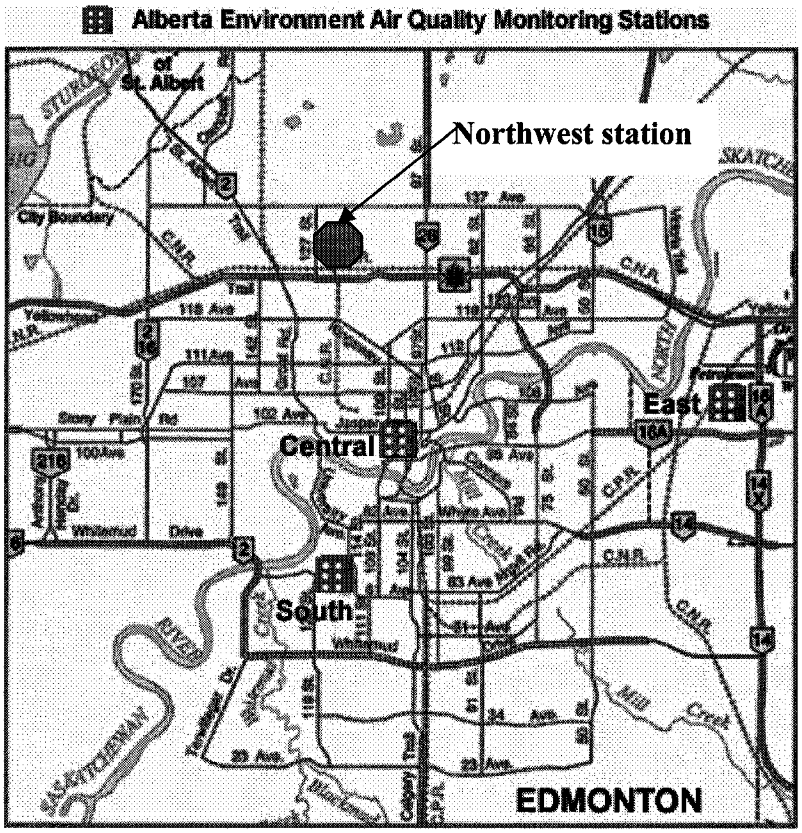
Map 2: Location of Fort McKay Air Monitoring Station in Wood Buffalo Air Shed.



(WBEA, 2006)

Metropolitan Edmonton has a population of one million people and it is located in central Alberta (Map 1). Major industries include petroleum refineries and chemical manufacturing facilities. The automobile exhaust in the urban area is the main and most severe source of air pollutant emission, which contributes mainly nitrogen oxides, hydrocarbons, CO, SO_2, PM and ozone (formed from its precursors NO_x and THC). Alberta Environment maintains a network of air monitoring stations in the city (CASA, 2006i). Data from the Edmonton Northwest station (a former air monitoring station) and East station (for SO_2) were used for this study (Map 3).

Map 3: Location of Northwest Station and East Station in Edmonton.



(Alberta Environment, 2006)

5.0 METHODOLOGY[1]

5.1 Tools and method

5.1.1 Tools

Calculations (data processing and trend analysis) were undertaken using Microsoft Excel® with Visual Basic Application (VBA). A procedure of data filtering, sorting, calculation of cumulative frequency distribution, and statistical analyses using the Mann-Kendall test and Sen's test were carried out using programs developed with Excel macros and VBA. These programs were developed to save computation time. All hourly average concentration values were examined to remove missing and erroneous data.

5.1.2 Benefits of Trend Analysis with Non-parametric Statistics

The number of indices to be tested for a trend represented a small number (i.e. <30). For example, 50th percentile concentration values for an eight-year period only resulted in eight values being tested for a trend (which is much less than 30). Because of this, t-test or ANOVA regression methods should ideally not be used for trend testing.

Non-parametric methods such as the Mann-Kendall test and Sen's test should give more convincible results for trends because they do not require the same assumptions as parametric methods (e.g. normality) except independence of data. The Mann-Kendall test and Sen's test do not have the deficiency of the least squares method in which outliers in the data will produce biased estimates of slope. In addition, these two non-parametric tests are suitable for datasets with missing values and non-detectable values.

Most non-parametric tests cannot quantify the magnitude of a trend, i.e., the rate of change expressed in the gradient of a trend; however, using the combination of these two

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[1] A version of this chapter has been accepted for publication by the Annual Conference of AWMA, 2006.

non-parametric tests – the Mann-Kendall test and Sen's test, detection of the presence/absence of a trend (change) and quantification of the magnitude of this trend can be achieved without the requirement of a normal distribution. Autocorrelation can increase the probability of rejecting the null hypothesis when there is actually no trend (Hamed and Rao, 1998). Except for air quality data extracted from annual cumulative frequency distribution curves, autocorrelation can be ignored and the data can be considered as independent data. Seasonal effects can also be ignored because of the power of using the cumulative frequency distribution within the time interval of a year.

5.2 Summary Procedures of Data Processing and Calculations

1. Data preliminary analysis and trend analysis were undertaken using Microsoft Excel® with Visual Basic Application.
2. Hourly average data for the Fort McKay and Edmonton stations were obtained from the Clean Air Strategic Alliance (CASA) Data Warehouse website (http://www.casadata.org).
3. Missing values and flagged values (non-numerical data) were eliminated from each annual dataset.
4. A minimum standard of 90% data completeness was used to determine whether to carry an annual dataset forward for trend analysis.
5. Cumulative frequency distribution values were calculated and the distribution curves were drawn for each annual dataset after sorting remaining hourly concentration values in ascending order.
6. Annual means, medians, complete percentages, and percentages of measurements below detection limits were calculated and examined. Yearly one-hour minimum concentrations and yearly one-hour maximum concentrations were also examined.
7. From the annual cumulative frequency distribution of each pollutant in each year, concentrations corresponding to 50th, 65th, 75th, 80th, 90th, 95th, and 98th percentile values were determined and recorded.

8. The first year (1997 for the Edmonton Northwest and East station, and 1999 for the Fort McKay station) was taken as a baseline year and concentrations corresponding to 50th, 65th, 75th, 80th, 90th, 95th, and 98th percentile values for these years were taken as "benchmark" concentrations. Annual hours exceeding these benchmark concentrations for each pollutant in subsequent years were calculated and recorded.
9. Indices derived from steps 7 and 8 were analyzed using the Mann-Kendall test and Sen's test (Gilbert, 1987) to determine trends (significance and slope of significant trend) for the indices for each pollutant.
10. Statistically significant trends were tested at three levels of significance. Initially a significance level $\alpha=0.01$ was used to test for statistical significance. If no trend was indicated, a significance at a level of $\alpha=0.05$ was tested. If no trends was indicated, a significance at $\alpha=0.10$ was tested. Finally, if no trend was indicated at $\alpha=0.10$, no further testing was undertaken and the indices were deemed to not represent any trend over the time period at a level of significance $\alpha=0.10$.

6.0 RESULTS AND DISCUSSION [2]

6.1 Fort McKay

Concentration indices for NO_2, O_3, $PM_{2.5}$, THC, and SO_2 that correspond to the 50th, 65th, 80th, 90th, 95th and 98th percentile values at the Fort McKay station are depicted in Figures 1 to 5, respectively, for the six-year period spanning from 1999 to 2004. Indications of a changing trend, i.e., the statistical significance of the changing trend at a certain significance level less than 0.1(α=0.10), were tested using the Mann-Kendall test and Sen's method. These statistical results from historical data in the Fort McKay station indicated that no statistically significant trends existed for these concentration indices at most cumulative frequency values at a significance level less than 0.1 (α=0.10), except for NO_2 concentration and $PM_{2.5}$ concentration corresponding to a 98th percentile value. The percentile values ranged from 50th to 98th for the concentrations of all pollutants (NO_2, O_3, $PM_{2.5}$, THCs, SO_2), as shown in Figures 1 to 5. NO_2 concentration and $PM_{2.5}$ concentration corresponding to a 98th percentile value exhibited a significantly increasing trend at a changing rate of 1ppb/yr (α=0.10) and 1.13 $\mu g/m^3/yr$ (α=0.05), respectively. Specifically, the null hypothesis (H_0) could not be rejected and therefore it was concluded that insufficient data were available to demonstrate a trend for concentration of O_3, THCs and SO_2 at cumulative frequency values from 50th to 98 h, and $PM_{2.5}$ and NO_2 at cumulative frequency values from 50th to 95th in Fort McKay during the 6 year observation period spanning from 1999 to 2004 (α=0.10). More data are required to reach a stronger conclusion.

Nevertheless, the significant increasing of trends for NO_2 and $PM_{2.5}$ concentrations corresponding to the 98th percentile value contains meaningful information. The concentration corresponding to a 98th percentile value represents the concentration that is exceeded for an accumulative total of seven days in one year. The European Union Directives regarding air quality are based on daily means at the 98th percentile value. The

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[2] A version of this chapter has been accepted for publication by the Annual Conference of AWMA, 2006.

Canadian Objective on $PM_{2.5}$ (maximum of 24-hour average is 30 $\mu g/m^3$) is based on an annual 98th percentile value averaged over three consecutive years. Although the concentration corresponding to a 98th percentile value may only reflect minor, unusual, or accidental situations of air quality without representing general conditions, it still deserves notice. The objective or guideline based on this value means more stringent regulation for air quality. More attention has been paid to the pollutants by public or government agencies because of the concerns about the potential severe effects, of occasionally higher concentrations of air pollutants, on human health.

The significantly increasing trends for NO_2 and $PM_{2.5}$ concentrations at the 98th percentile value deserve notice, although the maximum concentrations did not exceed either the Canadian or the Alberta objective. NO_2 and $PM_{2.5}$ can be primary pollutants in industrial areas for oil sand production and processing. NO_2 can be mainly released from emissions of fossil fuel combustion, oil refinery and oil processing production, whereas $PM_{2.5}$ can be mainly discharged from the operation of oil sand mining. $PM_{2.5}$ can also be a secondary pollutant produced from NO_2 and may show some consistency and correlation in concentration fluctuation with the air contaminant NO_2. Surface, opencast mining in oil sands production may be the main contributor to the increasing concentration of $PM_{2.5}$. The less stringent regulations regarding NO_2 compared to SO_2 leads to a lower degree of NO_2 release prevention in process design and treatment and an increase in the release of NO_2. The higher concentrations and long term trends should be monitored, documented, and noted.

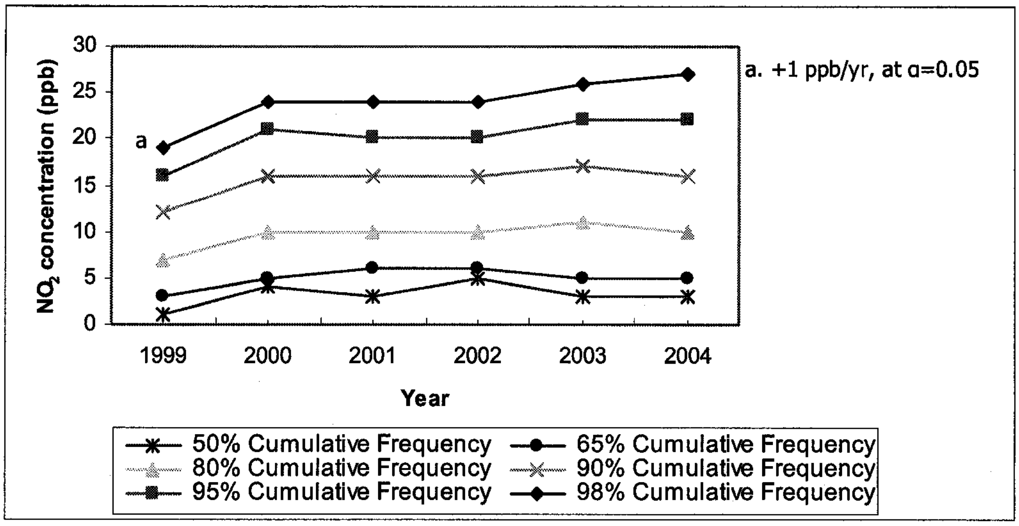

Figure 1: Trends of NO$_2$ concentrations corresponding to different percentile values at Fort McKay station (1999 and 2004) are illustrated.

(no statistically significant trends detected at all percentile values, α=0.10)[a]

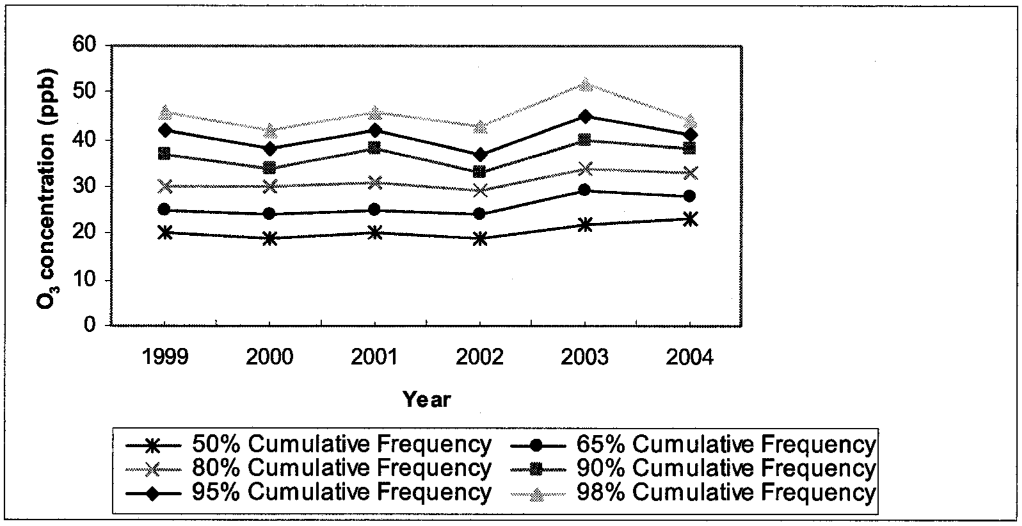

Figure 2: Trends of O$_3$ concentrations corresponding to different percentile values at Fort McKay station (1999 and 2004) are illustrated. (statistically significant trends not detected at all percentile values, α=0.10)[b]

Note (a, b): The labels refer to changing rates and their respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

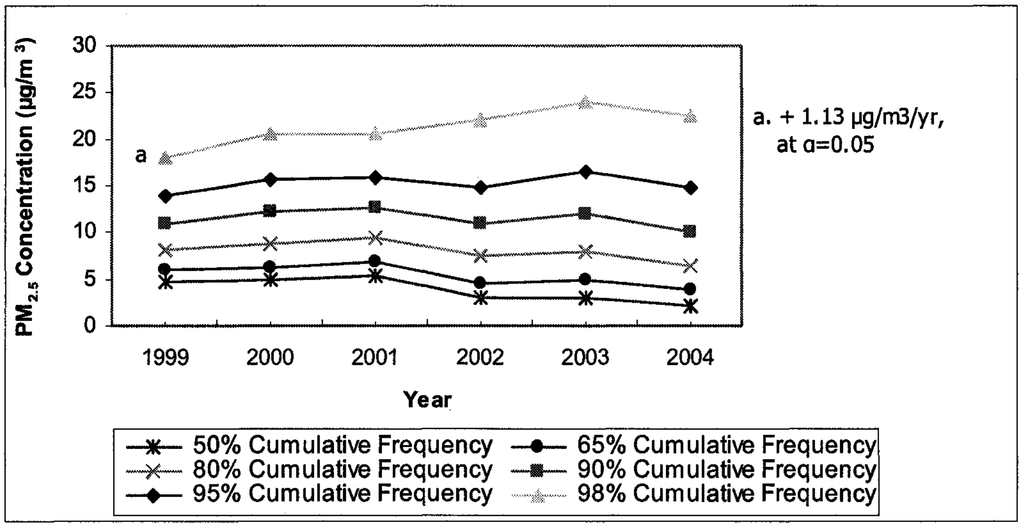

Figure 3: Trends of $PM_{2.5}$ concentrations corresponding to different percentile values at Fort McKay station (1999 and 2004) are illustrated

(no statistically significant trends detected at all percentile values, α=0.10)[c]

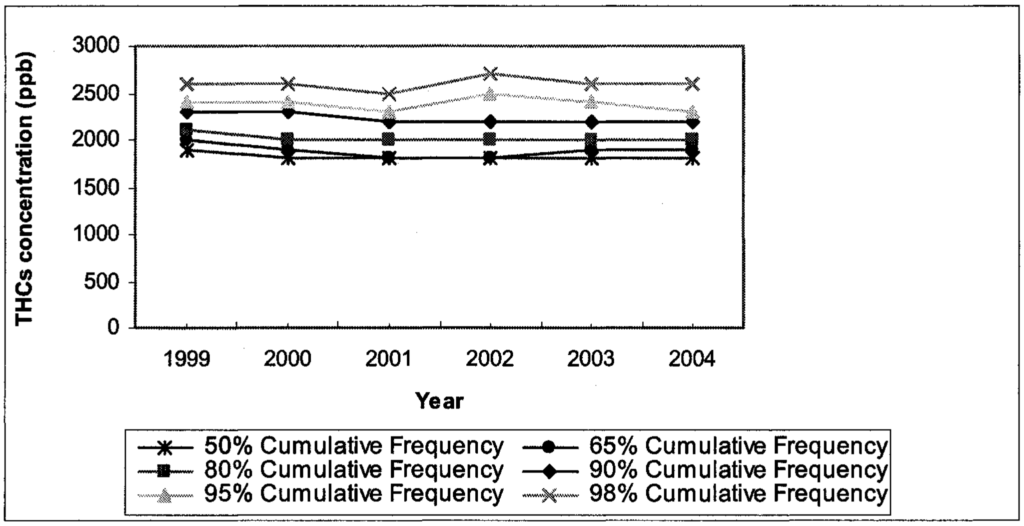

Figure 4: Trends of THCs concentrations corresponding to different percentile values at Fort McKay station (1999 and 2004) are illustrated

(no statistically significant trends detected at all percentile values, α=0.10)[d]

Note (c, d): The labels are changing rates and respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

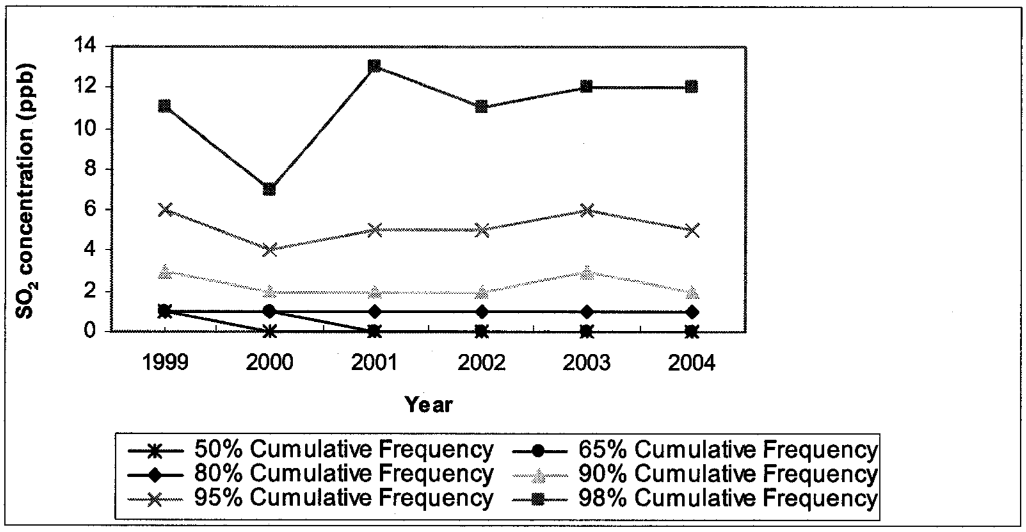

Figure 5: Trends of SO_2 concentrations corresponding to different percentile values at Fort McKay station (1999 and 2004) are illustrated

(no statistically significant trends detected at all percentile values, α=0.10)[e]

Note (e): The labels are changing rates and respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

Annual hours (number of hours per year) exceeding concentration benchmarks for the five pollutants (NO_2, O_3, $PM_{2.5}$, THC, SO_2) corresponding to 50th, 65th, 75th, 80th, 90th, 95th and 98th percentile values at the Fort McKay station are depicted in Figures 6 to 10, respectively, for the period from 1999 to 2004. These data were tested to verify whether indications of a changing trend were significant at a less than 0.1 significance level (α=0.10). The statistical significance and changing rates of the changing trends at a significance level less than 0.1 (α=0.10) were derived using the Mann-Kendall test and

Sen's method. Results similarly indicated that no statistically significant trends existed for these concentration benchmarks for all pollutants (α=0.10).

An exception was noted for annual hours exceeding a concentration of 1 ppb for SO_2 (Figure 10). Strictly speaking, the null hypothesis H_0 could not be rejected, as the evidence supplied by the data is not sufficient to prove a trend. More data are required to reach a stronger conclusion, except for annual hours of exceeding the 1 ppb benchmark concentration of SO_2 in Fort McKay.

It was noted that the annual hours exceeding 1 ppb SO_2 decreased at a rate of 65.5 hr/yr (α=0.05). There were no indications of decreasing trends for other benchmark concentrations tested (i.e. for 3 and 6 ppb benchmarks), at a significance level less than 0.1 (α=0.1), (Figure 10). In addition, no statistically significant trends existed for SO_2 concentration indices (α=0.1) (Figure 5). Thus, the total pollution level of SO_2 in Fort McKay decreased during the six years.

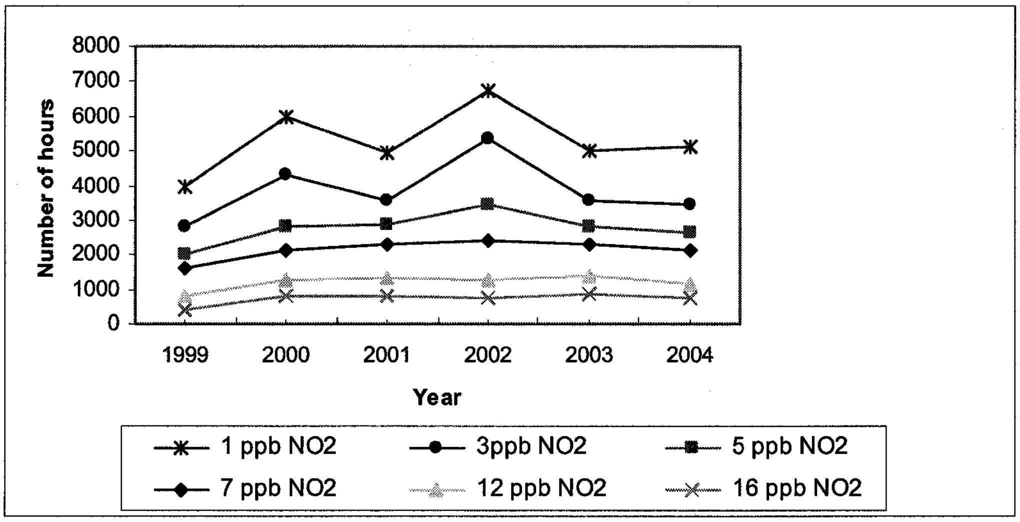

Figure 6: NO_2 trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Fort McKay station (1999 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentrations values, α=0.10)

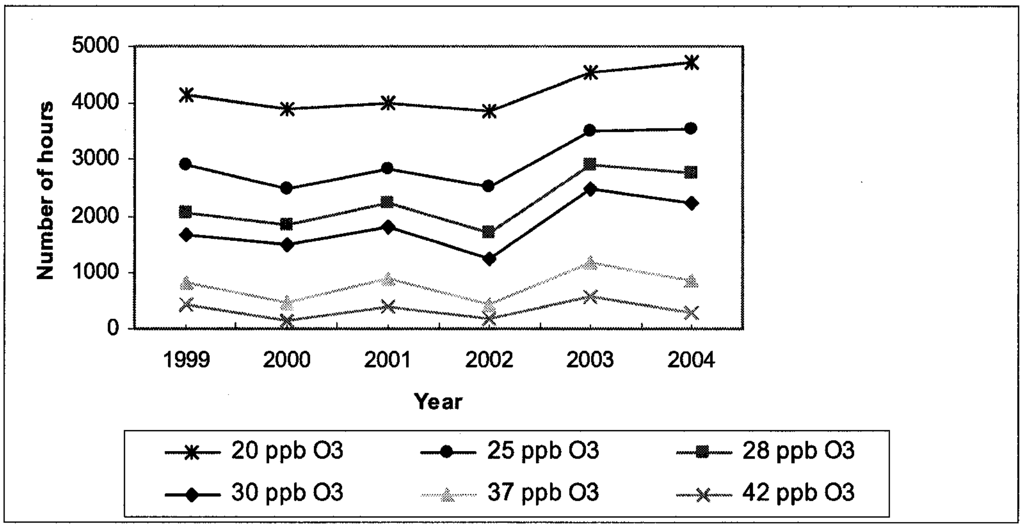

Figure 7: O_3 trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Fort McKay station (1999 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentrations values, α=0.10)

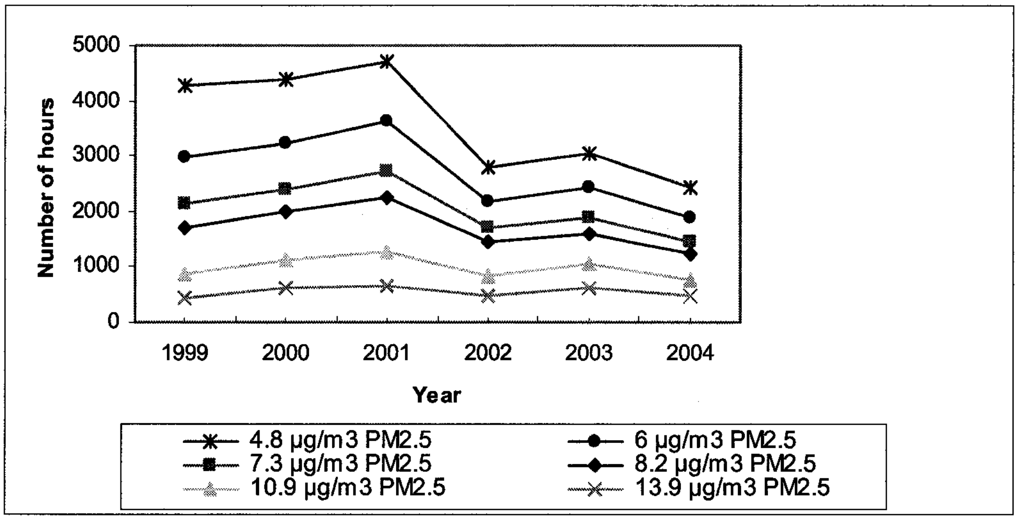

Figure 8: $PM_{2.5}$ trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Fort McKay station (1999 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentrations values, α=0.10)

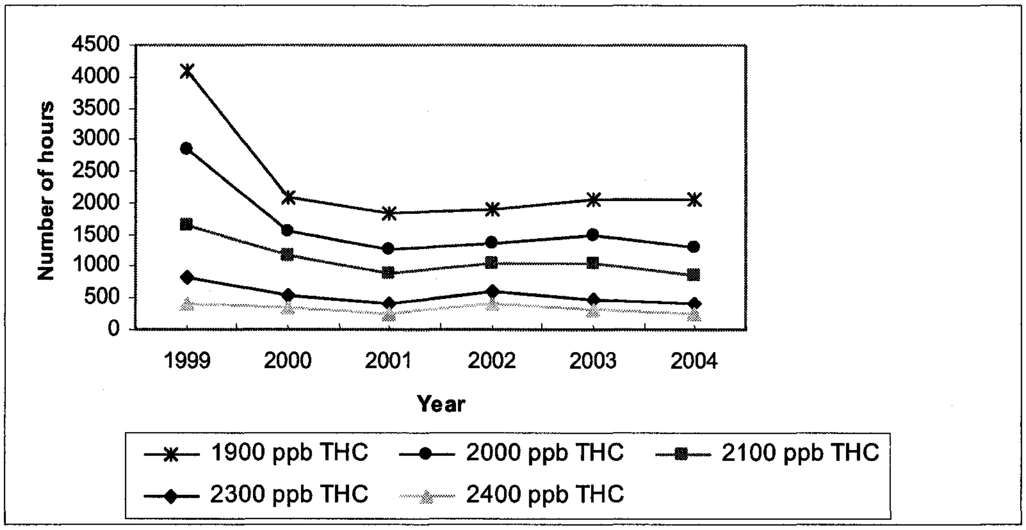

Figure 9: THCs trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Fort McKay station (1999 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentrations values, α=0.10)

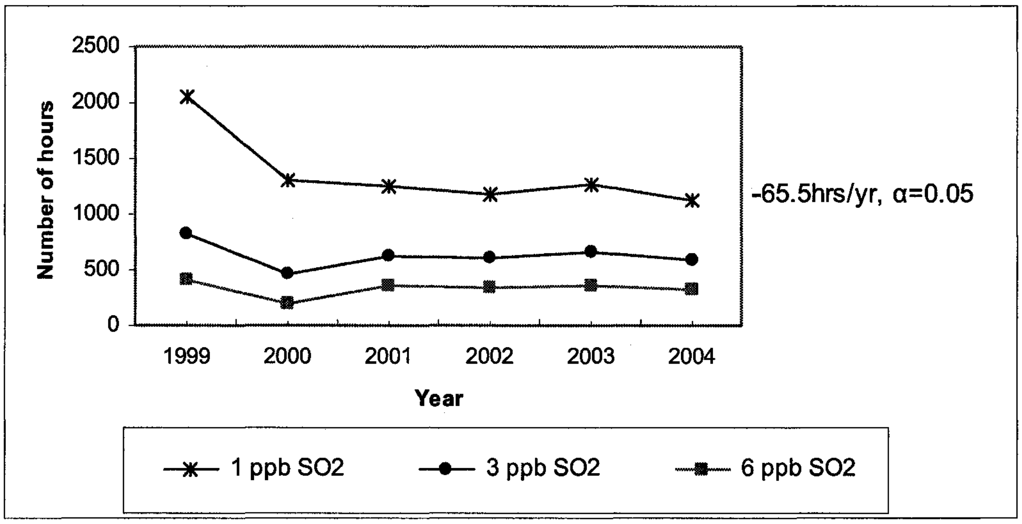

Figure 10: SO_2 trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Fort McKay station (1999 to 2004) are illustrated.

(significant trends and the respective significance level (α) given where detected)

6.2 Edmonton

Concentration trends for NO_2, O_3, $PM_{2.5}$, CO, THCs, SO_2, and H_2S corresponding to 50th, 65th, 80th, 90th, 95th and 98th percentile values at the Edmonton stations (Northwest and East stations) are depicted in Figures 11 to 17, respectively for the eight-year period spanning from 1997 to 2004. Indications of a changing trend and slopes of the significant trend were tested using the Mann-Kendall and Sen's method at a significance level of less than 0.1 (α=0.10, α=0.05, or α=0.01). Statistically significant decreasing trends were detected for $PM_{2.5}$, CO and SO_2 (Figure 13, 14 and 16), respectively) at a significance level of less than 0.1 (α=0.10, α=0.05, or α=0.01). On the other hand, no statistically significant decreasing trends were detected for NO_2, O_3, THCs and H_2S (Figure 11, 12, 15 and 17) at a significance level of less than 0.1 (α=0.10).

Annual hours exceeding concentration benchmarks for the seven pollutants (NO_2, O_3, $PM_{2.5}$, CO, THCs, SO_2 and H_2S) corresponding to 50th, 65th, 75th, 80th, 90th, 95th and 98th percentile values at the Edmonton station are depicted in Figures 18 to 24), respectively, for the 8-year period spanning 1997 to 2004. These data were tested to verify indications of a changing trend (i.e. whether or not there were statistically significant trends in the data) at a significance level less than 0.1 (α=0.10, α=0.05, or α=0.01) using the Mann-Kendall test. Slopes of statistically significant trends were tested using the Sen's method at a significance level less than 0.1 (α=0.10, α=0.05, or α=0.01).

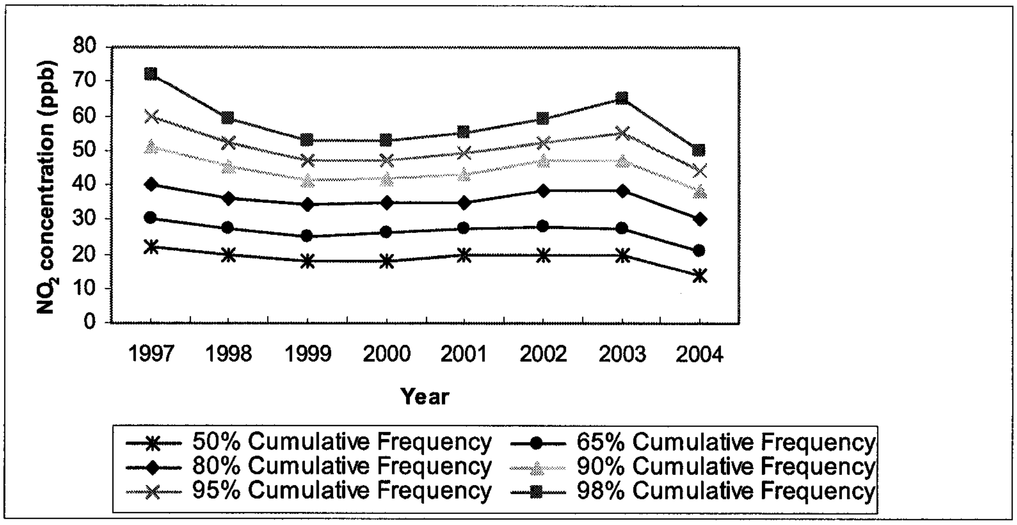

Figure 11: Trends of NO_2 concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all percentile values, $\alpha=0.10$)[f]

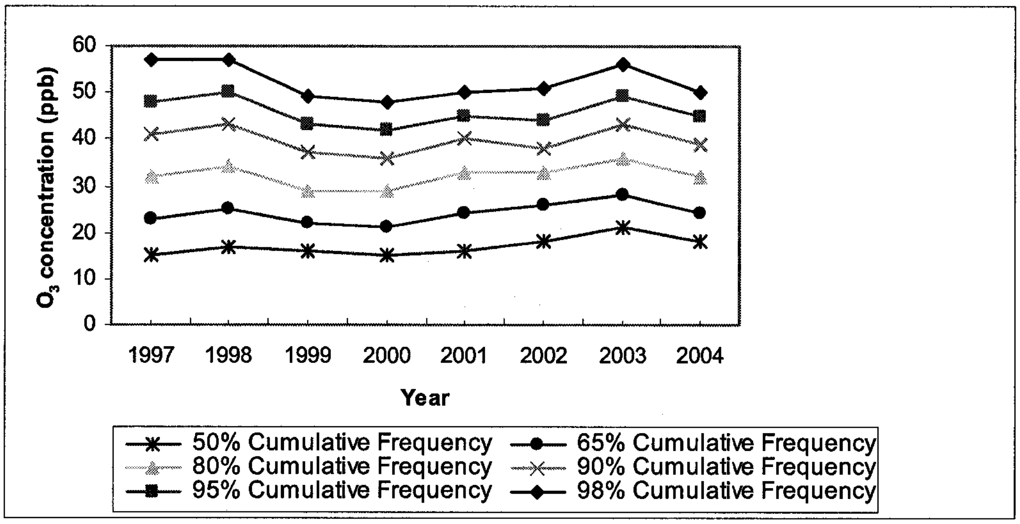

Figure 12: Trends of O_3 concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all percentile values, $\alpha=0.10$)[g]

Note (f,g): The labels are changing rates and respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than $\alpha=0.1$ significance levels.

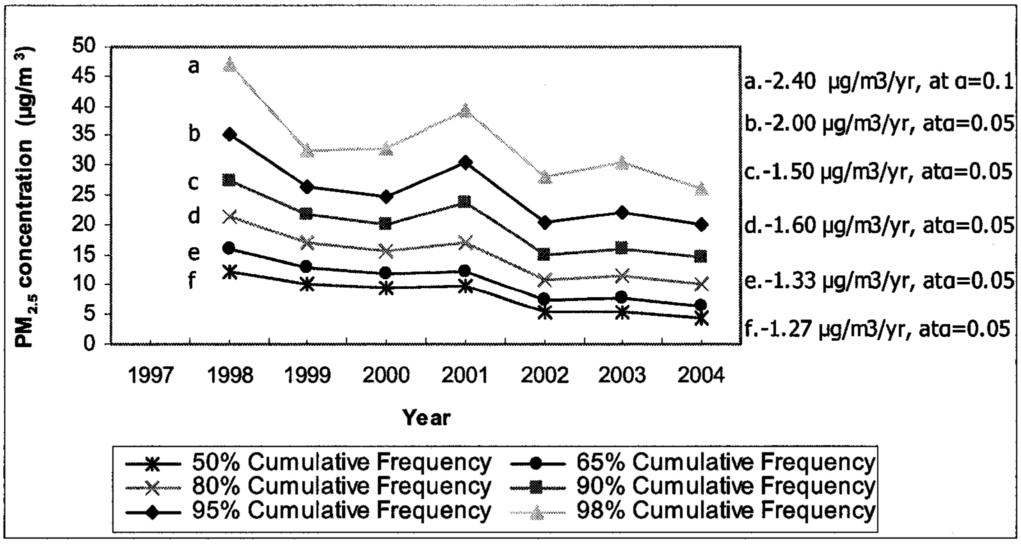

Figure 13: Trends of $PM_{2.5}$ concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(significant trends and the respective significance level (α) of the various percentile values are given)[h]

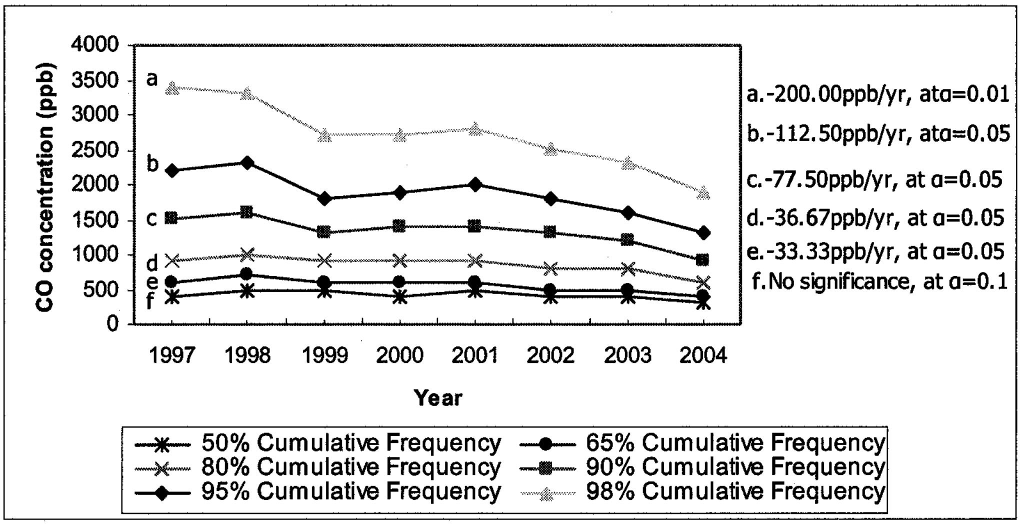

Figure 14: Trends of CO concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(significant trends and the respective significance level (α) of the various percentile values are given)[i]

Note (h,i): The labels are changing rates and respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

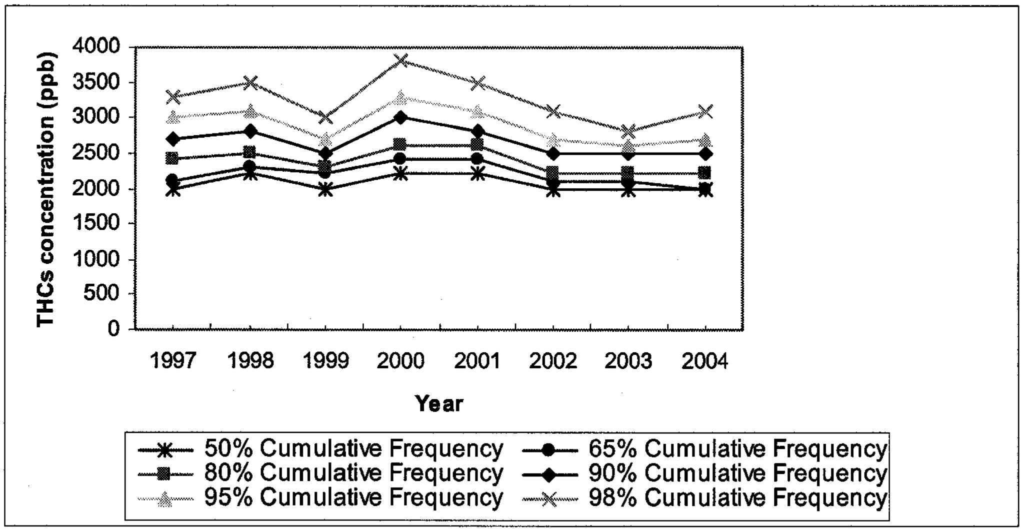

Figure 15: Trends of THCs concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all percentile values, α=0.10)[j]

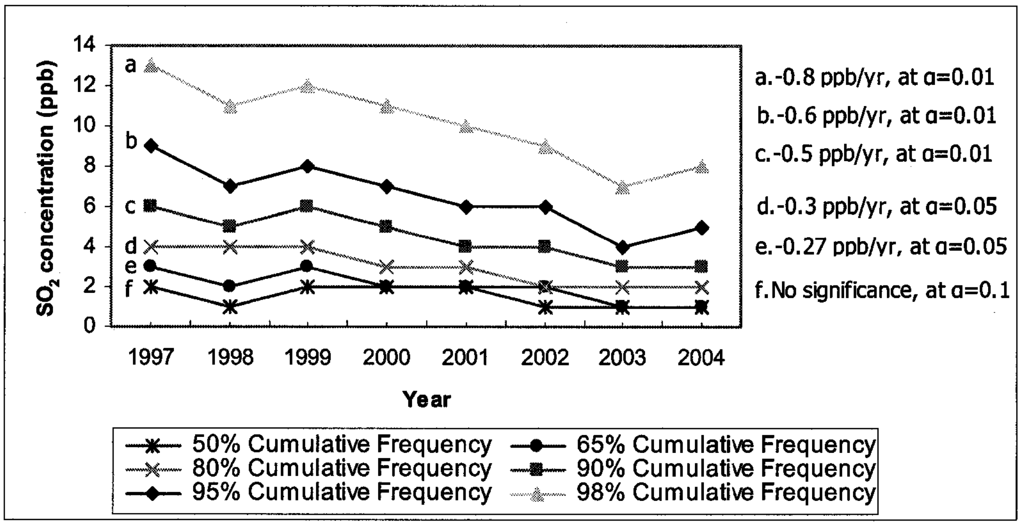

Figure 16: Trends of SO_2 concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(significant trends and the respective significance level (α) of the various percentile values are given)[k]

Note (j,k): The labels are changing rates and respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

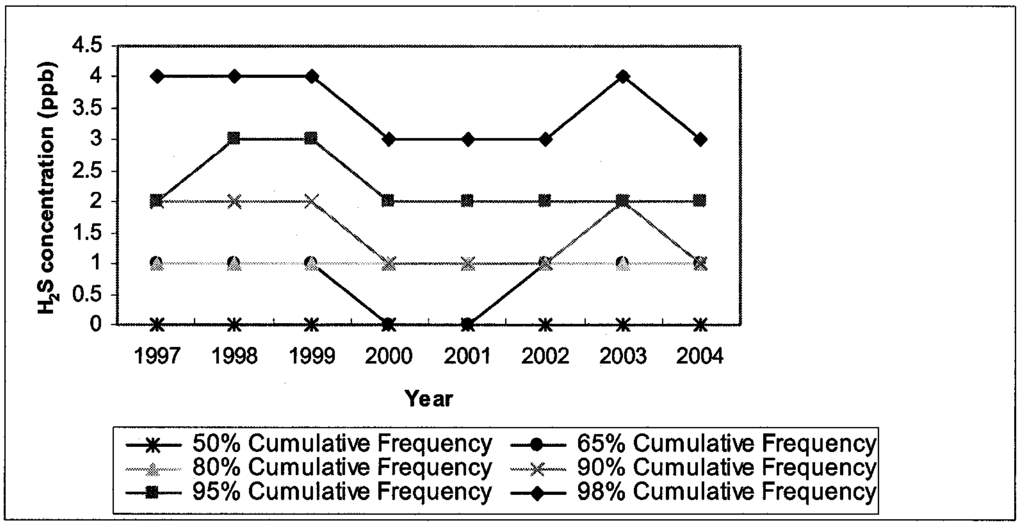

Figure 17: Trends of H_2S concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all percentile values, α=0.10)[1]

Note (l): The labels are changing rates and respective significance levels. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

As shown in Figure 18 to 24, the data from Edmonton's Northwest and East stations indicate similar results to those observed in Figures 11 to 17. Statistically significant trends do exist at a significance level of less than 0.1 (α=0.10, α=0.05, or α=0.01) for annual hours exceeding the five benchmark concentrations of $PM_{2.5}$, CO and SO_2 in Edmonton (Figure 20 to 22, respectively). However, there are no statistically significant trends at significance levels of less than 0.1 (α=0.10) for the five benchmark concentrations of NO_2, O_3, THC and H_2S (Figure 18, 19, 23 and 24). Again, the null hypothesis H_0 could not be rejected for the existence of trends in annual hours exceeding NO_2, O_3, THC and H_2S concentration benchmarks. It was concluded that insufficient data are available to prove a trend for these pollutants for the eight-year period spanning 1997 to 2004. Since the data does not provide enough evidence to prove a trend, more data are required to reach a stronger conclusion. On the contrary, the null hypothesis H_0 can be rejected for the number of hours per year in which the five benchmark concentrations of $PM_{2.5}$, CO and SO_2 were exceeded in Edmonton. Consequently, these results are consistent for the concentration indices of NO_2, O_3, $PM_{2.5}$, CO, THC, SO_2 and H_2S corresponding to 50th, 65th, 80th, 90th, 95th and 98th percentile values, for the data of annual hours exceeding different benchmark concentrations of NO_2, O_3, $PM_{2.5}$, CO,THC, SO_2 and H_2S.

Since the majority of the above seven air pollutants in a large city are generated from motor vehicles, the results are consistent with the fact that there are ongoing stringent regulations on $PM_{2.5}$ and SO_2 and improved technology for vehicle exhaust catalytic reactors. On the other hand, NO_x is generated from the combustion of fuel with nitrogen from the air and from the fuel that has not been reduced, while H_2S has little to do with vehicles. O_3 and $PM_{2.5}$ are regarded as two major secondary pollutants in ambient air. Firstly, the $PM_{2.5}$ concentration is mainly influenced by concentrations of SO_2 and NO_x. Secondly, O_3 concentration is greatly related to the concentrations of THC and NO_x, which are released from traffic, industrial and other non-industrial emissions. These releases have not been reduced. The results also show the consistency between the primary pollutants and secondary pollutants, since SO_2 concentration decreases greatly and NO_2 concentration has no significantly changing trend.

In summary, there is a statistically significant decreasing trend for $PM_{2.5}$, CO and SO_2 at a given significance level, but no statistically significant trends were seen for NO_2, O_3, THC and H_2S at a significance level of less than 0.1 (α=0.10) in Edmonton. These results are consistent with the ongoing stringent situation of regulations for automobile exhaust in a large city. The main source of air pollution in a large community is caused by emissions from motor vehicles. As primary or secondary pollutants, CO, NO_2, THC, SO_2 and $PM_{2.5}$ come from fuel combustion, and THC comes from vaporization of fuel. The exception is H_2S, which comes from natural sources, waste water treatment processes or landfills.

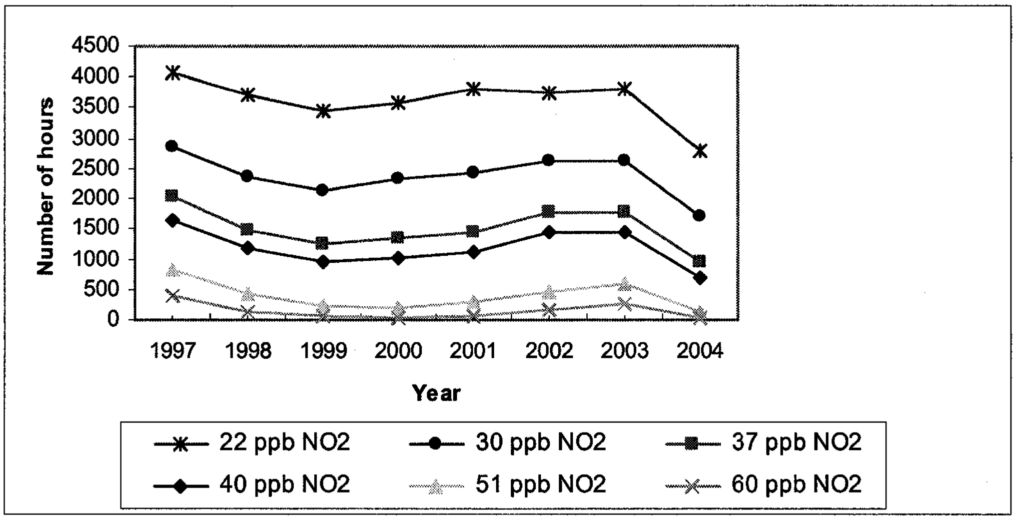

Figure 18: NO_2 trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentration values, α=0.10)

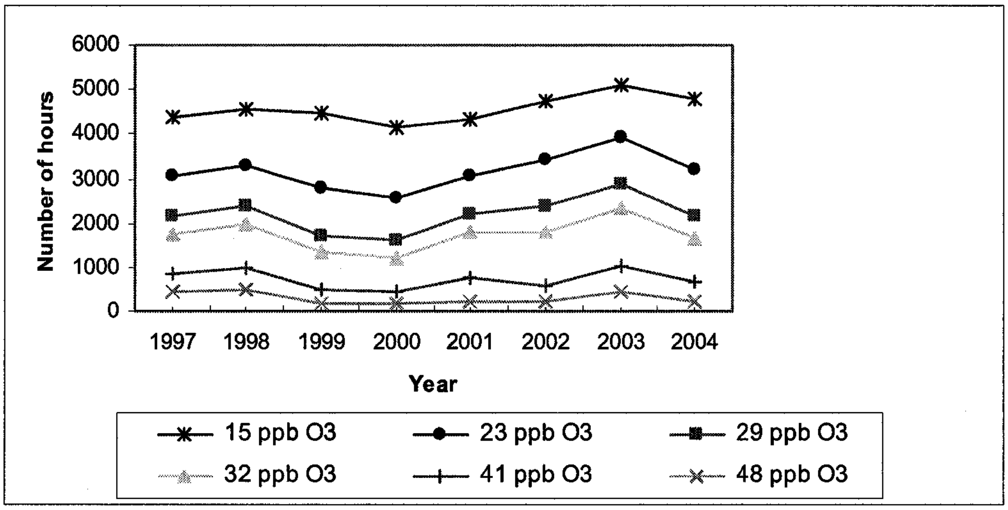

Figure 19: O_3 trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentration values, α=0.10)

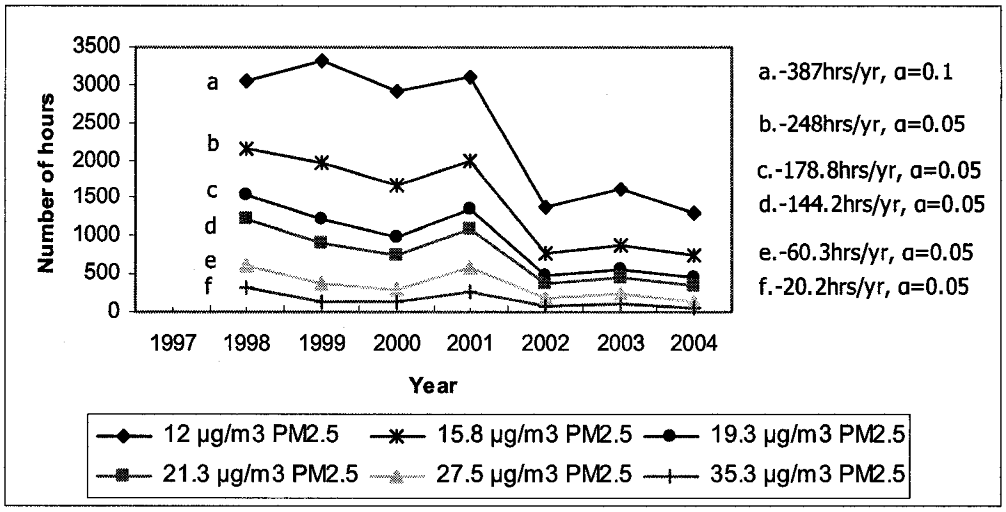

Figure 20: $PM_{2.5}$ trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(significant trends and the respective significance level [α] of the various benchmark concentration values are given)

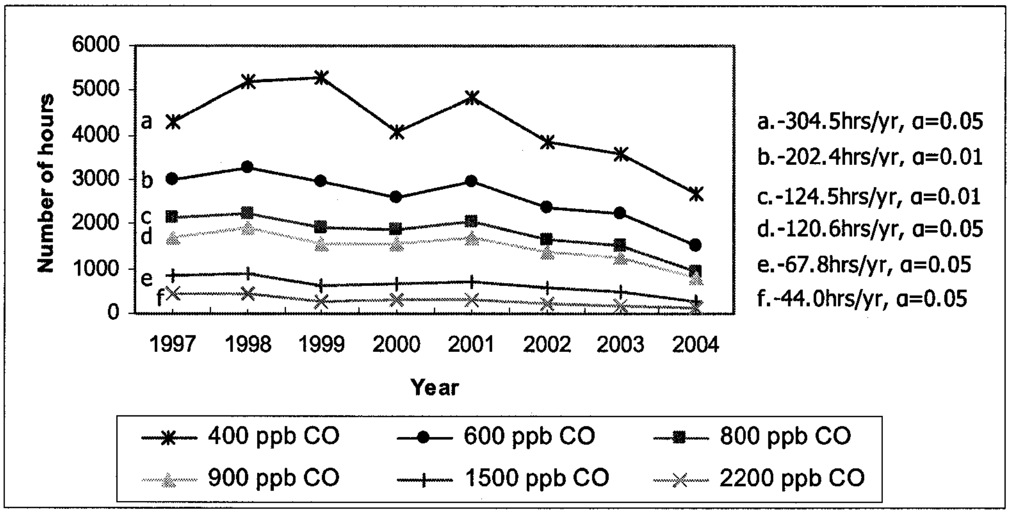

Figure 21: CO trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(significant trends and the respective significance level [α] of the various benchmark concentration values are given)

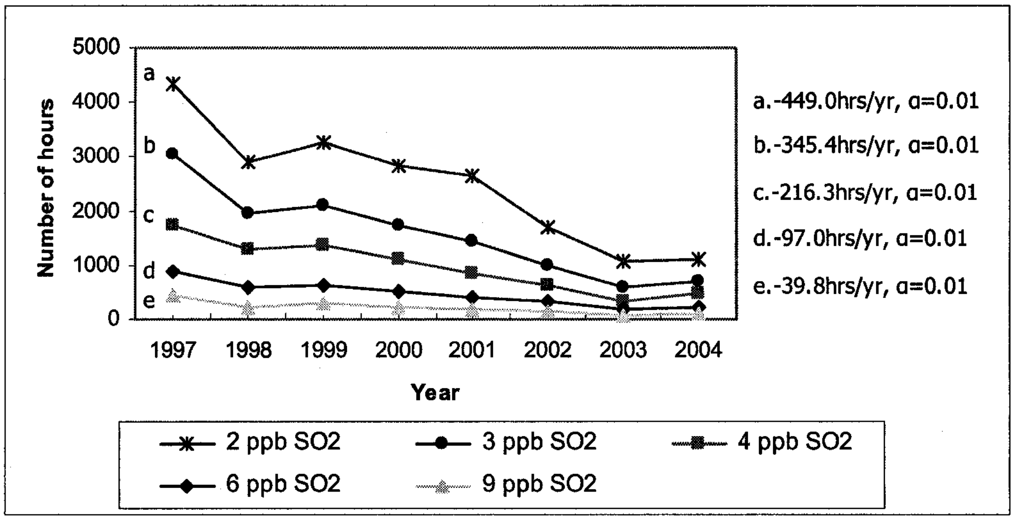

Figure 22: SO_2 trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(significant trends and the respective significance level [α] of the various benchmark concentration values are given)

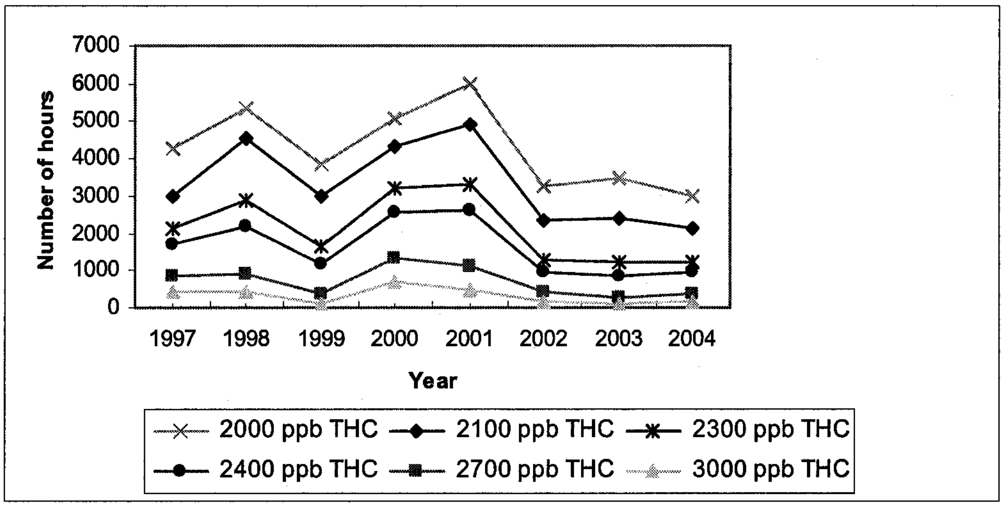

Figure 23: THCs trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentration values, α=0.10)

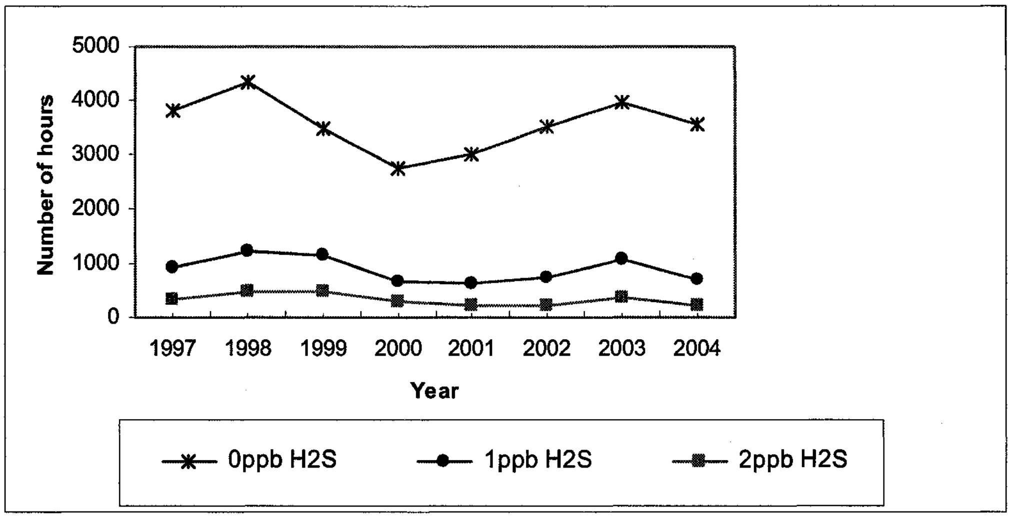

Figure 24: H_2S trends in annual hours exceeding benchmark concentrations corresponding to different percentile values at Edmonton station (1997 to 2004) are illustrated.

(no statistically significant trends detected at all benchmark concentration values, α=0.10)

The human population and the number of private vehicles increased steadily in the city of Edmonton during the years 1997 to 2004 (Department of Transportation and Streets, City of Edmonton, 2005), as shown in Figure 25 (The significance of the trends and the corresponding rates are derived from Mann-Kendall test and Sen's method). The emissions, due to fuel combustion in stationary and mobile sources, also increased. As much as 95th of all CO emissions may come from automobile exhaust in cities (USEPA, 2006a). Based on emission profiles, carbon monoxide has been linked to transportation as a major urban air pollutant source in Alberta (Alberta Environment, 1996). Statistically significant decreasing CO concentration trends indicate an overall improvement in air quality at the Edmonton stations, despite an approximately 16 % increase in the number of private vehicles in Edmonton between 1997 and 2004 (Department of Transportation and Streets, City of Edmonton, 2005). This trend may be related to better emission controls for automobiles. Environment Canada Criteria Air Contaminants Emission Summaries and National Pollutant Release Inventory (NPRI) for Alberta (Environment Canada, 2006a; Environment Canada, 2006b) demonstrated consistent overall decreases in CO emissions from automobiles during the same time period. These decreases are credited to improvements and advances in engine performance and fuel quality. The improved technology of exhaust catalytic treatment also reduced CO emission as well as primary PM emission.

Statistically significant deceasing $PM_{2.5}$ and SO_2 concentration trends indicate an overall improvement in air quality at the Edmonton station. Environment Canada Criteria Air Contaminants Emission Summaries and National Pollutant Release Inventory (NPRI) for Alberta (Environment Canada, 2006a; Environment Canada, 2006b) also demonstrated decreases (starting in 1994) in $PM_{2.5}$, SO_2, and $PM_{2.5}$-related and SO_x-related precursor emissions from motor vehicles. The data show continuous decreases despite a projected increase in the number of motor vehicles on roads in Alberta. These results provide a plausible explanation for statistically significant decreasing trends (α=0.10, α=0.05, or α=0.01) observed at the Edmonton station for $PM_{2.5}$, CO, and SO_2. Furthermore, the more stringent regulations on sulfur content in gasoline and diesel lead to reductions in direct SO_2 emissions and, as a result, secondary PM emissions. Simultaneously, this also improved the catalytic efficiency of exhaust catalytic treatment and mitigated catalyst poisoning and deactivation, and reinforcing the reduction of emissions of CO and primary PM. All of these lead to significant decreasing trends for $PM_{2.5}$, CO and SO_2. The other four pollutants should have weaker trends because NO_2 comes from the oxidation of N_2 in the air and nitrogen content in fuels, both of which are unchanging. THCs from road traffic and H_2S in ambient air have also not been reduced by mitigation measurements. O_3, which is mainly related to THC, NO_2 and partially to CO, maintains an unchanging trend.

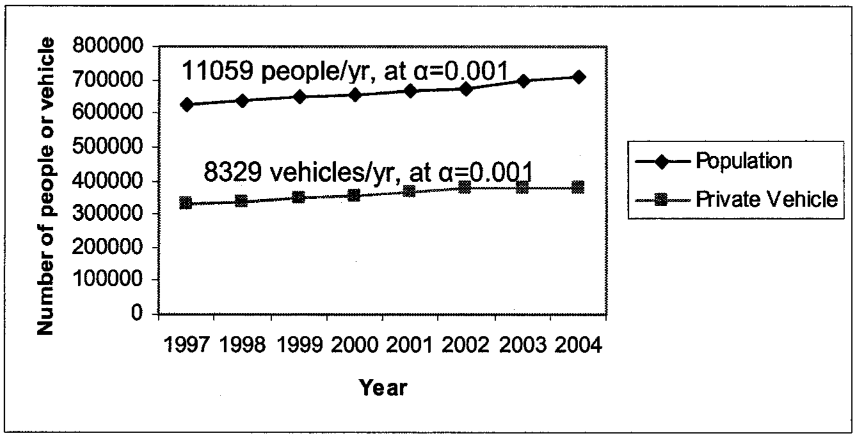

Figure 25: Increasing trends in population and number of private vehicles between 1997 and 2004 in Edmonton are illustrated.

Note: (1).The label is the changing rate at a certain significance level α=0.001).

(2). Data domain is urban area of Edmonton excluding suburb area.

The period of study over which trends were examined was less than a decade which is considered to be a short study period. Changes or lack of changes observed in air quality do not necessarily provide an indication of what may happen over the long-term. However, results generally supported that, despite increasing economic and other development activity in Edmonton, air quality appears to have improved and/or remained unchanged during the last six to eight years. As for the community of Fort McKay, which continues to see increased oil sands development surrounding it, air quality remained unchanged during the last six.

6.3 Comparison of Air Quality between Edmonton and Fort McKay

Figures 26 to 31 shows the changing trends in concentrations of NO_2, $PM_{2.5}$, SO_2, O_3 and THCs corresponding to a 75th percentile value (or SO_2, 75th and 90th percentiles), which can be a representative for the whole frequency distribution data in both the Edmonton and Fort McKay stations. This comparison demonstrates significant decreasing trends in $PM_{2.5}$ and SO_2 in Edmonton. However, there were no significant changing trends in any of the selected criteria air pollutants in Fort McKay. These are consistent with the changing trends of concentrations for NO_2, $PM_{2.5}$, SO_2, O_3 and THCs corresponding to percentile values other than the 75th in both stations. On the other hand, the general concentrations of all the selected criteria air pollutants in Edmonton were much higher than those in Fort McKay, with the exception of O_3 and THCs.

For SO_2, the concentration in Edmonton decreased greatly, while the concentration in Fort McKay was stable. In fact, the SO_2 concentration corresponding to the 90th percentile in Edmonton decreased to a level close to that in Fort McKay. The O_3 and THCs concentrations and the changing trends in Edmonton and Fort McKay were always similar to each other. This shows a correlation relationship between them; however, the sources contributing to the O_3 and THCs concentrations in each area are different. Although O_3 is the main secondary pollutant from THCs, THCs in Edmonton, a large city, are mainly due to releases from road traffic; while THCs in Fort McKay, an industrial area with a small population, are mainly emitted from the oil mining and processing in the area. The results show that the problem of THCs released from vehicles in large cities and the related O_3 problem is very important and even exceed fugitive emissions in the industrial area of Fort McKay which has an intensive oil mining and processing. The higher NO_2 concentration can enhance O_3 formation from higher THCs levels. Higher ambient temperature induced from heat islands enhancing O_3 formation, and the poor dispersion conditions in a large city, result in this higher O_3 concentration.

In addition, NO_2 is another important precursor of O_3. Although the concentration of NO_2 in Edmonton is much higher than that in Fort McKay, it does not lead to higher O_3

concentration in Edmonton. This can be explained in two ways. Firstly, NO_2 can be consumed by NH_3, which is relatively abundant in the air of Alberta. Excess NO_2 can react with THCs, which is a little higher in Edmonton than in Fort McKay, to produce HNO_3 through various intermediates. Secondly, O_3 can be consumed by NO, which is the intermediate of NO_2. O_3 can also react with excess THCs to produce more stable and soluble compounds. Therefore, the problems of THCs and NO_2 pollution in large cities, and related O_3 pollution problem, deserve attention.

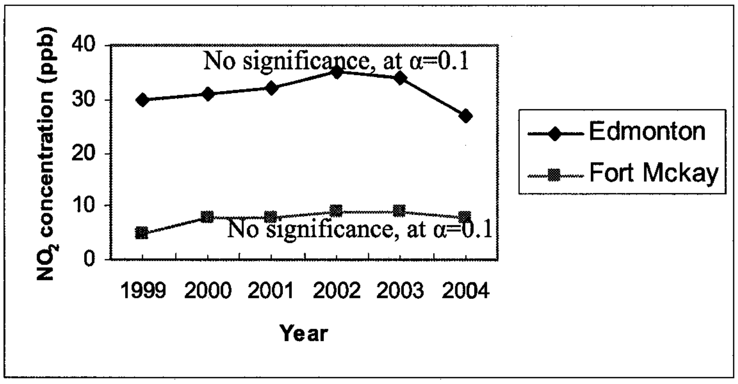

Figure 26: Comparison of NO_2 Concentration (ppb) Corresponding to the 75th Percentile between Edmonton and Fort McKay is illustrated. [m]

Note (m): The label is the changing rate at a certain significance level. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

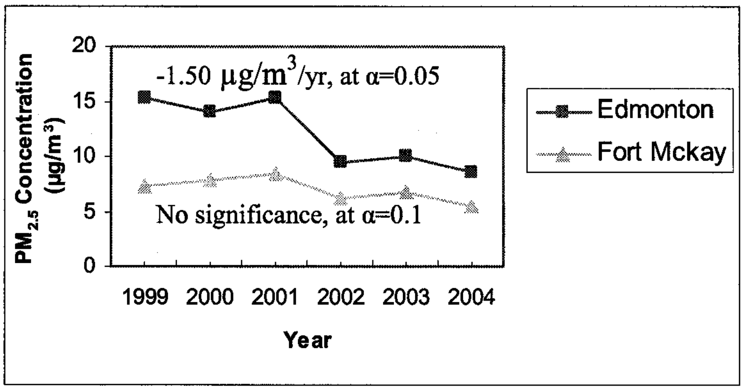

Figure 27: Comparison of $PM_{2.5}$ Concentration ($\mu g/m^3$) Corresponding to the 75th Percentile between Edmonton and Fort McKay is illustrated. [n]

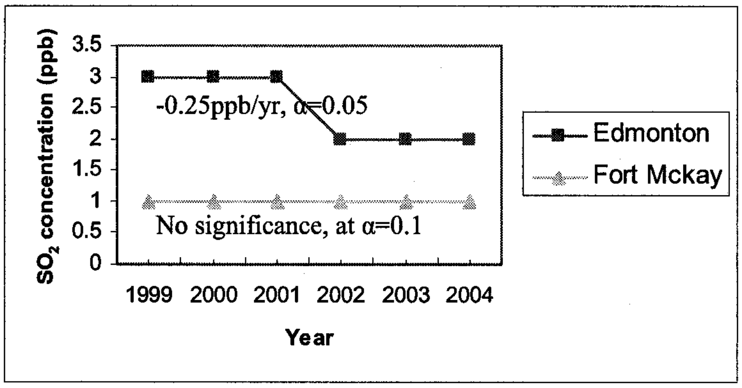

Figure 28: Comparison of SO_2 Concentration (ppb) Corresponding to the 75th Percentile between Edmonton and Fort McKay is illustrated. [o]

Note (n, o): The label is the changing rate at a certain significance level. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

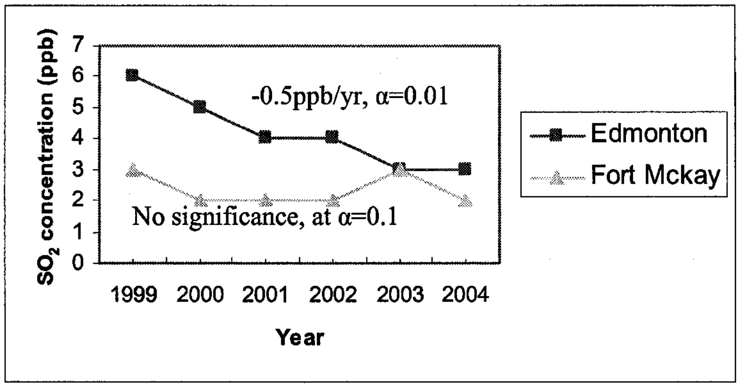

Figure 29: Comparison of SO_2 Concentration (ppb) Corresponding to the 90th Percentile between Edmonton and Fort McKay is illustrated. [p]

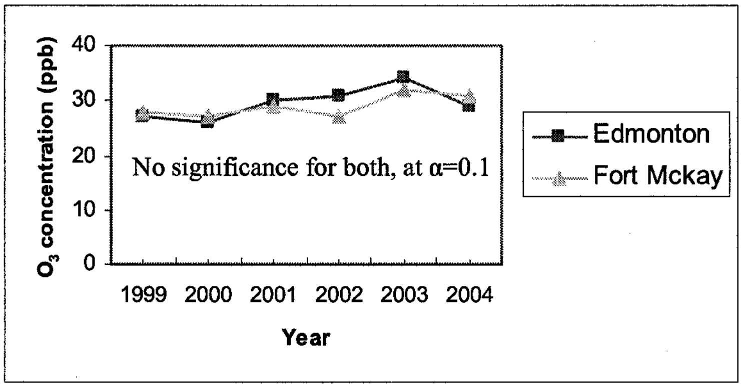

Figure 30: Comparison of O_3 Concentration (ppb) Corresponding to the 75th Percentile between Edmonton and Fort McKay is illustrated. [q]

Note (p, q): The label is the changing rate at a certain significance level. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

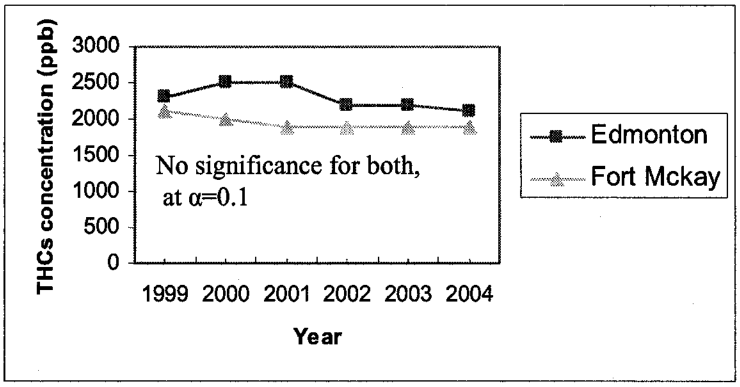

Figure 31: Comparison of THC Concentration (ppb) Corresponding to the 75th Percentile between Edmonton and Fort McKay is illustrated. [r]

Note (r): The label is the changing rate at a certain significance level. Those not being labeled show the fluctuation of criteria air pollutant concentration without existing significant trend (increasing or decreasing) at less than α=0.1 significance levels.

Environmental regulations and standards, which will become more and more stringent in future years, require low emissions of sulfur. Strict regulations on sulfur content in diesel and gasoline are being implemented throughout the world. For example, the Environmental Protection Agency of the United States (EPA) promulgated a regulation to achieve a 97th reduction in the sulfur content of diesel fuel from the previous 500 ppm standard to less than 15 ppm (McFarland, 1999). Among the pollutants from fossil fuel combustion, especially in motor vehicles, only sulfur and nitrogen pollution can not be removed completely from the processes of combustion. In order to prevent the transfer of pollutants from manufacturing process areas to populated areas of cities, a more stringent regulation of the sulfur content in fuels would be effective. This is strongly supported and proved in this research by the comparison of SO_2 pollution between the city area and the industrial area (Figure 22; Figure 28, 29).

7.0 CONCLUSIONS

The air quality and changing trends in the large city of Edmonton and in the small community of Fort McKay were investigated and analyzed by non-parametric statistical tests. A comparison between these two representative air sheds was also made.

As a whole, there is no statistically significant trend for concentrations of NO_2, O_3, $PM_{2.5}$, THC and SO_2 at a significance level less than 0.1 in Fort McKay. Currently available data do not provide sufficient evidence to prove a significant trend for the five criteria pollutants in Fort McKay during a six year period spanning 1999 to 2004. More monitoring data are required to reach a stronger conclusion. The exceptions are NO_2 concentration and $PM_{2.5}$ concentration corresponding to 98th percentile value, which exhibited a significant increasing trend at a changing rate of 1ppb/yr (α=0.10) and 1.13 $\mu g/m^3/yr$ (α=0.05), respectively. Although maximum concentrations did not exceed the Canadian objective or Alberta objective, higher values and trends of NO_2 concentration and $PM_{2.5}$ concentration in Fort McKay area may deserve attention.

For concentrations of NO_2, O_3, $PM_{2.5}$, CO, THC, SO_2 and H_2S spanning from 1997 to 2004 in Edmonton, there exist statistically significant decrease trends for concentrations of $PM_{2.5}$, CO and SO_2 at a significance level of less than 0.1. There exists no statistically significant trend for concentrations of NO_2, O_3, THC and H_2S at a significance level less than 0.1. The significance levels and slope values (changing rate) of significant trends at a certain significance level less than 0.1 were derived from the Mann-Kendall test and Sen's method.

The main sources of air pollution in a large city are related to population factors and the number of vehicles. Factors affecting air quality in areas like Fort McKay would be expected to be related to change in production, processing and manufacturing capacity of the oil sands industry. With the increasing trend of crude oil production and processing between 1999 and 2004 in the Fort McKay area, the lack of a statistically significant change in air pollution levels may be credited to the fact that the dilution and degrading capacity of the air shed has not been exceeded. Effective pollution control measures in industrial production may also play a role.

Although there are statistically significant decrease trends for concentrations of $PM_{2.5}$, CO, and SO_2 in Edmonton, general concentration levels of all the selected criteria air pollutants in Edmonton, aside from those of O_3 and THC, are much higher than those in Fort McKay. In both areas, fugitive emission levels of THC have always been similar.

In summary, although changes or lack thereof observed in air quality do not necessarily provide an indication of what may happen over the long-term, the results generally support that despite increasing economic and other development activity in Edmonton and continuous oil sands development surrounding the community of Fort MacKay, air quality remains unchanged during the previous six to eight years, 1997 to 2004 and 1999 to 2004 for Edmonton and Fort MacKay respectively.

8.0 RECOMMENDATIONS

It is usually difficult to simulate and predict the air pollutant concentrations in the ambient air, and their diurnal, weekly, and seasonal styles because of the complexity of influencing factors and complex mechanisms of interaction, formation, transportation, attenuation, and deposition of pollutants in the atmosphere. Artificial neural network (ANN) has been used in the field of air quality research for many years. The performance of ANN model can be improved greatly by the combination of methodologies of parsimonious principle, systematic optimization and moving windows. This ANN simulation model can be used to estimate missing data and predict air quality in the future. Therefore, this simulation can improve the trend analysis of air quality and further forcast the future trend of air quality.

The time periods from which data were extracted and tested for nonparametric trend analysis are relative short. Further analysis for air quality trend should be pursued as more monitored data are available in the coming year, so that not only more reliable results can be achieved but also urbanization and industrial development will be monitored continuously. Mitigation and follow-up measures can be implemented when there is a significant increasing trend for a criteria air pollutant, and valuable information for policy decision-making can be obtained when an obvious, decreasing trend of criteria air pollutant occurs.

Nonparametric statistical methods are recommended for environmental data analysis. Higher values and significantly increasing trends of NO_2 concentration and $PM_{2.5}$ concentration in Fort McKay area should be noted and monitored for a long term. Before a new oil sands mining or a new plant is approved and put into production, environmental impact assessment (EIA) should be conducted to ensure that the clean air objectives will be met. Many dispersion models have been promulgated and being upgraded continually by US EPA (USEPA, 2006b). These models can be used to simulate and predict the temporal and spatial concentrations of air pollutants in an air shed. This simulation will be valuable in EIA, particularly in evaluating the environmental and ecological impacts of a new industrial development project.

There is an important issue to be noted especially for oil production and processing industrial areas. The emissions and concentrations of pollutants may be higher during startup and shutdown of production instruments, unstable operation or accidents of production, and sweeping and cleaning of instruments before the examination and repair plants. The higher concentrations of pollutants over a short time caused by the above unusual events may not be reflected by average values over a longer period or by trend analyses based upon annual indices. Because of the potential adverse impacts of severe air pollution over a short time on public health and ecosystems involving fauna and flora, air quality in Fort McKay should be monitored and recorded in shorter time intervals, and compared to reference values in regulations during and after periods of these special events and activities.

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APPENDICES

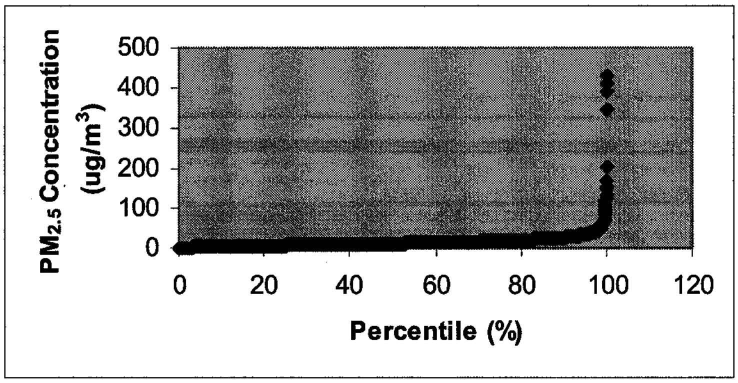
Appendix 1. Raw Data Statistics and Percentile Distribution Curves of Annual Hourly Data of Edmonton

Note: Data come from Northwest station except SO_2 data from East station.

$PM_{2.5}$ ($\mu g/m^3$):

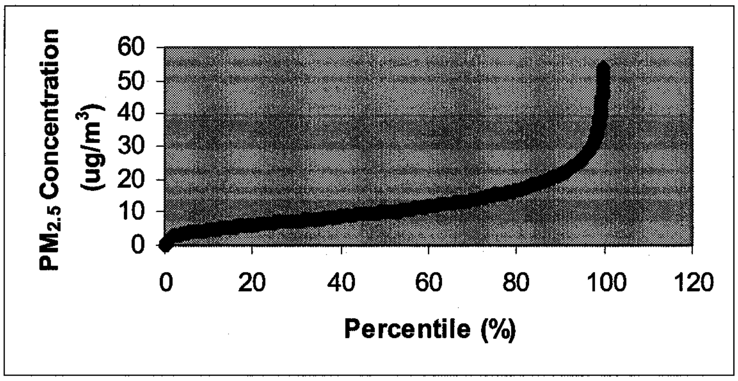
1998:

Median ($\mu g/m^3$):	12
Max ($\mu g/m^3$):	431.3
Min ($\mu g/m^3$):	0
Average ($\mu g/m^3$):	15.228
Completeness:	69.78%
Below Detection Limit:	0.40%



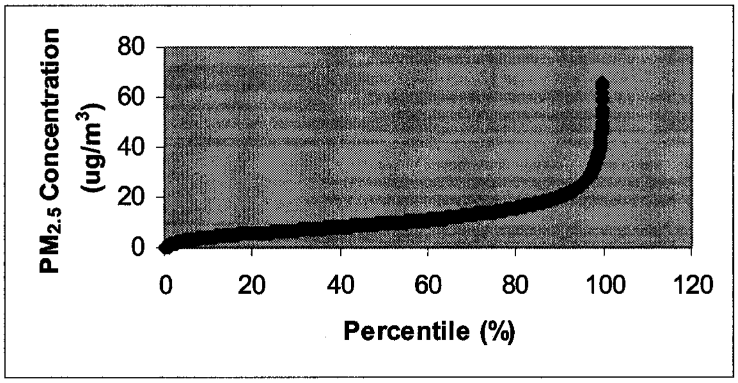
1999:

Median ($\mu g/m^3$):	10
Max ($\mu g/m^3$):	216.5
Min ($\mu g/m^3$):	0
Average ($\mu g/m^3$):	11.999
Completeness:	99.89%
Below Detection Limit:	0.50%



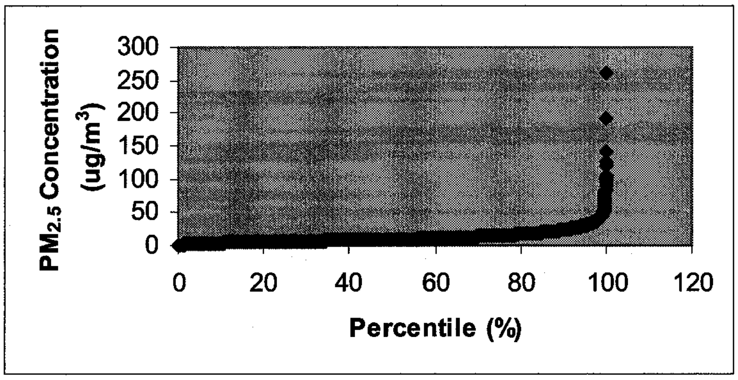
2000:

Median (μg/m^3):	9.3
Max (μg/m^3):	231.3
Min (μg/m^3):	0
Average (μg/m^3):	11.200
Completeness:	99.51%
Below Detection Limit:	0.82%



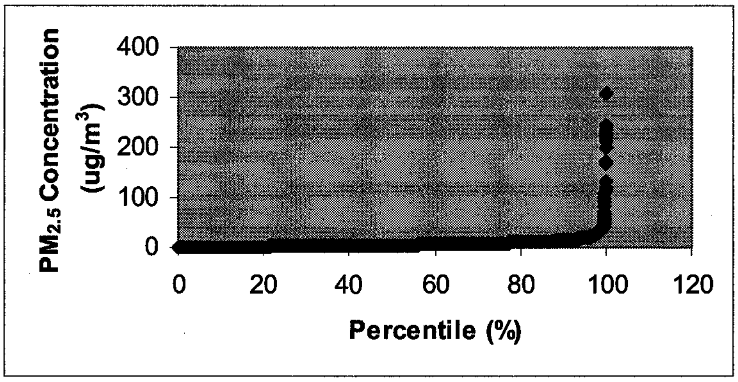
2001:

Median (μg/m^3):	9.8
Max (μg/m^3):	261.3
Min (μg/m^3):	0
Average (μg/m^3):	12.443
Completeness:	98.08%
Below Detection Limit:	0.50%



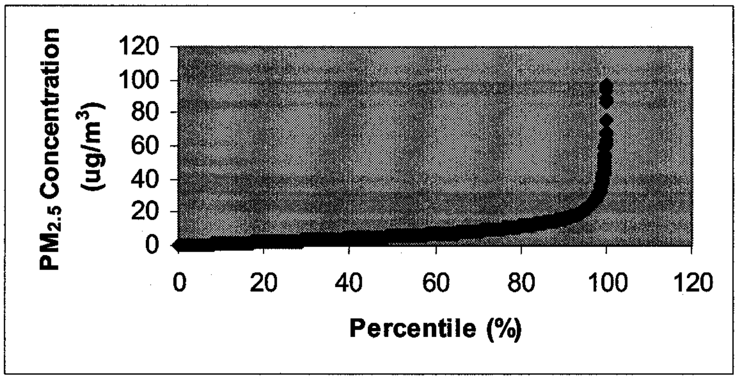
2002:

Median (µg/m^3):	5.3
Max (µg/m^3):	307.5
Min (µg/m^3):	0
Average (µg/m^3):	7.433
Completeness:	98.84%
Below Detection Limit:	6.32%



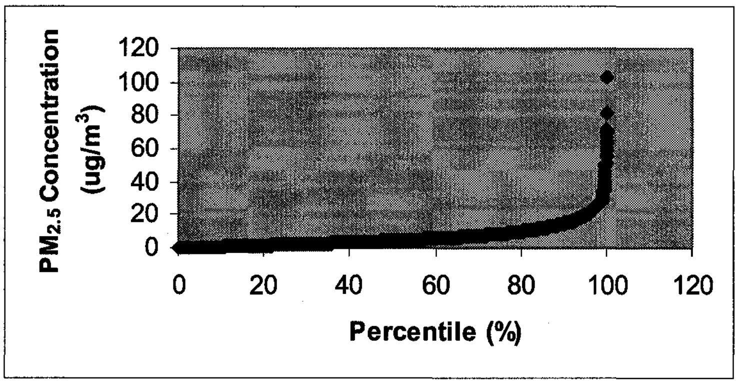
2003:

Median (µg/m^3):	5.5
Max (µg/m^3):	97.1
Min (µg/m^3):	0
Average (µg/m^3):	7.608
Completeness:	99.51%
Below Detection Limit:	4.63%



2004:

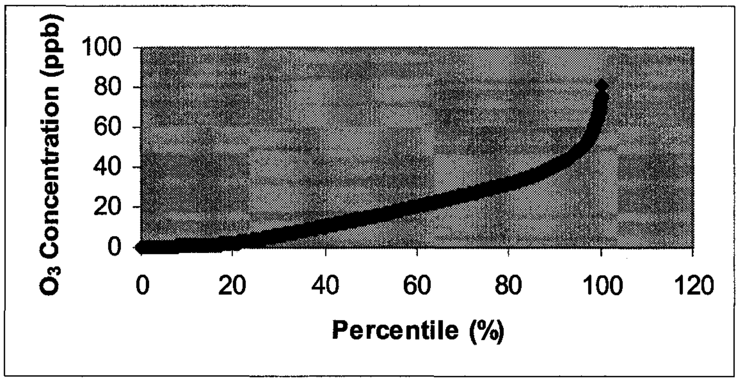
Median ($\mu g/m^3$):	4.4
Max ($\mu g/m^3$):	102.7
Min ($\mu g/m^3$):	0
Average ($\mu g/m^3$):	6.467
Completeness:	98.99%
Below Detection Limit:	6.42%



O_3:

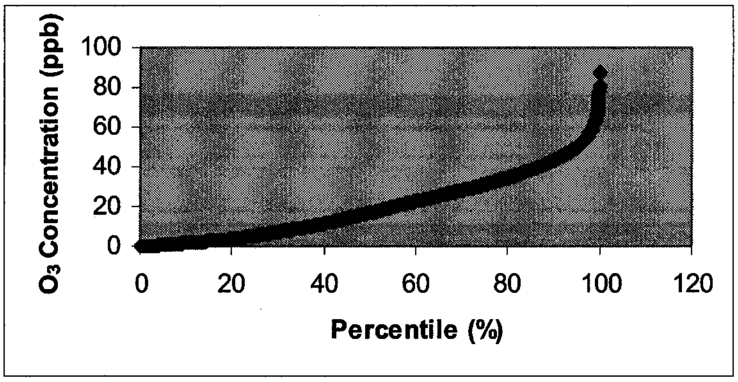
1997:

Median (ppb):	15
Max (ppb):	81
Min (ppb):	0
Average (ppb):	18.199
Completeness:	99.44%
Below Detection Limit:	7.64%



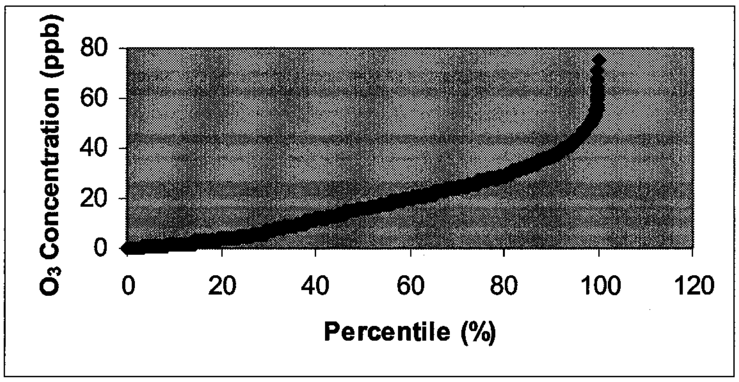
1998:

Median (ppb):	17
Max (ppb):	88
Min (ppb):	0
Average (ppb):	19.879
Completeness:	98.70%
Below Detection Limit:	3.77%



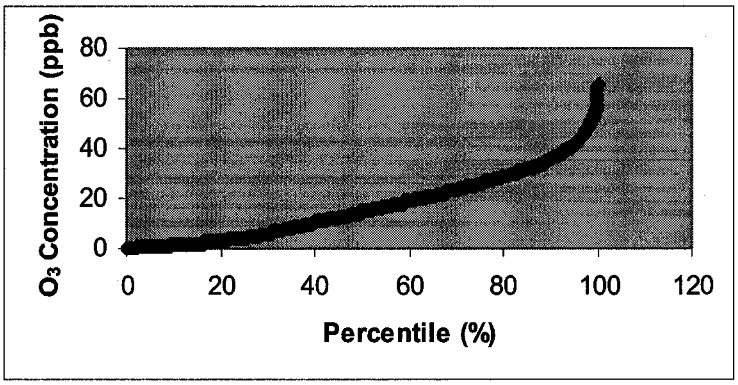
1999:

Median (ppb):	16
Max (ppb):	75
Min (ppb):	0
Average (ppb):	17.560
Completeness:	99.46%
Below Detection Limit:	3.34%



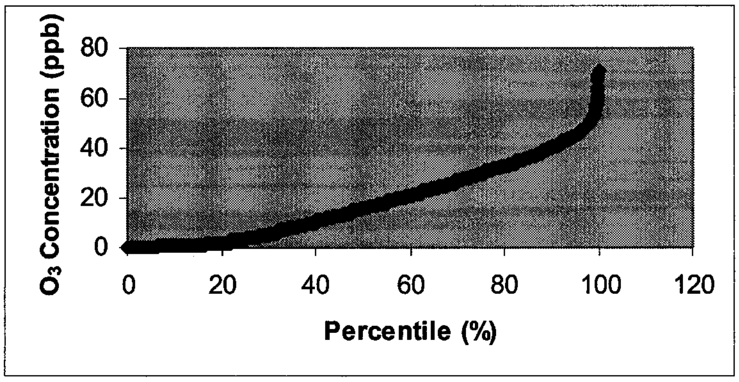
2000:

Median (ppb):	15
Max (ppb):	66
Min (ppb):	0
Average (ppb):	16.788
Completeness:	98.94%
Below Detection Limit:	2.17%



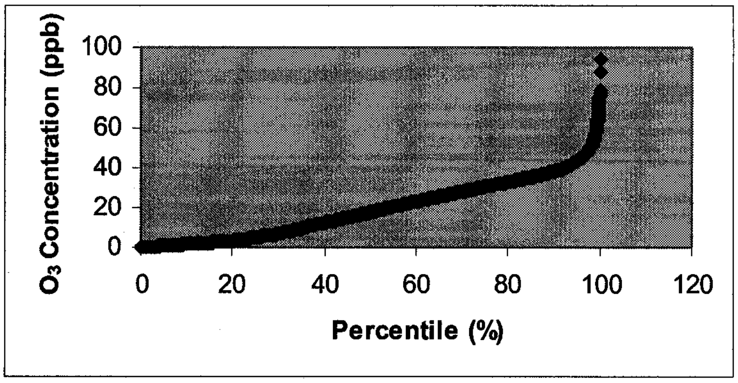
2001:

Median (ppb):	16
Max (ppb):	71
Min (ppb):	0
Average (ppb):	18.155
Completeness:	98.29%
Below Detection Limit:	6.31%



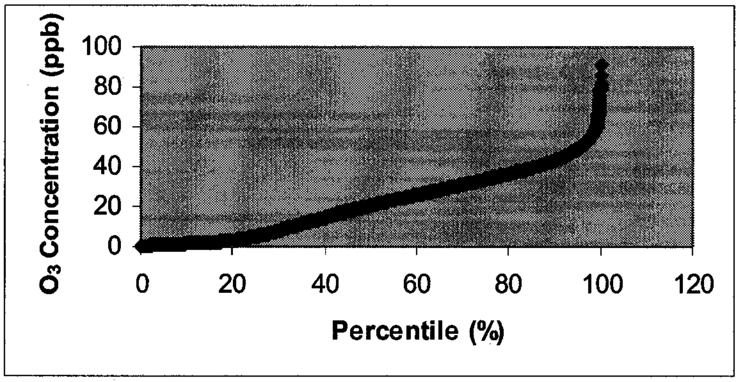
2002:

Median (ppb):	18
Max (ppb):	94
Min (ppb):	0
Average (ppb):	19.095
Completeness:	99.69%
Below Detection Limit:	3.96%



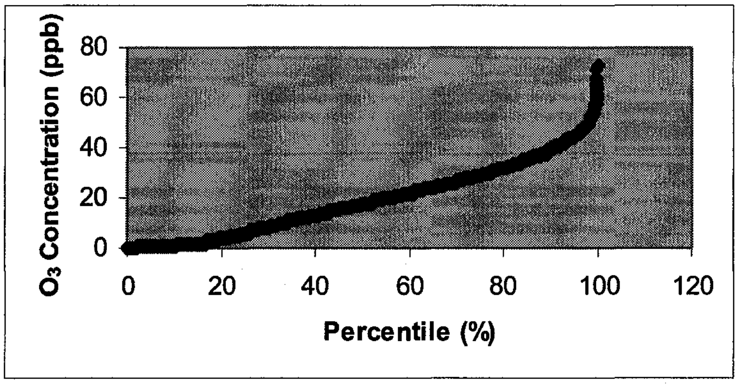
2003:

Median (ppb):	21
Max (ppb):	91
Min (ppb):	0
Average (ppb):	21.329
Completeness:	99.43%
Below Detection Limit:	2.27%



2004:

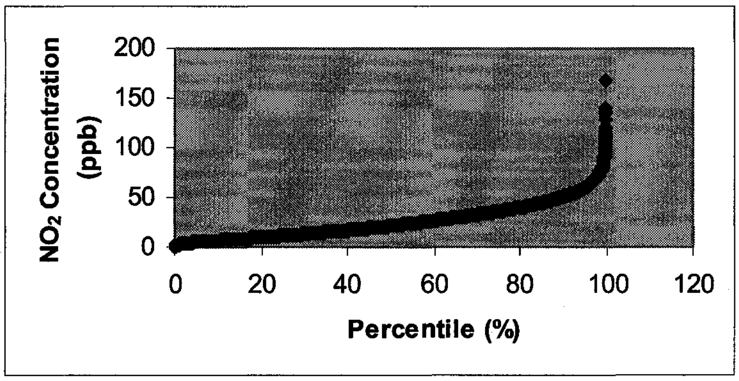
Median (ppb):	18
Max (ppb):	73
Min (ppb):	0
Average (ppb):	19.028
Completeness:	99.20%
Below Detection Limit:	2.08%



NO$_2$:

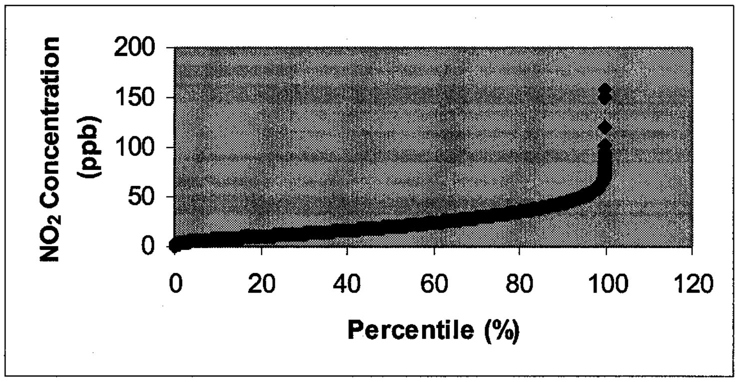
1997:

Median (ppb):	22
Max (ppb):	169
Min (ppb):	1
Average (ppb):	26.243
Completeness:	93.26%
Below Detection Limit:	0.00%



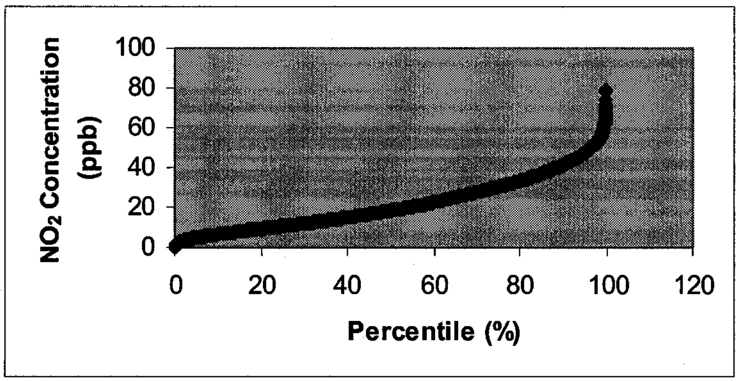
1998:

Median (ppb):	20
Max (ppb):	158
Min (ppb):	0
Average (ppb):	23.546
Completeness:	95.76%
Below Detection Limit:	0.08%



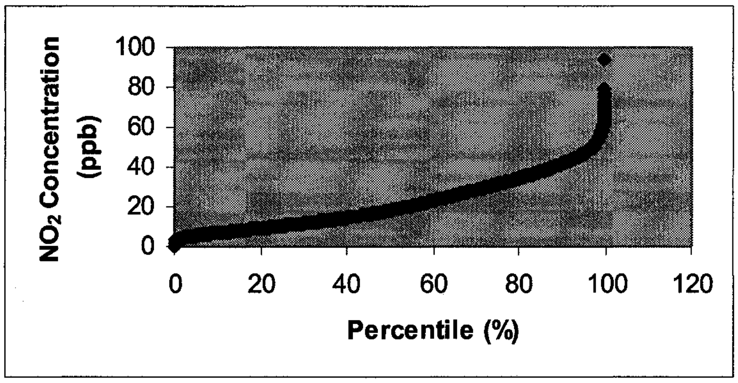
1999:

Median (ppb):	18
Max (ppb):	79
Min (ppb):	0
Average (ppb):	21.512
Completeness:	98.05%
Below Detection Limit:	0.01%



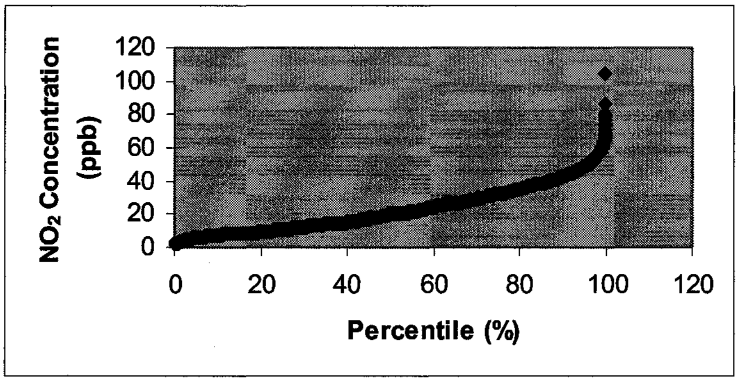
2000:

Median (ppb):	18
Max (ppb):	94
Min (ppb):	0
Average (ppb):	21.698
Completeness:	99.29%
Below Detection Limit:	0.01%



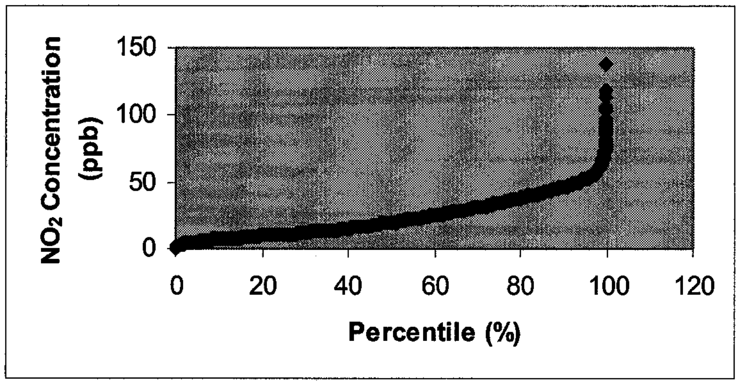
2001:

Median (ppb):	20
Max (ppb):	104
Min (ppb):	2
Average (ppb):	22.644
Completeness:	99.45%
Below Detection Limit:	0.00%



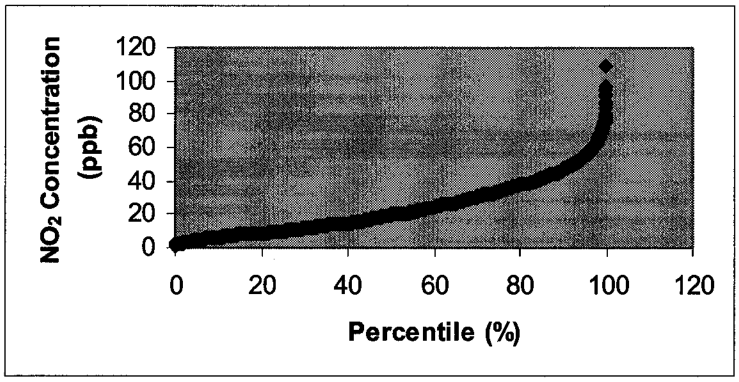
2002:

Median (ppb):	20
Max (ppb):	138
Min (ppb):	0
Average (ppb):	23.817
Completeness:	95.64%
Below Detection Limit:	0.09%



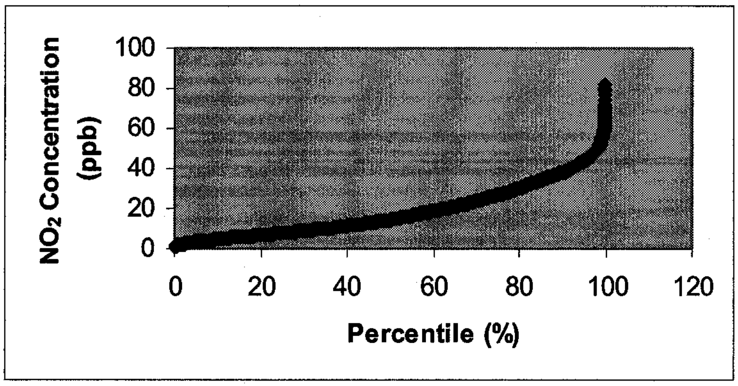
2003:

Median (ppb):	20
Max (ppb):	109
Min (ppb):	1
Average (ppb):	23.644
Completeness:	99.44%
Below Detection Limit:	0.00%



2004:

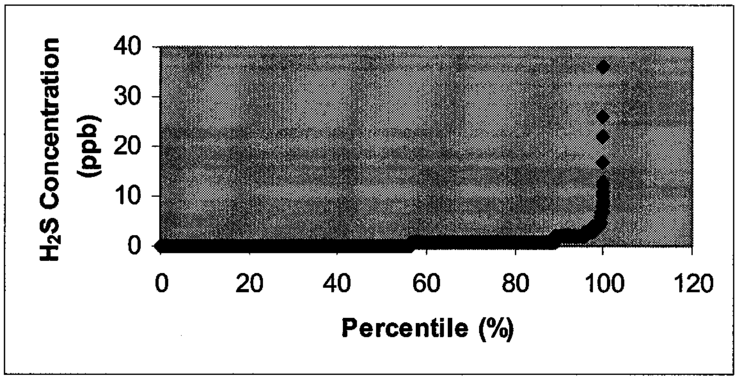
Median (ppb):	14
Max (ppb):	82
Min (ppb):	1
Average (ppb):	18.460
Completeness:	99.27%
Below Detection Limit:	0.00%



H_2S :

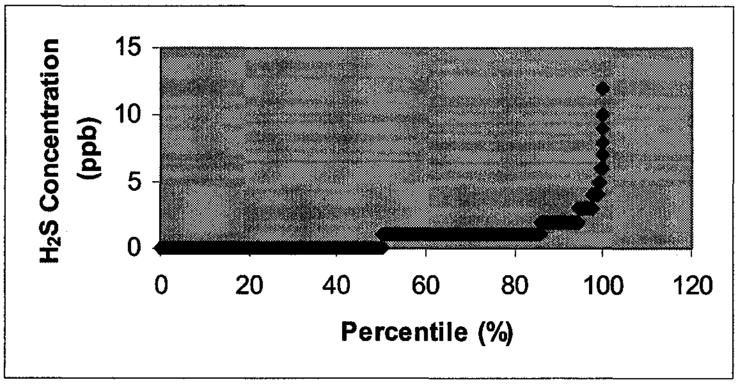
1997:

Median (ppb):	0
Max (ppb):	36
Min (ppb):	0
Average (ppb):	0.647
Completeness:	99.14%
Below Detection Limit:	55.75%



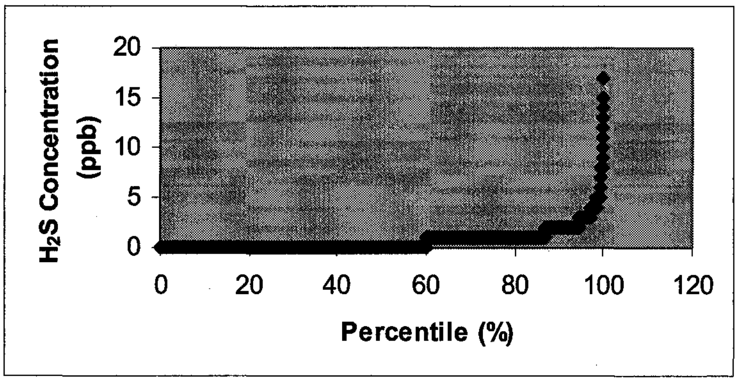
1998:

Median (ppb):	0
Max (ppb):	12
Min (ppb):	0
Average (ppb):	0.737
Completeness:	99.24%
Below Detection Limit:	49.78%



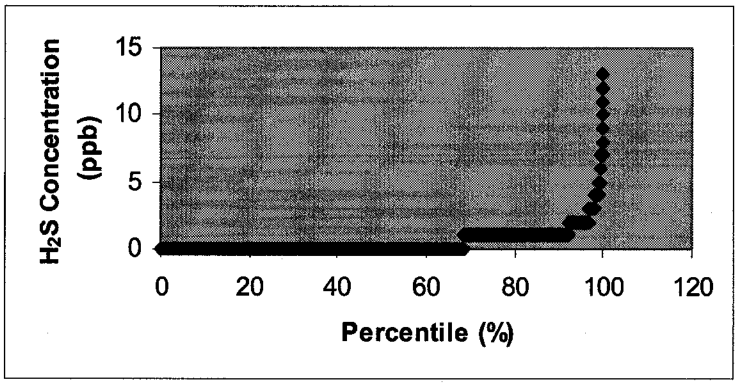
1999:

Median (ppb):	0
Max (ppb):	17
Min (ppb):	0
Average (ppb):	0.651
Completeness:	99.19%
Below Detection Limit:	59.50%



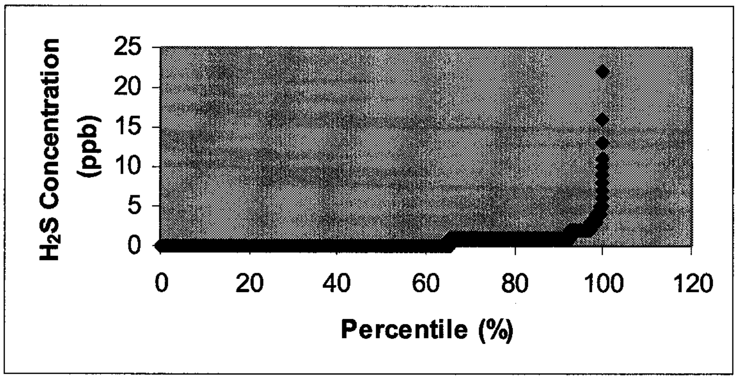
2000:

Median (ppb):	0
Max (ppb):	29
Min (ppb):	0
Average (ppb):	0.482
Completeness:	99.49%
Below Detection Limit:	68.33%



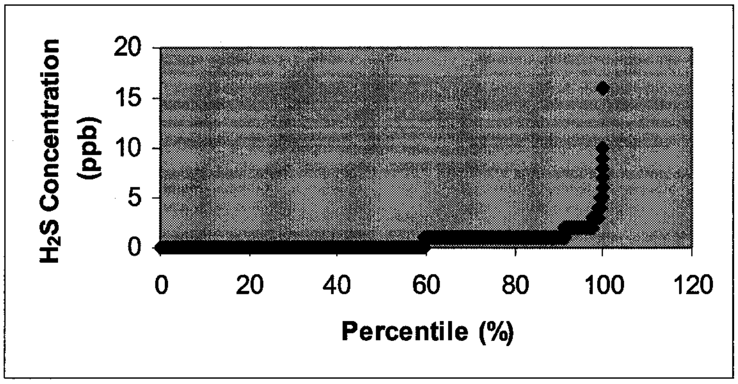
2001:

Median (ppb):	0
Max (ppb):	22
Min (ppb):	0
Average (ppb):	0.473
Completeness:	99.65%
Below Detection Limit:	65.34%



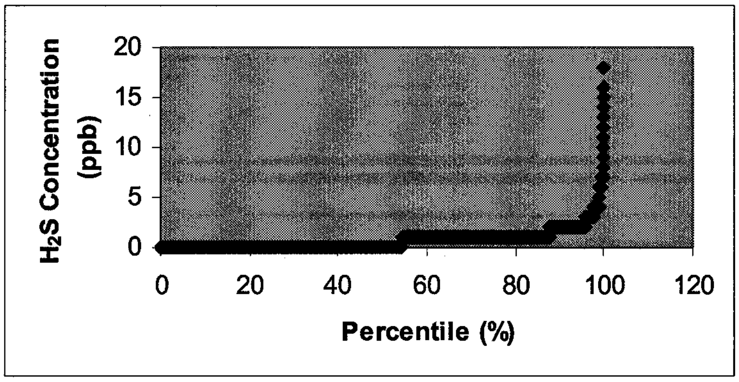
2002:

Median (ppb):	0
Max (ppb):	16
Min (ppb):	0
Average (ppb):	0.536
Completeness:	99.38%
Below Detection Limit:	59.14%



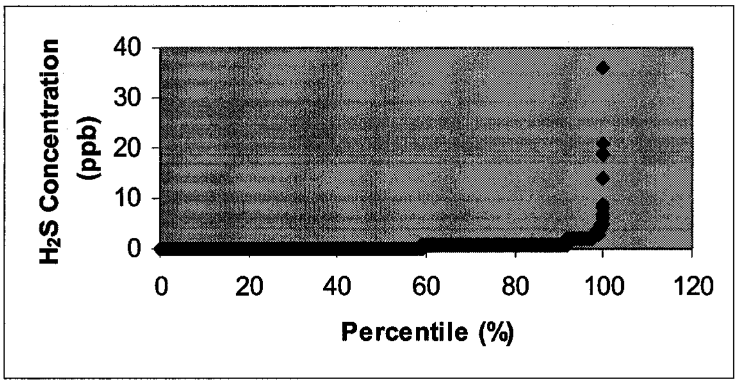
2003:

Median (ppb):	0
Max (ppb):	18
Min (ppb):	0
Average (ppb):	0.684
Completeness:	99.59%
Below Detection Limit:	54.18%



2004:

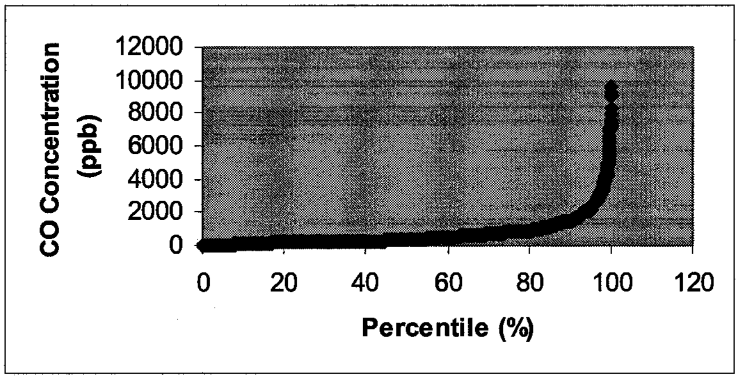
Median (ppb):	0
Max (ppb):	36
Min (ppb):	0
Average (ppb):	0.546
Completeness:	98.79%
Below Detection Limit:	58.21%



CO:

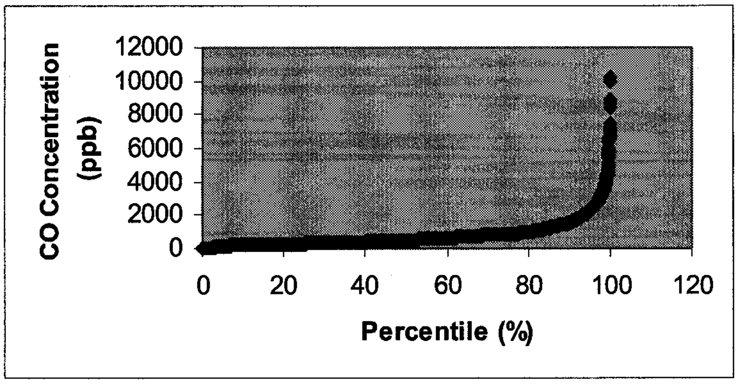
1997:

Median (ppb):	400
Max (ppb):	9600
Min (ppb):	0
Average (ppb):	669.738
Completeness:	98.11%
Below Detection Limit:	7.81%



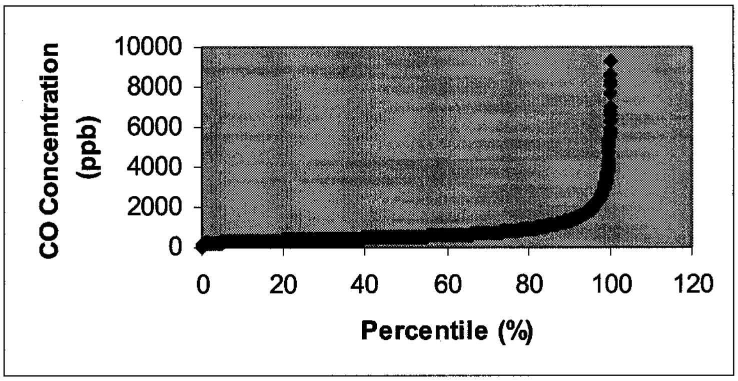
1998:

Median (ppb):	500
Max (ppb):	10200
Min (ppb):	0
Average (ppb):	764.779
Completeness:	98.74%
Below Detection Limit:	2.95%



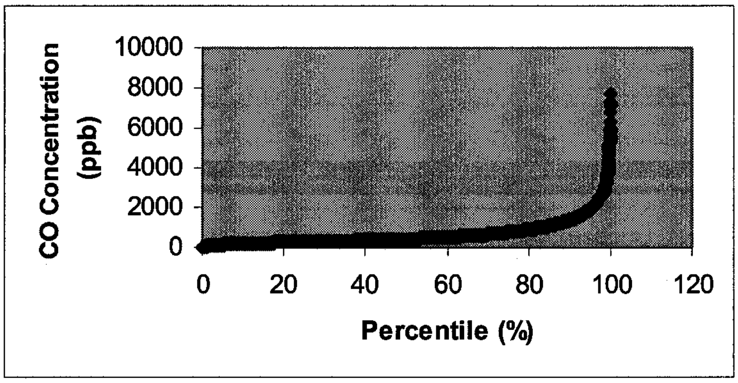
1999:

Median (ppb):	500
Max (ppb):	9300
Min (ppb):	0
Average (ppb):	707.758
Completeness:	99.61%
Below Detection Limit:	0.05%



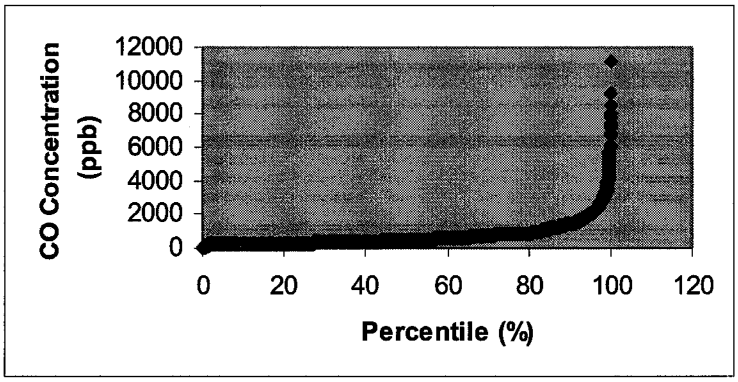
2000:

Median (ppb):	400
Max (ppb):	7700
Min (ppb):	0
Average (ppb):	648.536
Completeness:	99.16%
Below Detection Limit:	1.13%



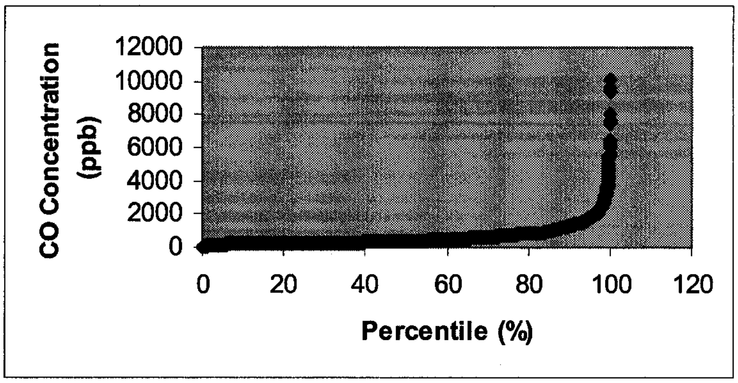
2001:

Median (ppb):	500
Max (ppb):	11200
Min (ppb):	0
Average (ppb):	717.396
Completeness:	98.29%
Below Detection Limit:	0.53%



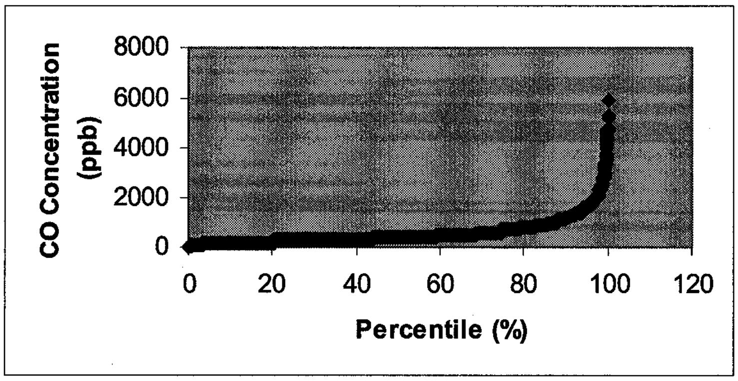
2002:

Median (ppb):	400
Max (ppb):	10100
Min (ppb):	0
Average (ppb):	615.166
Completeness:	98.89%
Below Detection Limit:	0.95%



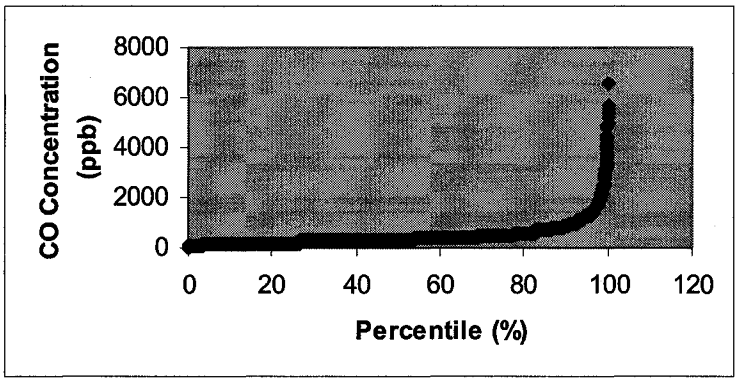
2003:

Median (ppb):	400
Max (ppb):	5900
Min (ppb):	0
Average (ppb):	573.179
Completeness:	99.50%
Below Detection Limit:	0.31%



2004:

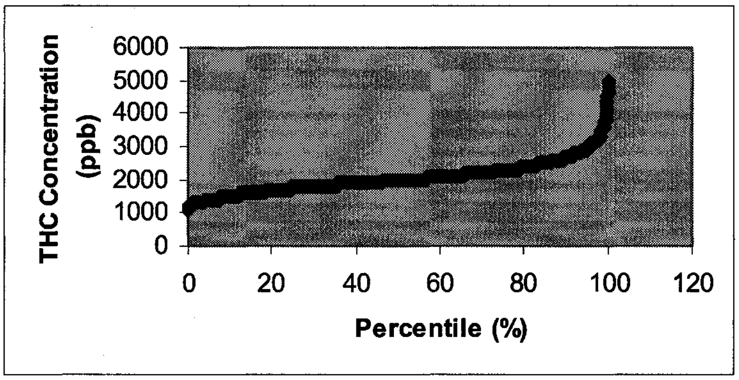
Median (ppb):	300
Max (ppb):	6600
Min (ppb):	0
Average (ppb):	476.825
Completeness:	99.32%
Below Detection Limit:	0.01%



THC:

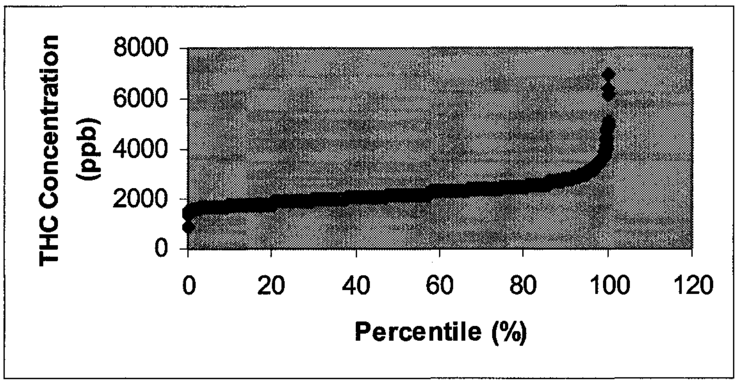
1997:

Median (ppb):	2000
Max (ppb):	5000
Min (ppb):	1100
Average (ppb):	2054.888
Completeness:	97.84%
Below Detection Limit:	0.00%



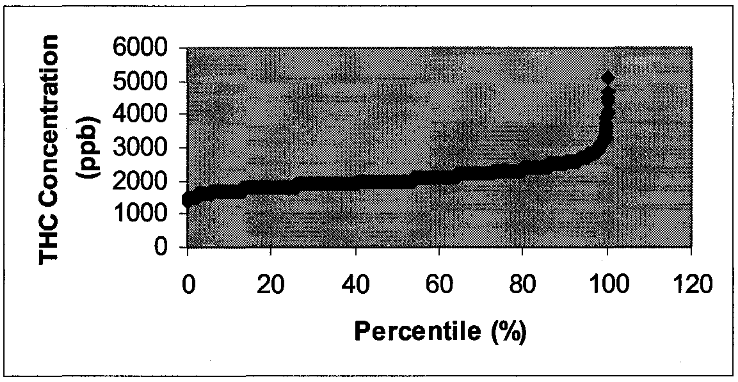
1998:

Median (ppb):	2200
Max (ppb):	7000
Min (ppb):	900
Average (ppb):	2237.579
Completeness:	98.14%
Below Detection Limit:	0.00%



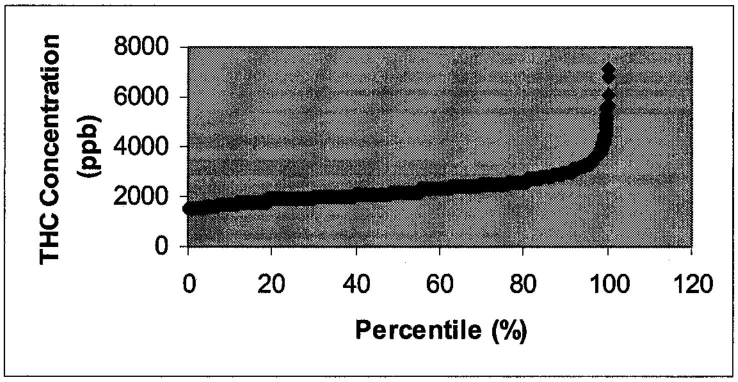
1999:

Median (ppb):	2000
Max (ppb):	5100
Min (ppb):	1400
Average (ppb):	2086.838
Completeness:	95.48%
Below Detection Limit:	0.00%



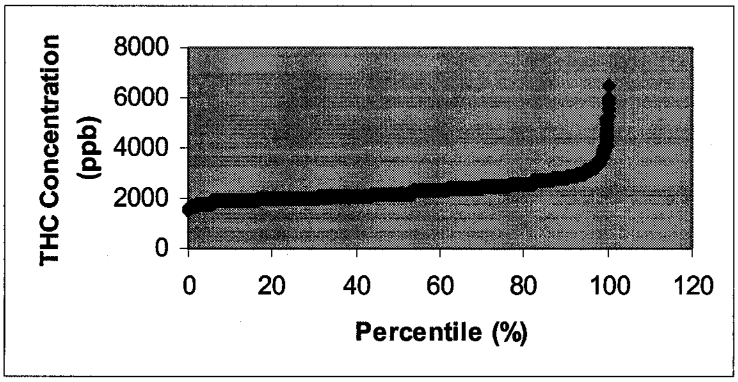
2000:

Median (ppb):	2200
Max (ppb):	7100
Min (ppb):	1500
Average (ppb):	2283.728
Completeness:	95.77%
Below Detection Limit:	0.00%



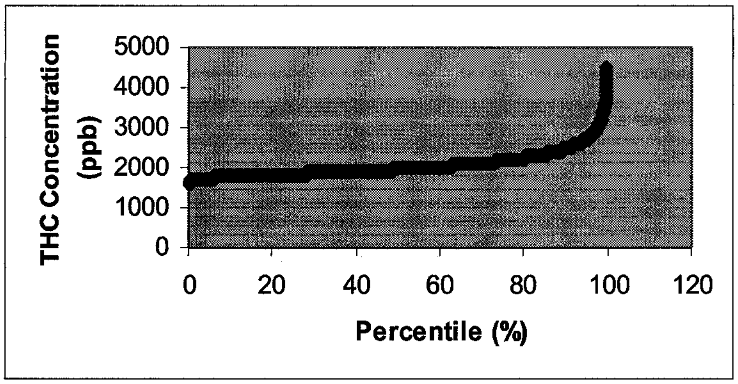
2001:

Median (ppb):	2200
Max (ppb):	6500
Min (ppb):	1500
Average (ppb):	2314.512
Completeness:	99.34%
Below Detection Limit:	0.00%



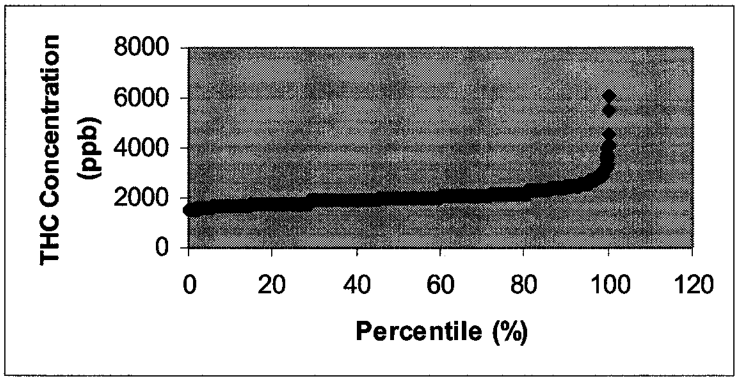
2002:

Median (ppb):	2000
Max (ppb):	6500
Min (ppb):	1600
Average (ppb):	2061.744
Completeness:	99.77%
Below Detection Limit:	0.00%



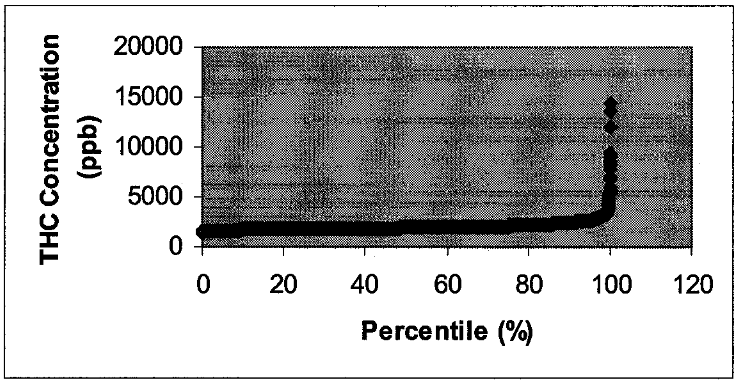
2003:

Median (ppb):	2000
Max (ppb):	6100
Min (ppb):	1500
Average (ppb):	2036.797
Completeness:	98.42%
Below Detection Limit:	0.00%



2004:

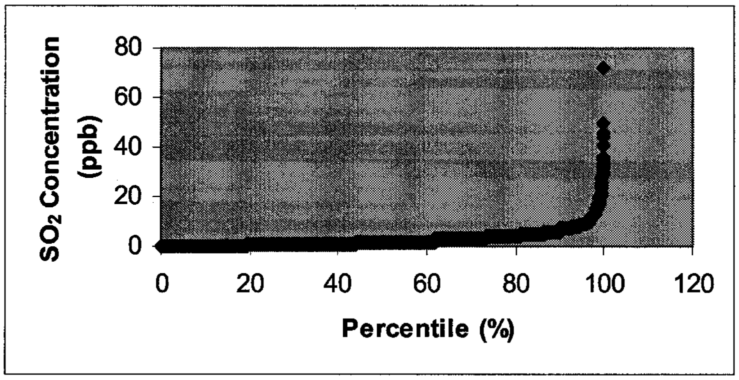
Median (ppb):	2000
Max (ppb):	14500
Min (ppb):	1500
Average (ppb):	2058.029
Completeness:	99.24%
Below Detection Limit:	0.00%



SO_2 (EdmontonEast):

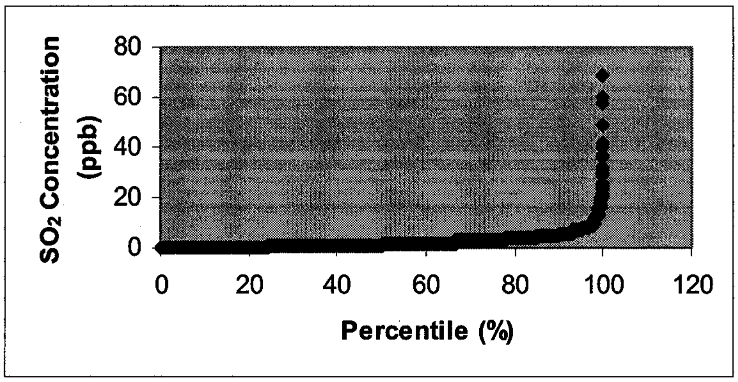
1997:

Median (ppb):	2
Max (ppb):	72
Min (ppb):	0
Average (ppb):	2.877
Completeness:	99.21%
Below Detection Limit:	18.95%



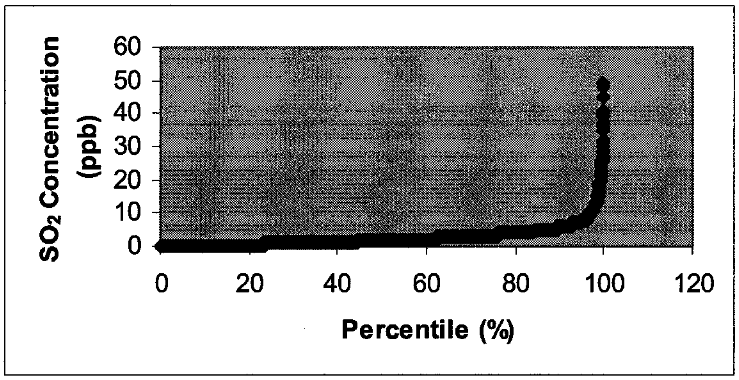
1998:

Median (ppb):	1
Max (ppb):	69
Min (ppb):	0
Average (ppb):	2.378
Completeness:	99.21%
Below Detection Limit:	24.19%



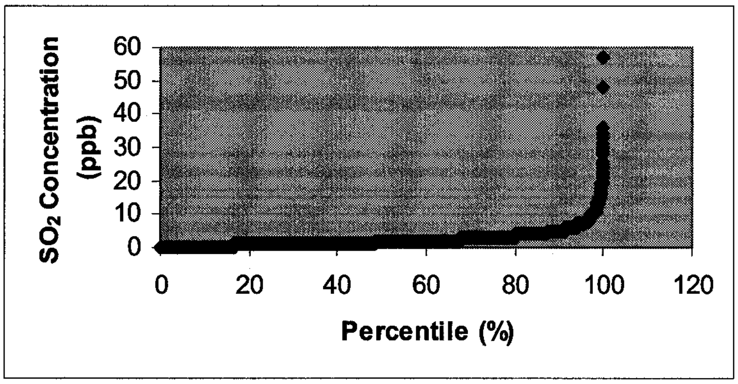
1999:

Median (ppb):	2
Max (ppb):	49
Min (ppb):	0
Average (ppb):	2.603
Completeness:	99.37%
Below Detection Limit:	23.21%



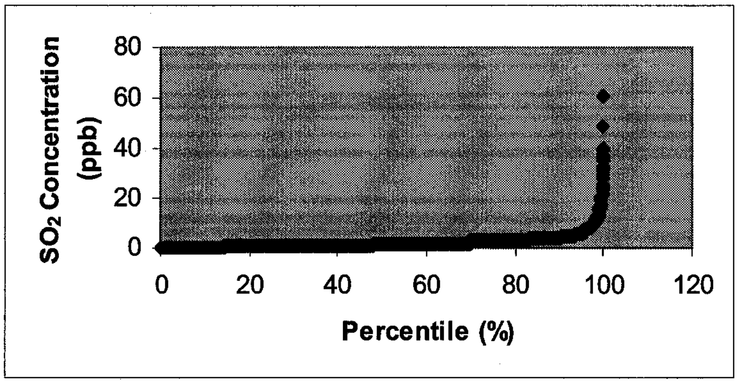
2000:

Median (ppb):	2
Max (ppb):	57
Min (ppb):	0
Average (ppb):	2.373
Completeness:	99.20%
Below Detection Limit:	16.62%



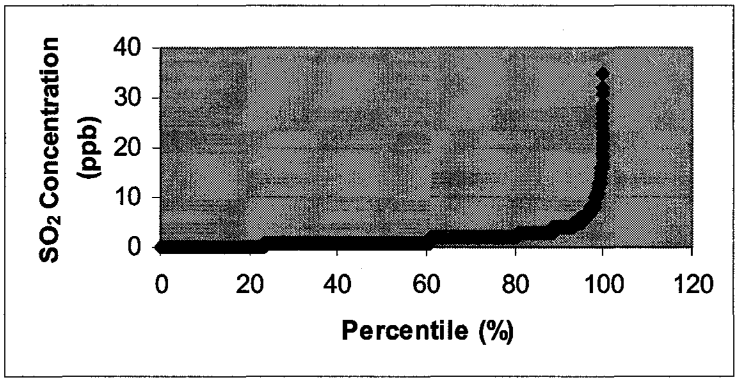
2001:

Median (ppb):	2
Max (ppb):	61
Min (ppb):	0
Average (ppb):	2.281
Completeness:	99.67%
Below Detection Limit:	14.22%



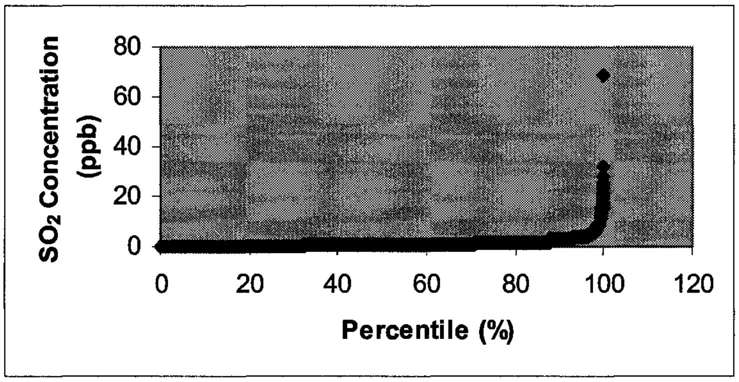
2002:

Median (ppb):	1
Max (ppb):	35
Min (ppb):	0
Average (ppb):	1.764
Completeness:	99.67%
Below Detection Limit:	23.31%



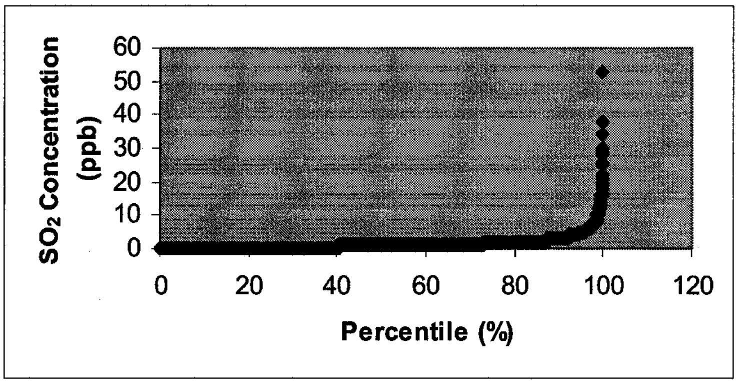
2003:

Median (ppb):	1
Max (ppb):	69
Min (ppb):	0
Average (ppb):	1.341
Completeness:	99.57%
Below Detection Limit:	32.17%



2004:

Median (ppb):	1
Max (ppb):	53
Min (ppb):	0
Average (ppb):	1.310
Completeness:	97.60%
Below Detection Limit:	39.48%

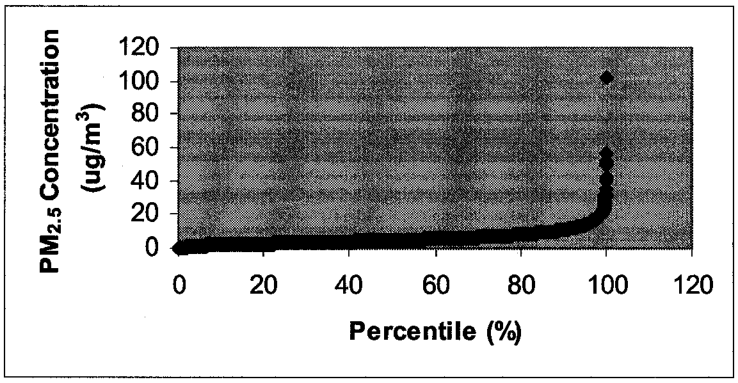


Appendix 2. Raw Data Statistics and Percentile Distribution Curves of Annual Hourly Data of Fort McKay

$PM_{2.5}$ (µg/m^3):

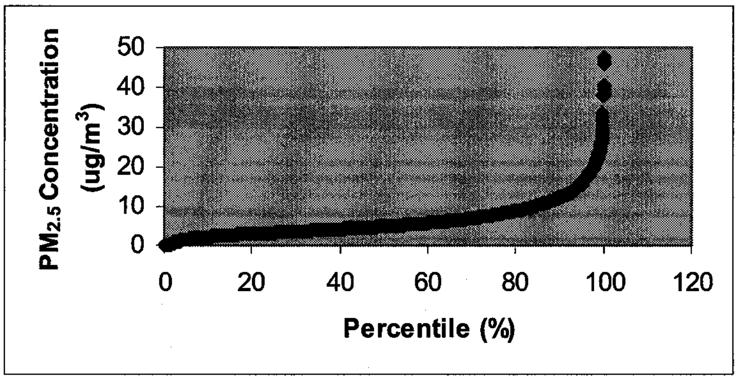
1999:

Median (µg/m^3):	4.8
Max (µg/m^3):	101.5
Min (µg/m^3):	0
Average (µg/m^3):	5.888
Completeness:	97.34%
Below Detection Limit:	0.98%



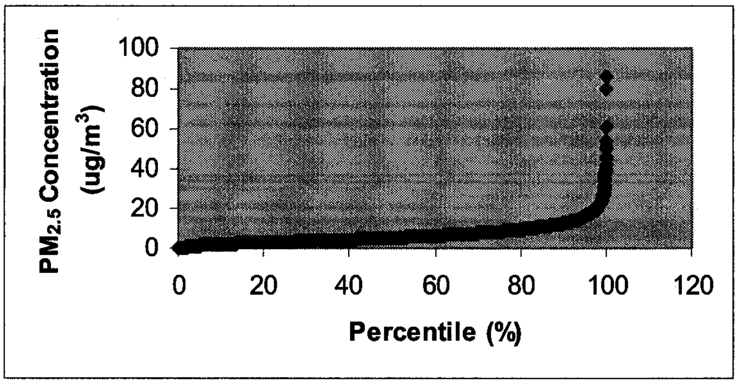
2000:

Median (µg/m^3):	4.9
Max (µg/m^3):	47.6
Min (µg/m^3):	0
Average (µg/m^3):	6.259
Completeness:	98.82%
Below Detection Limit:	0.99%



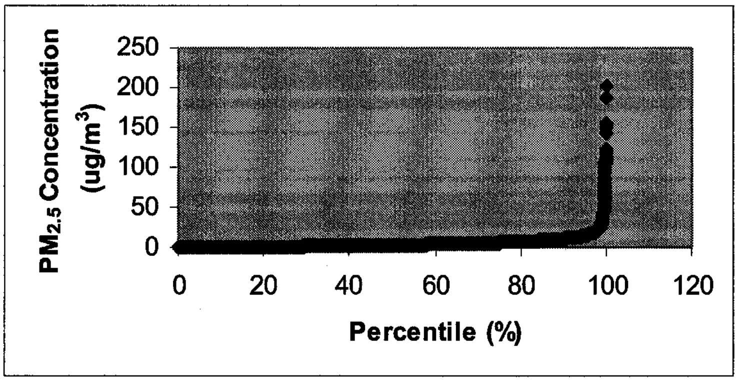
2001:

Median (μg/m^3):	5.3
Max (μg/m^3):	86.4
Min (μg/m^3):	0
Average (μg/m^3):	6.612
Completeness:	98.56%
Below Detection Limit:	1.10%



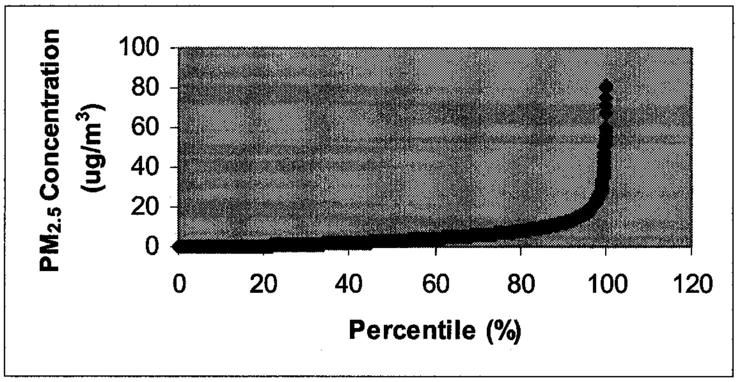
2002:

Median (μg/m^3):	3
Max (μg/m^3):	203.5
Min (μg/m^3):	0
Average (μg/m^3):	4.955
Completeness:	95.07%
Below Detection Limit:	13.20%



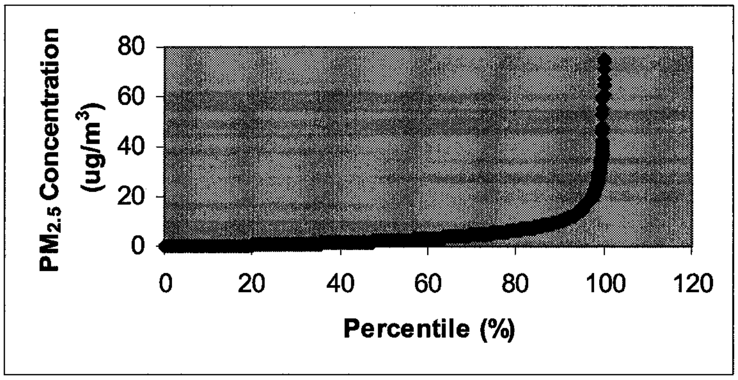
2003:

Median (μg/m³):	3.1
Max (μg/m³):	80.9
Min (μg/m³):	0
Average (μg/m³):	4.993
Completeness:	97.15%
Below Detection Limit:	15.42%



2004:

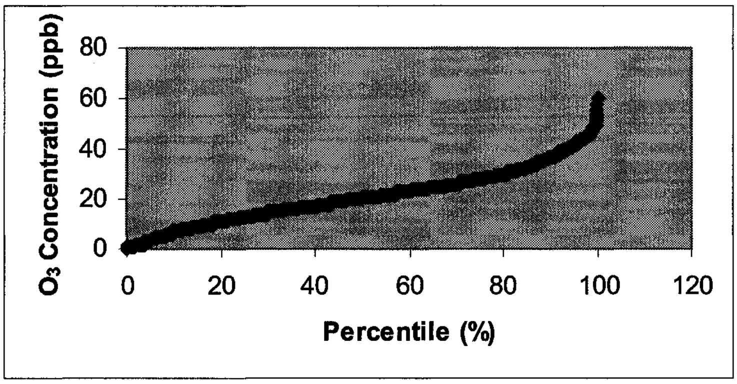
Median (μg/m³):	2.2
Max (μg/m³):	74.9
Min (μg/m³):	0
Average (μg/m³):	4.207
Completeness:	98.58%
Below Detection Limit:	6.63%



O_3:

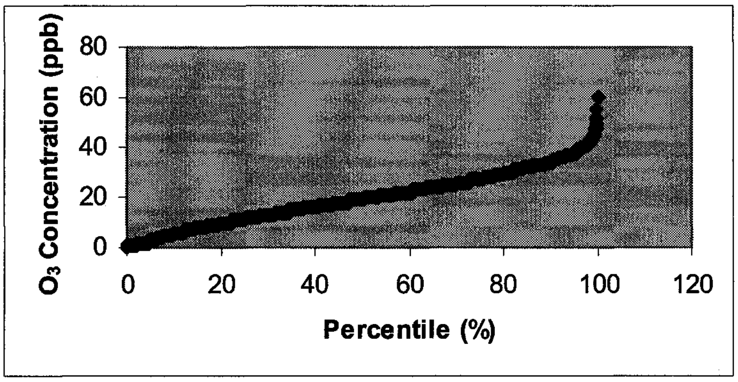
1999:

Median (ppb):	20
Max (ppb):	60
Min (ppb):	0
Average (ppb):	21.032
Completeness:	94.49%
Below Detection Limit:	0.01%



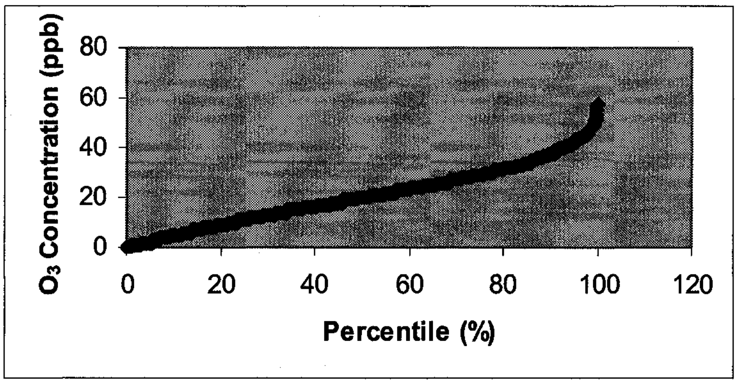
2000:

Median (ppb):	19
Max (ppb):	60
Min (ppb):	0
Average (ppb):	19.742
Completeness:	94.84%
Below Detection Limit:	0.08%



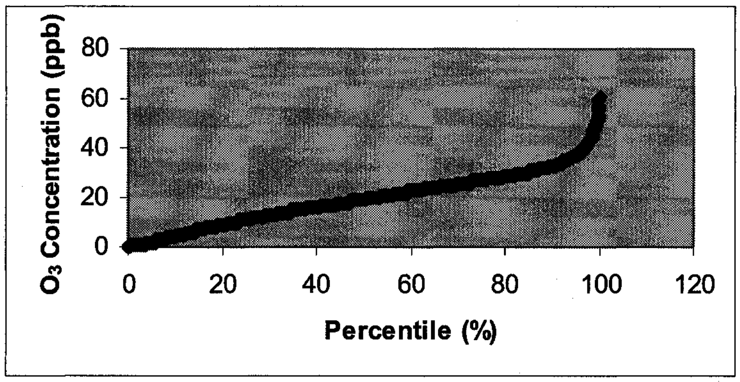
2001:

Median (ppb):	20
Max (ppb):	58
Min (ppb):	0
Average (ppb):	20.662
Completeness:	94.60%
Below Detection Limit:	0.98%



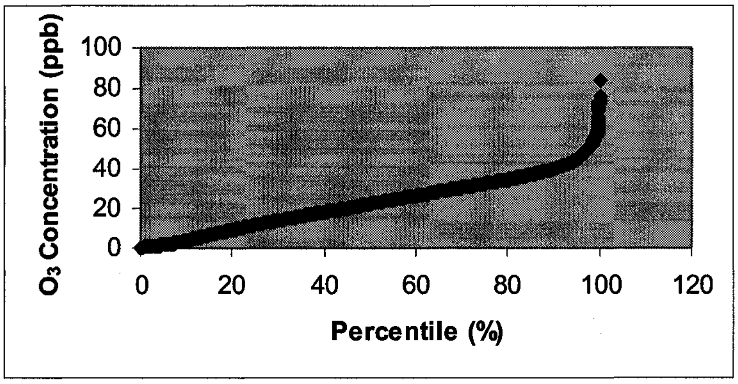
2002:

Median (ppb):	19
Max (ppb):	61
Min (ppb):	0
Average (ppb):	19.455
Completeness:	94.77%
Below Detection Limit:	0.34%



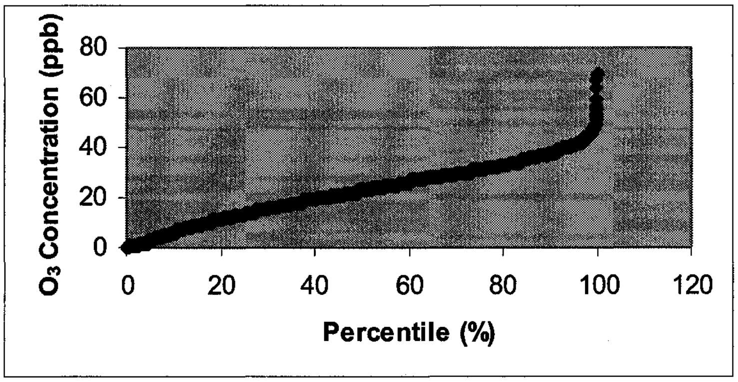
2003:

Median (ppb):	22
Max (ppb):	84
Min (ppb):	0
Average (ppb):	22.581
Completeness:	94.53%
Below Detection Limit:	0.61%



2004:

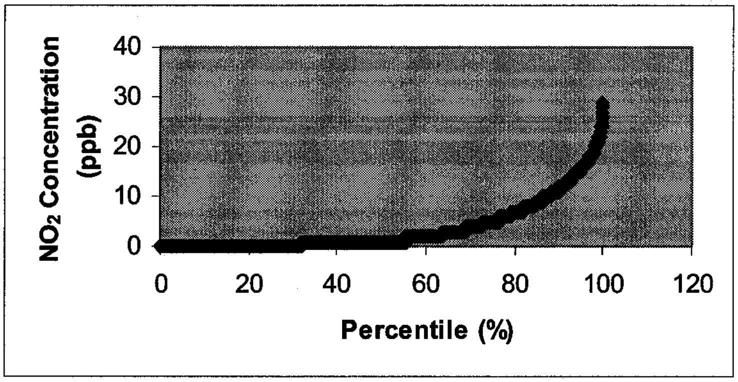
Median (ppb):	23
Max (ppb):	70
Min (ppb):	0
Average (ppb):	22.466
Completeness:	95.05%
Below Detection Limit:	0.24%



NO_2:

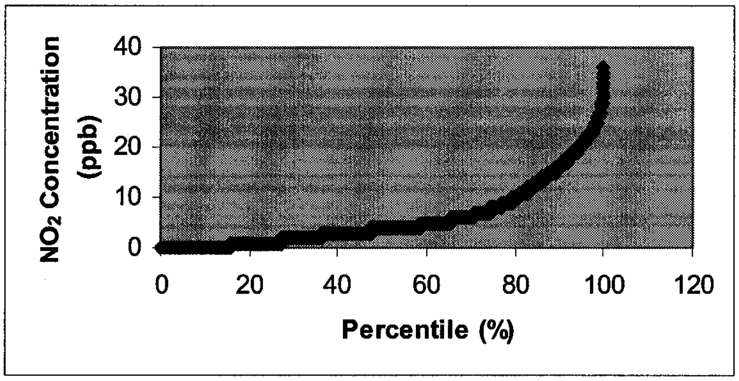
1999:

Median (ppb):	1
Max (ppb):	29
Min (ppb):	0
Average (ppb):	3.637
Completeness:	91.26%
Below Detection Limit:	29.20%



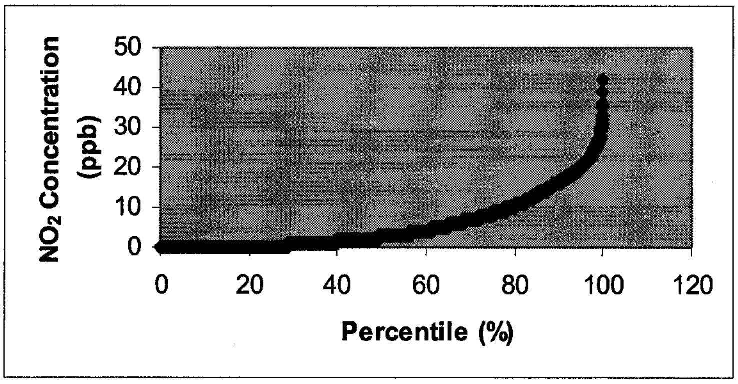
2000:

Median (ppb):	4
Max (ppb):	36
Min (ppb):	0
Average (ppb):	5.892
Completeness:	93.98%
Below Detection Limit:	14.53%



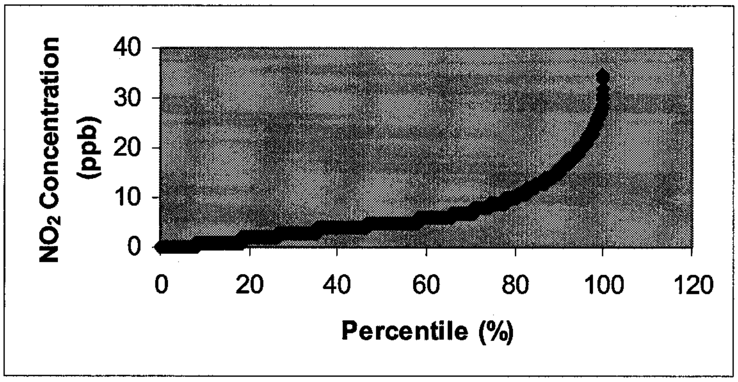
2001:

Median (ppb):	3
Max (ppb):	42
Min (ppb):	0
Average (ppb):	5.484
Completeness:	93.86%
Below Detection Limit:	26.78%



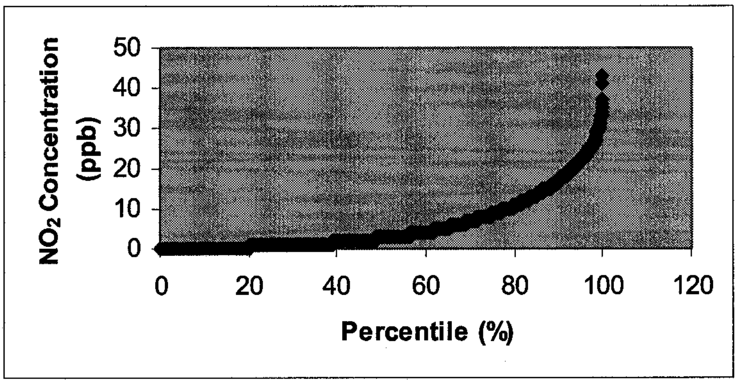
2002:

Median (ppb):	5
Max (ppb):	35
Min (ppb):	0
Average (ppb):	6.530
Completeness:	94.20%
Below Detection Limit:	7.53%



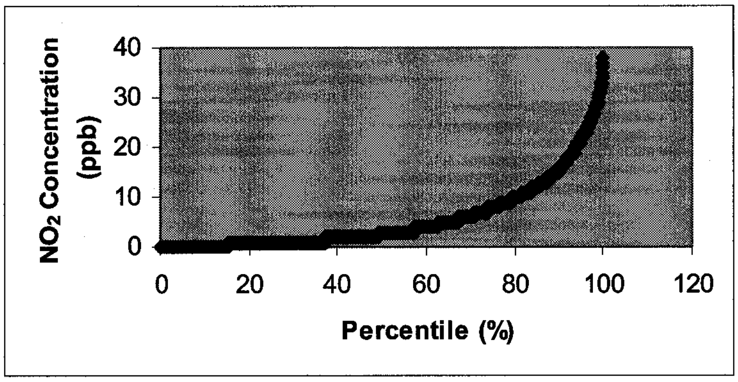
2003:

Median (ppb):	3
Max (ppb):	43
Min (ppb):	0
Average (ppb):	5.815
Completeness:	93.23%
Below Detection Limit:	18.90%



2004:

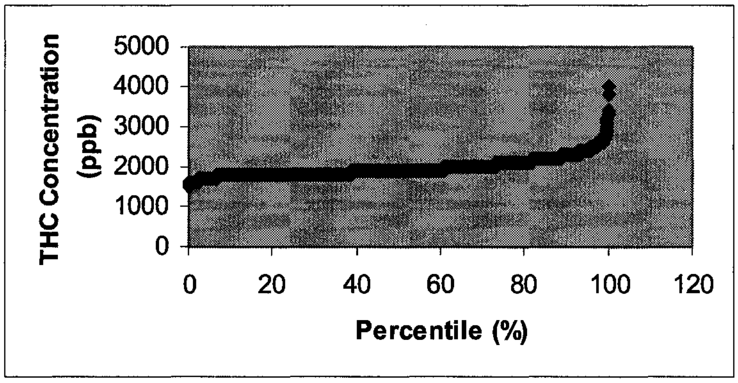
Median (ppb):	3
Max (ppb):	38
Min (ppb):	0
Average (ppb):	5.617
Completeness:	92.05%
Below Detection Limit:	14.07%



THC :

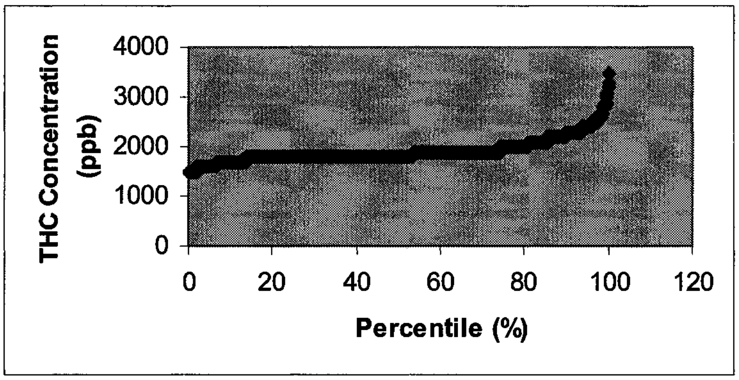
1999:

Median (ppb):	1900
Max (ppb):	4000
Min (ppb):	1500
Average (ppb):	1965.631
Completeness:	93.36%
Below Detection Limit:	0.00%



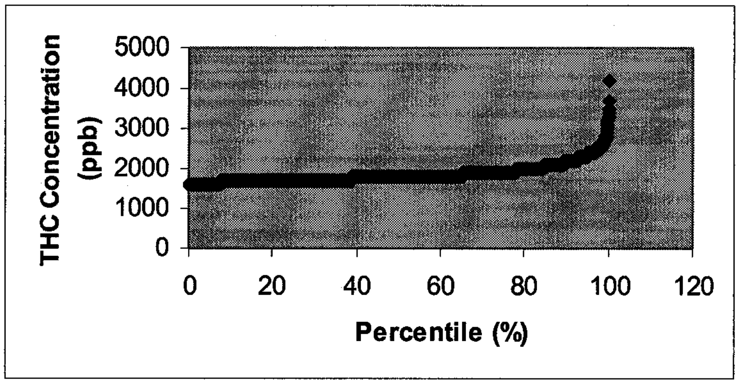
2000:

Median (ppb):	1800
Max (ppb):	3500
Min (ppb):	1500
Average (ppb):	1912.345
Completeness:	92.49%
Below Detection Limit:	0.00%



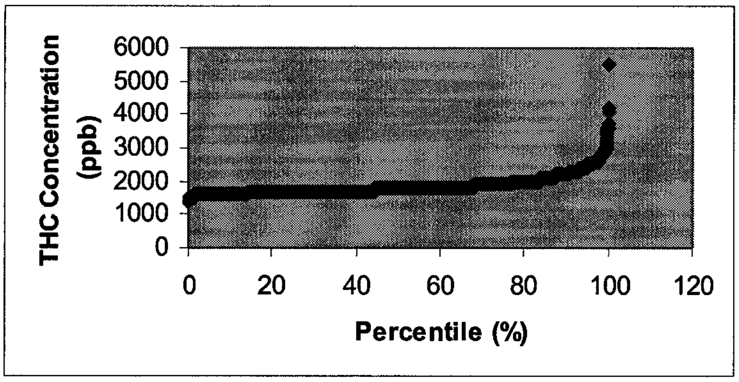
2001:

Median (ppb):	1800
Max (ppb):	4200
Min (ppb):	1600
Average (ppb):	1858.043
Completeness:	94.16%
Below Detection Limit:	0.00%



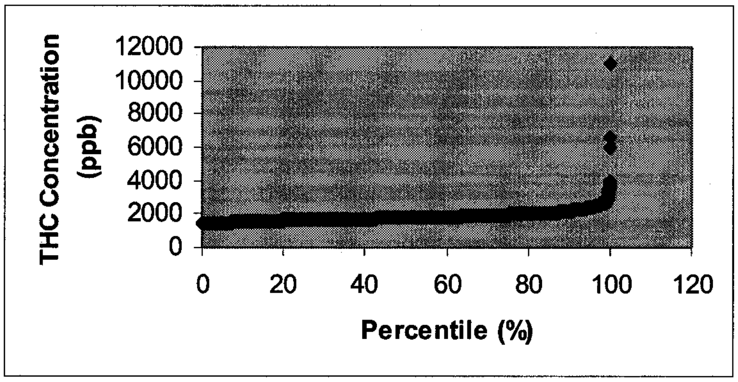
2002:

Median (ppb):	1800
Max (ppb):	5500
Min (ppb):	1400
Average (ppb):	1856.229
Completeness:	94.55%
Below Detection Limit:	0.00%



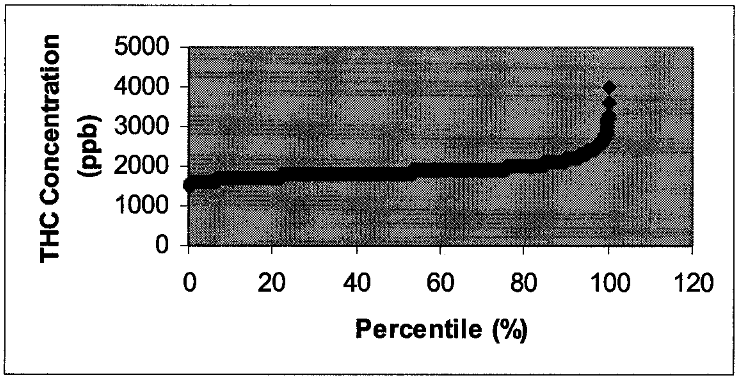
2003:

Median (ppb):	1800
Max (ppb):	11100
Min (ppb):	1400
Average (ppb):	1848.994
Completeness:	94.19%
Below Detection Limit:	0.00%



2004:

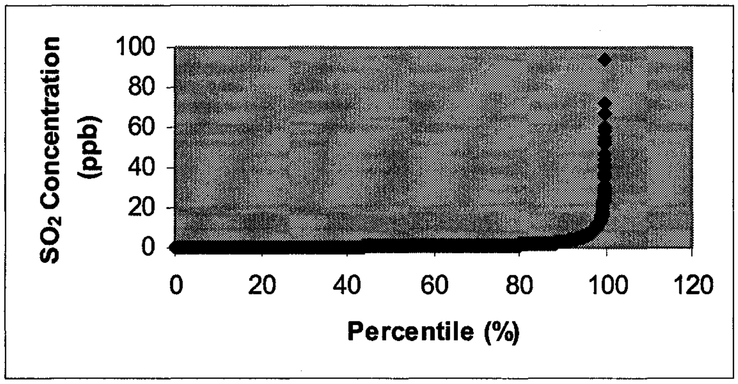
Median (ppb):	1800
Max (ppb):	4000
Min (ppb):	1500
Average (ppb):	1888.367
Completeness:	94.72%
Below Detection Limit:	0.00%



SO_2:

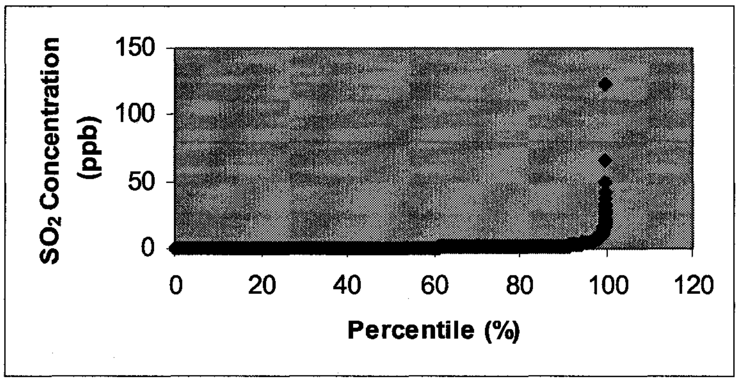
1999:

Median (ppb):	1
Max (ppb):	94
Min (ppb):	0
Average (ppb):	1.418
Completeness:	94.10%
Below Detection Limit:	41.05%



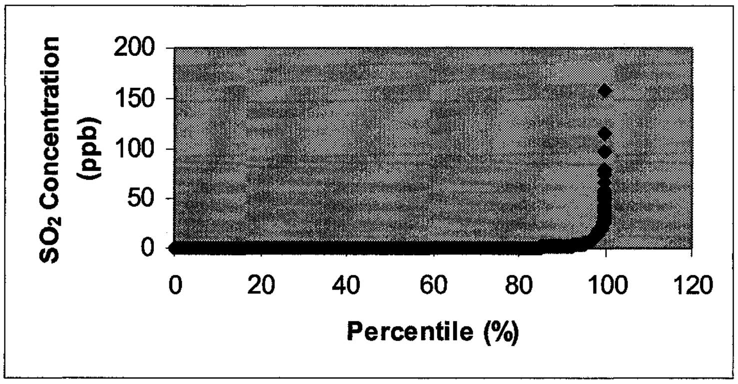
2000:

Median (ppb):	0
Max (ppb):	123
Min (ppb):	0
Average (ppb):	0.931
Completeness:	94.13%
Below Detection Limit:	57.50%



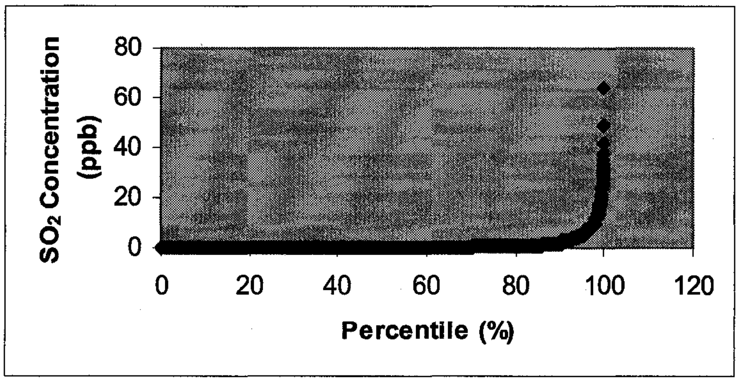
2001:

Median (ppb):	0
Max (ppb):	158
Min (ppb):	0
Average (ppb):	1.210
Completeness:	94.67%
Below Detection Limit:	64.91%



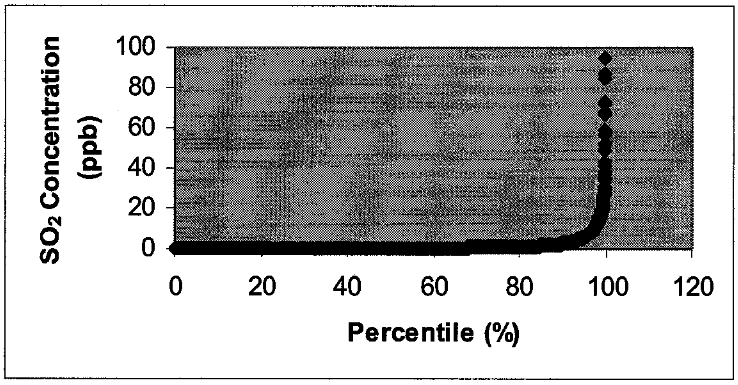
2002:

Median (ppb):	0
Max (ppb):	64
Min (ppb):	0
Average (ppb):	1.011
Completeness:	94.71%
Below Detection Limit:	66.58%



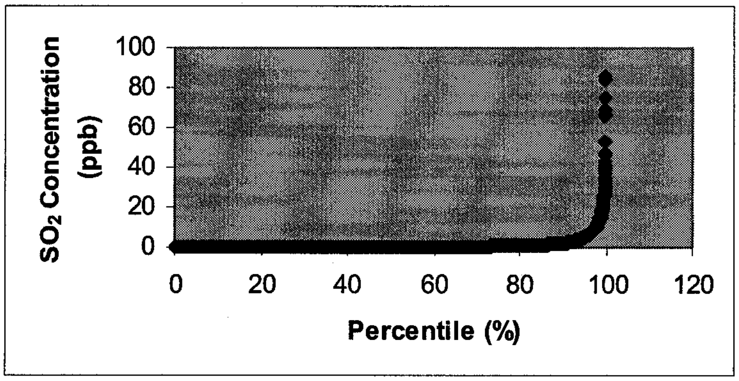
2003:

Median (ppb):	0
Max (ppb):	95
Min (ppb):	0
Average (ppb):	1.192
Completeness:	94.29%
Below Detection Limit:	64.28%



2004:

Median (ppb):	0
Max (ppb):	86
Min (ppb):	0
Average (ppb):	1.068
Completeness:	94.55%
Below Detection Limit:	69.00%



Appendix 3.Calculation Procedure Summary of Regression, Mann-Kendall Test and Sen's Test

A3.1 Regression

1. Simple linear regression

   In the simple linear regression model, the dependent variable (response) is related to only one independent variable (regressor), as $Y=\beta_0+\beta_1X+\varepsilon$, (24)

   where ε is the random error term, the parameters β_0 and $\beta_1$are regression coefficients (Montgomery, 2004).

2. Multiple linear regression

   In a multiple linear regression model, the dependent variable (response) is related to k independent variables (regressors), as $Y=\beta_0+\beta_1X+\beta_2X_2+\ldots+\beta_kX_k+\varepsilon$, (25)

   where ε is the random error term, the parameters β_j ($j=0,1,2,\ldots,k$)are regression coefficients (Montgomery, 2004).

3. High order linear Regression (2nd Order and 3rd Order Polynomial Regression)

   The polynomial regression such as second-order regression and the cubic regression can also be considered and analyzed as a multiple linear regression. The 2nd Order and 3rd Order Polynomial Regression have the equation forms as follows respectively, $Y= a+bX+cX^2$ and $Y= a+bX+cX^2+dX^3$ (Montgomery, 2004).

   For fitting a polynomial regression, a calculation should be made to reduce the multicollinearity in the data to obtain more reliable and precise coefficients estimations. In this calculation, each observation is subtracted the average value of each corresponding regressor respectively (centering the regressors) and then these centered regressors are used to obtain the corresponding terms in the model (Gibbons and Coleman, 2001).

4. Regression coefficients estimation by least squares method

   Many computer software such as Excel, Minitab, Matlab, S-Plus, etc., can be used to estimate regression coefficients for fitting a regression model based on the least squares method (Montgomery, 2004).

5. Testing hypotheses in simple linear regression and multiple linear regression by t-test

For testing the null hypothesis that the slope β_1 equals a constant $\beta_{1,0}$, the appropriate hypotheses are: H_0: $\beta_1= \beta_{1,0}$
H1: $\beta_1\neq \beta_{1,0}$

The criterion for rejecting H_0 is: $|T_0|>T_{\alpha/2,n-2}$, where $T_0=(\beta_1\hat{}-\beta_{1,0})/stv(\beta_1\hat{})$ and standard deviation (stv) $\beta_1\hat{}=(\sigma^2/S_{xx})^{1/2}$
(Montgomery, 2004).
A specific case of the hypotheses are: H_0: $\beta_1=0$ and H_1: $\beta_1\neq0$. For this type of hypothesis and simultaneously at the linear regression situation, rejecting H_0 can mean either that the straight-line model is adequate, or that the addition of higher order polynomial terms in X should give better results though there is a linear effect of X,. Failure to reject H_0 leads to the conclusion that there is no linear relationship between X and Y. That is to say, X is of little value in explaining the variation in Y, and the best estimator of Y for any X is $Y\hat{}=Y^{-}$, where $Y\hat{}$ and Y^{-} is the model prediction value and average value of Y, respectively; or the true relationship between X and Y is not linear (Montgomery, 2004).

6. Testing hypotheses in simple linear regression and multiple linear regression by ANOVA

The analysis of variance (ANOVA) partitions the Total Sum of Squares SS_T into Residual Sum of Squares (or Error Sum of Squares) SS_E and Regression Sum of Squares (or Model Sum of Squares) SS_R. In practical meanings, SS_E is a measure of unexplained variability in the dependent variables Y, and SS_R measures variability explained by the regression model (Montgomery, 2004):

$$SS_T= SS_E \quad + \quad SS_R \quad =$$

$$\boldsymbol{TotalSS = RegrSS + ErrorSS}$$

$$\sum_{i=1}^{n}(Y_i-\bar{Y})^2=\sum_{i=1}^{n}(\hat{Y}_i-\bar{Y})^2+\sum_{i=1}^{n}(Y_i-\hat{Y}_i)^2, \qquad (26)$$

on the other hand, the Coefficient of Determination (R^2) (Domain: $0\leq R^2\leq1$) measures the proportion of variability explained and accounted for by the regression model in the total observed dependent variable change (Montgomery, 2004):

$$R^2=1-SS_E/SS_T=SS_R/SS_T \qquad (27)$$

A large value of R^2 indicates the good performance of the model in explaining the variability in the response, whereas a small R^2 value indicates the necessary of an alternative model (Montgomery, 2004).

ANOVA can be used to test for the significance of a regression as follows. The hypotheses are:

Null hypothesis $H_0: \beta_1 = 0$

Alternative hypothesis $H_1: \beta_1 \neq 0$

The rejection criterion of H_0 is: $F_0 > F_{\alpha,1,n-2}$, where $F_0 = MS_R/MS_E$, and $MS_R = SS_R/1$, $MS_E = SS_E/(n-p)$, p is the number of independent variables (Montgomery, 2004).

7. Comparison of t-test and ANOVA F-test

The t-test and ANOVA F-test should produce identical results for significance test of a regression. Actually, although rounding may affect the results, the square of the computed value of the t-test statistic t_0 is equal to the computed value of the ANOVA F-test statistic F_0 (Montgomery, 2004). In general, the square of a t random variable with r degrees of freedom is equal to an F random variable with one numerator degree of freedom and r denominator degrees of freedom (Montgomery, 2004).

Under the assumption that the observation data are normally distributed and independent, a 100(1-α)% confidence interval for the slope β_1 in simple linear regression is (Montgomery, 2004):

$$\beta_1\hat{} - t_{\alpha/2,n-2}\, stv(\beta_1\hat{}) \le \beta_1 \le \beta_1\hat{} + t_{\alpha/2,n-2}\, stv(\beta_1\hat{}) \qquad (28)$$

where $stv(\beta_1\hat{})$ is the standard deviation of the slope, $stv(\beta_1\hat{}) = (\sigma^2/S_{xx})^{1/2}$, and $S_{xx} =$

$$\sum_{i=1}^{n}(X_i - \bar{X})_i^2$$

(Montgomery, 2004)

A3.2 Mann-Kendall Test

1. For the number of data n ≤ 40, the calculating procedure is as follows (Gilbert, 1987):

- Firstly, arrange the data in time order: $X_1, X_2, \ldots, X_n$, where X_i is the datum at time i.
- Secondly, determine the sign of all $C_n^2 = n(n-1)/2$ possible differences $X_j - X_k$, where j>k. The differences $X_2 - X_1$, $X_3 - X_1$, …,

X_n-X_1, X_3-X_2, X_4-X_2, …, X_n-X_2,…, X_{k+1}-X_k, X_{k+2}-X_k,…, X_n-X_k,…, X_{n-1}-X_{n-2}, X_n-X_{n-2}, x_n-X_{n-1}, can be calculated clearly with the following Table 5 (Gilbert, 1987).

Table 5: Differences in data values for computing the Mann-Kendall statistic S

X_1	X_2	X_3	X_4	……	X_{n-1}	X_n	Number of + Signs	Number of - Signs
	X_2-X_1	X_3-X_1	X_4-X_1	……	X_{n-1}-X_1	X_n-X_1		
		X_3-X_2	X_4-X_2	……	X_{n-1}-X_2	X_n-X_2		
			X_4-X_3	……	X_{n-1}-X_3	X_n-X_3		
				……	……	……		
					X_{n-1}-X_{n-2}	X_n-X_{n-2}		
						X_n-X_{n-1}		
						S=∑	(sum of + signs)	(sum of - signs)

(Source: Gilbert, 1987. Used by permission)

Thirdly, let sgn(X_j-X_k) be an indicator function with values 1, 0, or -1 according to the sign of X_j-X_k, i.e.,

$$\begin{aligned} \mathrm{Sgn}(X_j-X_k) &= 1, \text{ if } X_j-X_k>0 \\ &= 0, \text{ if } X_j-X_k=0 \\ &= -1, \text{ if } X_j-X_k<0 \end{aligned} \qquad (29)$$

Then compute the Mann-Kendall statistics

$$S=\sum_{k=1}^{n-1}\sum_{j=k+1}^{n} sgn\,(x_j-x_k) \qquad (30)$$

(Gilbert, 1987)

(1). For an one-sided (one tail) test, in which the null hypothesis H_0, is of no trend, and the alternative hypothesis H_1 is of only one single monotonous trend (an upward trend or downward trend alternatively) over time, Mann (1945) proposed the statistical conclusion as follows.

The fundamental conclusion should be interpreted by the Mann-Kendall statistics S. If Mann-Kendall statistics S value is a large positive number, that represents an increasing upward trend; or if Mann-Kendall statistics S value is a large negative number, that represents a decreasing downward trend (Gilbert, 1987).

If the probability value in Table 6 (Probabilities for the Mann-Kendall Nonparametric Test for Trend) corresponding to a computed absolute value of Mann-Kendall statistics S is larger than the preconcerted significance level α value, e.g., 0.05, H_0 will fail to be rejected, and one cannot conclude there will be difference or trend at a 95% level of confidence. On the contrary, if the probability value in Table 6 corresponding to a computed absolute value of Mann-Kendall statistics S is less than the preconcerted significance level (α value), e.g., 0.05, then at a 95% level of confidence, H_0 is rejected in favor of H_1, if S is positive for testing H_0 of no trend against H_1 of an upward trend; or H_0 is rejected and H_1 is accepted, if S is negative for testing H_0 against H_1 of a downward trend (Gilbert, 1987).

(2).For a two-sided (two tail) test, the null hypothesis H_0 is: there is no trend, and the alternative hypothesis H_1 is: there is a trend including two possibility of trends (both of an upward and downward trend). In this situation, the probability value corresponding to the absolute value of S in Table 6 should be doubled. The statistical conclusion should be: H_0 will be rejected if the doubled probability value is less than the preconcerted significance level (α value) (Gilbert, 1987).

Table 6: Probabilities for the Mann-Kendall nonparametric test for trend

	Values of n					Values of n		
S	4	5	8	9	S	6	7	10
0	6.25E-01	5.92E-01	5.48E-01	5.40E-01	1	5.00E-01	5.00E-01	5.00E-01
2	3.75E-01	4.08E-01	4.52E-01	4.60E-01	3	3.60E-01	3.86E-01	4.31E-01
4	1.67E-01	2.42E-01	3.60E-01	3.81E-01	5	2.35E-01	2.81E-01	3.64E-01
6	4.20E-02	1.17E-01	2.74E-01	3.06E-01	7	1.36E-01	1.91E-01	3.00E-01
8		4.20E-02	1.99E-01	2.38E-01	9	6.80E-02	1.19E-01	2.42E-01
10		8.30E-03	1.38E-01	1.79E-01	11	2.80E-02	6.80E-02	1.90E-01
12			8.90E-02	1.30E-01	13	8.30E-03	3.50E-02	1.46E-01
14			5.40E-02	9.00E-02	15	1.40E-03	1.50E-02	1.08E-01
16			3.10E-02	6.00E-02	17		5.40E-03	7.80E-02
18			1.60E-02	3.80E-02	19		1.40E-03	5.40E-02
20			7.10E-03	2.20E-02	21		2.00E-04	3.60E-02
22			2.80E-03	1.20E-02	23			2.30E-02
24			8.70E-04	6.30E-03	25			1.40E-02
26			1.90E-04	2.90E-03	27			8.30E-03
28			2.50E-05	1.20E-03	29			4.60E-03
30				4.30E-04	31			2.30E-03
32				1.20E-04	33			1.10E-03
34				2.50E-05	35			4.70E-04
36				2.80E-06	37			1.80E-04
					39			5.80E-05
					41			1.50E-05
					43			2.80E-06
					45			2.80E-07

(Source: Gilbert, 1987. Used by permission)

(Each table entry is the probability that the Mann-Kendall statistic S equals or exceeds the specified value of S when no trend is present.)

2. For the number of data n > 40, Kendall (1975) proposed a normal approximation test. This method can also be used for the number of data n as small as 10 ($n \geq 10$) as long as there are not many tied data in the data tested (Gilbert, 1987):

- Firstly, compute S by using equation (30).
- Secondly, as Kendall (1975) demonstrated, S is asymptotically normally distributed. Taking into account possible existing ties data in the tested data, compute the mean (M(S))and variance (VAR(S)) of S :

$M(S)=0$

$$VAR(S)=\frac{1}{18}\left[n(n-1)(2n+5)-\sum_{p=1}^{g}t_p(t_p-1)(2t_p+5)\right] \qquad (31)$$

Where g is the number of tied data groups, and t_p is the number of data in the pth group.

Then compute the test statistic Z with calculated S and VAR(S) as follows:

$$Z=(S-1)/[VAR(S)]^{1/2}, \quad \text{if } S>0$$
$$=0 \quad \text{if } S=0$$
$$=(S+1)/[VAR(S)]^{1/2} \quad \text{if } S<0 \qquad (32)$$

(Gilbert, 1987)

If the statistic Z has a standard normal distribution or approximate standard normal distribution, standard normal tables can be used to conclude whether to reject the null hypothesis H_0 of no tend. A positive (negative) value of Z represents the alternative hypothesis H_1: there exists an upward (downward) trend (Gilbert, 1987).

- For a two-sided test (H_1: there exists both possible situations (either upward or downward trend)) at α significance level, if the absolute value of Z is greater than $Z_{1-\alpha/2}$, where $Z_{1-\alpha/2}$ is obtained from standard tabulated data, then H_0 is rejected (Gilbert, 1987).

- For the one-sided test, if Z is greater than $Z_{1-\alpha}$, then H_0 is rejected with accepting the alternative hypothesis H_1: there exists an upward or downward trend at the α level of significance; if Z is negative and the absolute value of Z is greater than $Z_{1-\alpha}$, then H_0 is rejected with accepting the alternative hypothesis H_1 of a downward trend (Gilbert, 1987).

Kendall (1975) reported that using standard normal tables to judge the statistical significance of the Z test may introduce little error as long as $n \geq 10$ and groups of ties and ties within groups do not exist considerably in tested data (Gilbert, 1987).

Both Mann (1945) and Kendall (1975) calculated distributions of S for $n \geq 10$ and demonstrated that the normality assumption should be met even for small values of n, as long as the test statistic Z was calculated with the above formula. Therefore, this method can be used for $n \leq 10$ as long as the test statistic Z is used (Gilbert, 1987).

More importantly, this method may be useful when there are duplicated data. Van Belle and Hughes (1984) reported two methods: one was calculating the median or mean then the test statistic S; and another was treating these duplicated data as tied data and then calculating the modified variance and the test statistic S (Gilbert, 1987).

A3.3 Sen's Test

1. Firstly, calculate slope estimates Q for each datum pair with the total number of N'(Gilbert, 1987):

$Q=(X_{i'}-X_i)/(i'-i)$ (33)

where $X_{i'}$ and X_i are data values at times (or during time periods) i' and i, respectively, and i' >i; N' is the number of data pairs for which i' >i.

The median of these N' values of Q is Sen's estimator of slope. "If there is only one datum in each time period, then $N'=n(n-1)/2$, where n is the number of time periods. If there are multiple observations in one or more time periods, then $N'< n(n-1)/2$, where n is now the total number of observations. If an X_i is below the detection limit, one half the detection limit may be used for X_i "(Gilbert, 1987).

2. Secondly, Sen's estimator is obtained in the following way (Gilbert, 1987):

The N' slope estimates of Q are arranged in ascending order as $Q[1] \leq Q[2] \leq Q[3] \leq \ldots \leq Q[N'-1] \leq Q[N']$.

Then compute Sen's estimator
= median slope
$= Q[(N'+1)/2]$ if N' is odd
$= (Q[N'/2]+Q[N'+2)/2])/2$ if N' is even

Hollander and Wolfe (1973) as cited in Gilbert (1987) indicated the following simpler and generalized procedure of computing the 100(1-α)% two-sided confidence interval about the true slope for a situation where ties and/or multiple observations per time period are present. This procedure should be reliable for normal distribution data, $n \geq 10$ and less ties data exist (Gilbert, 1987):

- Choose the required significance level α and obtain $Z_{1-\alpha/2}$ in standard normal table.

- Calculate VAR(S) with Equation (31) or the equation used for situations with multiple observations per time period, then compute $C_{\alpha}=Z_{1-\alpha/2}[\mathrm{VAR(S)}]^{1/2}$,.
- Calculate $M_1=(N'-C_{\alpha})/2$ and $M_2=(N'+C_{\alpha})/2$.
- The confidence interval are between the M_1th largest and (M_2+1)th largest of Q values.
 (Gilbert, 1987)

Appendix 4. Sample Calculation

Take annual hours of exceeding 9 ppb SO_2 in Edmonton as an example:

Mann-Kendall Test

Firstly, arrange annual hours of exceeding 9 ppb SO_2 in time order: X_1= 434, X_2= 226, X_3= 277, X_4= 229, X_5= 198, X_6= 157, X_7= 89, X_8= 111, where X_i is the annual hours of exceeding 9 ppb SO_2 at year i.

Secondly, determine the sign of all n(n-1)/2 =8*(8-1)/2=28 possible differences X_j-X_k, where j>k. The differences X_2-X_1, X_3-X_1, …, X_8-X_1, X_3-X_2, X_4-X_2, …, X_8-X_2,…, X_{k+1}-X_k, X_{k+2}-X_k,…, X_8-X_k,…, X_7-X_6, X_8-X_6, X_8-X_7, can be calculated clearly in the following table.

Table 7: Computation of the Mann-Kendall trend statistic S

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	Number of + Signs	Number of - Signs
X_j	434	226	277	229	198	157	89	111		
X_j-X_1		-208	-157	-205	-236	-277	-345	-323	0	7
X_j-X_2			51	3	-28	-69	-137	-115	2	4
X_j-X_3				-48	-79	-120	-188	-166	0	5
X_j-X_4					-31	-72	-140	-118	0	4
X_j-X_5						-41	-109	-87	0	3
X_j-X_6							-68	-46	0	2
X_j-X_7								22	1	0
								S=-22	3	25

Thirdly, let sgn(X_j-X_k) be an indicator function with values 1, 0, or -1 according to the sign of X_j-X_k, i.e.,

$$\begin{aligned} \mathrm{Sgn}(X_j-X_k)&=1,\ \text{if } X_j-X_k>0 \\ &=0,\ \text{if } X_j-X_k=0 \\ &=-1,\ \text{if } X_j-X_k<0 \end{aligned} \qquad (29)$$

(Gilbert, 1987)

Then compute the Mann-Kendall statistics,

$$S=\sum \mathrm{Sgn}(X_j-X_k)=-22$$

One-side test is considered in this research, that the null hypothesis H_0 is of no trend, and the alternative hypothesis H_1, is of a monotonous trend over time, that means the Mann-Kendall statistics S is a large positive number representing an increasing upward trend or a large negative number representing a decreasing downward trend (Gilbert, 1987).

The probability value corresponding to the computed absolute value of Mann-Kendall statistics S =-22 in the Cumulative normal distribution table (Values of p corresponding to Z_p for the normal curve) is 0.0028. This value is less than 0.01, therefore H_0 should be rejected and the alternative hypothesis of a downward trend be accepted at a 99% level of confidence (Gilbert, 1987).

Generally speaking, the value obtained from Table 6 is the probability that S value is equal to or larger than the corresponding value at the corresponding n value when there is no monotone trend (upward or downward). If the probability value in Table 6 corresponding to the computed absolute value of Mann-Kendall statistics S is larger than the priori specified α value, say 0.05, H_0 will be fail to be rejected, that can not conclude there will be difference or trend at a 95% level of confidence. If the probability value in Table 6 corresponding to the computed absolute value of Mann-Kendall statistics S is less than the priori specified α value, say 0.05, then at a 95% level of confidence, H_0 is rejected in favor of H_1 if S is positive for testing H_0 of no trend against H_1 of an upward trend, or H_0 is rejected and H_1 is accepted if S is negative for testing H_0 against H_1 of a downward trend (Gilbert, 1987).

Sen's Test

Firstly, compute the slope estimates Q for data with the total number of N':

$$Q=(X_{i}'-X_{i})/(i'-i) \qquad (33)$$

where X_{i}' and X_i are data values at times (or during time periods) i' and i, respectively, and where i' >i; N' is the number of data pairs for which i' >i.

If there is only one datum in each time period, then $N'=C_n^2=n(n-1)/2=8*(8-1)/2=28$ pairs for which i' >i , where n is the number of time periods. (If there are multiple observations in one or more time periods, then N'< n(n-1)/2, where n is now the total number of observations. If a X_i is below the detection limit, half of the detection limit may be used for X_i) (Gilbert, 1987).

The values of individual slope estimates Q for these pairs are calculated by dividing the differences in Table 7 by i'-i. These 28 Q values are presented in Table 8.

Table 8: Computation of individual trend slopes (Q values) for Sen's test

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8
X_j	434.00	226.00	277.00	229.00	198.00	157.00	89.00	111.00
$(X_j-X_1)/(j-1)$		-208.00	-78.50	-68.33	-59.00	-55.40	-57.50	-46.14
$(X_j-X_2)/(j-2)$			51.00	1.50	-9.33	-17.25	-27.40	-19.17
$(X_j-X_3)/(j-3)$				-48.00	-39.50	-40.00	-47.00	-33.20
$(X_j-X_4)/(j-4)$					-31.00	-36.00	-46.67	-29.50
$(X_j-X_5)/(j-5)$						-41.00	-54.50	-29.00
$(X_j-X_6)/(j-6)$							-68.00	-23.00
$(X_j-X_7)/(j-7)$								22.00

Secondly, the median of these N' values of Q is Sen's estimator of slope. The median of the N' slope estimates is obtained in the following way (Gilbert, 1987).

The N' values of Q are arranged in ascending order as

$$Q[1] \leq Q[2] \leq Q[3] \leq \ldots \leq Q[N'-1] \leq Q[N'].$$

i.e. Q values at ascending order are:

-208.00, -78.50, -68.33, -68.00, -59.00, -57.50, -55.40, -54.50, -48.00, -47.00, -46.67, -46.14, -41.00, -40.00, -39.50, -36.00, -33.20, -31.00, -29.50, -29.00, -27.40, -23.00, -19.17, -17.25, -9.33, 1.50, 22.00, 51.00.

Then compute

Sen's slope= median slope

$$=Q[(N'+1)/2] \qquad \text{if } N' \text{ is odd}$$

$$=(Q[N'/2]+Q[N'+2)/2])/2 \qquad \text{if } N' \text{ is even}$$

(Gilbert, 1987)

Since N'=28, Sen's slope=(Q(14)+Q(15))/2=((-40.00)+(-39.50))/2=-39.75

Therefore, the Sen's estimate of the true slope, i.e., the average (median) change is 39.75 ppb per year.

Appendix 5. Consolidated Results of Non-parametric Statistics (Edmonton)

Table 9: Non-parametric statistical results for trend analysis of NO_2 (Edmonton North West) (1997 to 2004)

	Mann-Kendall trend		Sen's estimate	
Index	Test S	Significant	R	I
Annual hours of exceeding 22 ppb NO_2	-4	No	-51.67	3874.67
Annual hours of exceeding 30 ppb NO_2	-2	No	-30.67	2487.83
Annual hours of exceeding 37 ppb NO_2	-4	No	-48.28	1582.71
Annual hours of exceeding 40 ppb NO_2	-6	No	-35.05	1229.13
Annual hours of exceeding 51 ppb NO_2	-6	No	-37.08	459.21
Annual hours of exceeding 60 ppb NO_2	-6	No	-11.33	132.33
NO_2 Concentration (ppb) (50th Percentile)	-9	No	-0.37	20.92
NO_2 Concentration (ppb) (65th Percentile)	-7	No	-0.50	28.25
NO_2 Concentration (ppb) (75th Percentile)	-5	No	-0.50	33.25
NO_2 Concentration (ppb) (80th Percentile)	-6	No	-0.37	36.42
NO_2 Concentration (ppb) (90th Percentile)	-5	No	-0.67	45.67
NO_2 Concentration (ppb) (95th Percentile)	-6	No	-0.79	52.48
NO_2 Concentration (ppb) (98th Percentile)	-6	No	-0.96	59.40

Note:

(1).*: There exists the trend at α=0.05 level of significance

**: There exists the trend at α=0.01 level of significance

***: There exists the trend at α=0.001 level of significance

+: There exists the trend at α=0.1 level of significance

No: There does not exist the trend at α< 0.1 level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where: X: Ordinal number of year for index

Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at Xth year

R: Sen's slope (change in index per year)

I: Intercept

Table 10: Non-parametric statistical results for trend analysis of O_3 (Edmonton North West) (1997 to 2004)

	Mann-Kendall trend		Sen's estimate	
Index	Test S	Significant	R	I
Annual hours of exceeding 15 ppb O_3	12	No	71.70	4329.30
Annual hours of exceeding 23 ppb O_3	10	No	80.40	2894.20
Annual hours of exceeding 29 ppb O_3	4	No	61.40	2015.20
Annual hours of exceeding 32 ppb O_3	4	No	17.10	1726.05
Annual hours of exceeding 41 ppb O_3	0	No	-7.47	767.07
Annual hours of exceeding 48 ppb O_3	-2	No	-4.77	250.10
O_3 Concentration (ppb) (50th Percentile)	15	No	0.55	14.95
O_3 Concentration (ppb) (65th Percentile)	9	No	0.50	22.50
O_3 Concentration (ppb) (75th Percentile)	6	No	0.40	28.70
O_3 Concentration (ppb) (80th Percentile)	5	No	0.23	31.94
O_3 Concentration (ppb) (90th Percentile)	-1	No	-0.13	40.19
O_3 Concentration (ppb) (95th Percentile)	-1	No	-0.10	45.55
O_3 Concentration (ppb) (98th Percentile)	-4	No	-0.18	51.60

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance
**: There exists the trend at $\alpha=0.01$ level of significance
***: There exists the trend at $\alpha=0.001$ level of significance
+: There exists the trend at $\alpha=0.1$ level of significance
No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index
Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year
R: Sen's slope (change in index per year)
I: Intercept

Table 11: Non-parametric statistical results for trend analysis of $PM_{2.5}$ (Edmonton North West) (1997 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 12 μg/m^3 $PM_{2.5}$	-13	+	-387.00	4003.00
Annual hours of exceeding 15.8 μg/m^3 $PM_{2.5}$	-15	*	-248.00	2415.00
Annual hours of exceeding 19.3 μg/m^3 $PM_{2.5}$	-15	*	-178.83	1633.00
Annual hours of exceeding 21.3 μg/m^3 $PM_{2.5}$	-15	*	-144.17	1314.00
Annual hours of exceeding 27.5 μg/m^3 $PM_{2.5}$	-15	*	-60.33	558.33
Annual hours of exceeding 35.3 μg/m^3 $PM_{2.5}$	-13	+	-20.25	193.75
$PM_{2.5}$ Concentration (μg/m^3) (50% Percentile)	-17	*	-1.27	13.10
$PM_{2.5}$ Concentration (μg/m^3) (65% Percentile)	-17	*	-1.33	15.80
$PM_{2.5}$ Concentration (μg/m^3) (75% Percentile)	-16	*	-1.50	19.00
$PM_{2.5}$ Concentration (μg/m^3) (80% Percentile)	-15	*	-1.60	21.20
$PM_{2.5}$ Concentration (μg/m^3) (90% Percentile)	-15	*	-1.50	25.00
$PM_{2.5}$ Concentration (μg/m^3) (95% Percentile)	-15	*	-2.00	33.80
$PM_{2.5}$ Concentration (μg/m^3) (98% Percentile)	-13	+	-2.40	42.90

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance
**: There exists the trend at $\alpha=0.01$ level of significance
***: There exists the trend at $\alpha=0.001$ level of significance
+: There exists the trend at $\alpha=0.1$ level of significance
No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index
Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at Xth year
R: Sen's slope (change in index per year)
I: Intercept

Table 12: Non-parametric statistical results for trend analysis of CO (Edmonton NorthWest) (1997 to 2004)

	Mann-Kendall trend		Sen's slope	
Time series	Test S	Significant	R	I
Annual hours of exceeding 400 ppb CO	-18	*	-304.50	5392.25
Annual hours of exceeding 600 ppb CO	-22	**	-202.43	3381.02
Annual hours of exceeding 800 ppb CO	-22	**	-124.50	2248.75
Annual hours of exceeding 900 ppb CO	-20	*	-120.58	1962.13
Annual hours of exceeding 1500 ppb CO	-20	*	-67.80	894.70
Annual hours of exceeding 2200 ppb CO	-20	*	-43.95	441.79
CO Concentration(ppb) (50% Percentile)	-11	No	-17.14	494.29
CO Concentration(ppb) (65% Percentile)	-19	*	-33.33	683.33
CO Concentration(ppb) (75% Percentile)	-19	*	-36.67	896.67
CO Concentration(ppb) (80% Percentile)	-19	*	-36.67	996.67
CO Concentration(ppb) (90% Percentile)	-20	*	-77.50	1648.75
CO Concentration(ppb) (95% Percentile)	-19	*	-112.50	2256.25
CO Concentration(ppb) (98% Percentile)	-23	**	-200.00	3450.00

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance

**: There exists the trend at $\alpha=0.01$ level of significance

***: There exists the trend at $\alpha=0.001$ level of significance

+: There exists the trend at $\alpha=0.1$ level of significance

No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index

Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year

R: Sen's slope (change in index per year)

I: Intercept

Table 13: Non-parametric statistical results for trend analysis of H_2S (Edmonton NorthWest) (1997 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 0ppb H_2S	0	No	-8.86	3599.14
Annual hours of exceeding 1ppb H_2S	-8	No	-35.07	949.25
Annual hours of exceeding 2ppb H_2S	-14	No	-20.50	364.50
H_2S Concentration(ppb) (50% Percentile)	0	No	0.00	0.00
H_2S Concentration(ppb) (65% Percentile)	0	No	0.00	1.00
H_2S Concentration(ppb) (75% Percentile)	0	No	0.00	1.00
H_2S Concentration(ppb) (80% Percentile)	0	No	0.00	1.00
H_2S Concentration(ppb) (90% Percentile)	-10	No	0.00	1.50
H_2S Concentration(ppb) (95% Percentile)	-8	No	0.00	2.00
H_2S Concentration(ppb) (98% Percentile)	-10	No	0.00	3.50

Note:
(1).*: There exists the trend at $\alpha=0.05$ level of significance
**: There exists the trend at $\alpha=0.01$ level of significance
***: There exists the trend at $\alpha=0.001$ level of significance
+: There exists the trend at $\alpha=0.1$ level of significance
No: There does not exist the trend at $\alpha< 0.1$ level of significance
(2).Equation of trend line of Sen's estimation: $Y(X) = R^*(X-1) + I$
Where:
X: Ordinal number of year for index
Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^th year
R: Sen's slope (change in index per year)
I: Intercept

Table 14: Non-parametric statistical results for trend analysis of THC (Edmonton NorthWest) (1997 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 2000 ppb THC	-12	No	-194.92	4485.54
Annual hours of exceeding 2100 ppb THC	-12	No	-137.02	3250.60
Annual hours of exceeding 2300 ppb THC	-12	No	-134.83	2145.92
Annual hours of exceeding 2400 ppb THC	-8	No	-95.64	1662.75
Annual hours of exceeding 2700 ppb THC	-8	No	-88.43	929.72
Annual hours of exceeding 3000 ppb THC	-8	No	-47.21	463.11
THC Concentration(ppb) (50% Percentile)	-5	No	0.00	2000.00
THC Concentration(ppb) (65% Percentile)	-8	No	-29.17	2266.67
THC Concentration(ppb) (75% Percentile)	-13	No	-30.95	2373.81
THC Concentration(ppb) (80% Percentile)	-10	No	-30.95	2408.33
THC Concentration(ppb) (90% Percentile)	-9	No	-30.95	2708.33
THC Concentration(ppb) (95% Percentile)	-10	No	-63.33	3080.00
THC Concentration(ppb) (98% Percentile)	-8	No	-58.33	3450.00

Note:
(1).*: There exists the trend at $\alpha=0.05$ level of significance
**: There exists the trend at $\alpha=0.01$ level of significance
***: There exists the trend at $\alpha=0.001$ level of significance
+: There exists the trend at $\alpha=0.1$ level of significance
No: There does not exist the trend at $\alpha< 0.1$ level of significance
(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$
Where:
X: Ordinal number of year for index
Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year
R: Sen's slope (change in index per year)
I: Intercept

Table 15: Non-parametric statistical results for trend analysis of SO_2 (Edmonton NorthWest) (1997 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 2 ppb SO_2	-24	**	-449.02	4181.05
Annual hours of exceeding 3 ppb SO_2	-24	**	-345.43	2776.57
Annual hours of exceeding 4 ppb SO_2	-24	**	-216.29	1728.08
Annual hours of exceeding 6 ppb SO_2	-24	**	-97.00	808.50
Annual hours of exceeding 9 ppb SO_2	-22	**	-39.75	356.13
SO_2 Concentration(ppb) (50% Percentile)	-10	No	0.00	1.50
SO_2 Concentration(ppb) (65% Percentile)	-18	*	-0.27	2.94
SO_2 Concentration(ppb) (75% Percentile)	-19	*	-0.25	3.63
SO_2 Concentration(ppb) (80% Percentile)	-21	*	-0.33	4.17
SO_2 Concentration(ppb) (90% Percentile)	-22	**	-0.50	6.25
SO_2 Concentration(ppb) (95% Percentile)	-22	**	-0.60	8.90
SO_2 Concentration(ppb) (98% Percentile)	-23	**	-0.80	13.10

Note:
(1).*: There exists the trend at $\alpha=0.05$ level of significance
**: There exists the trend at $\alpha=0.01$ level of significance
***: There exists the trend at $\alpha=0.001$ level of significance
+: There exists the trend at $\alpha=0.1$ level of significance
No: There does not exist the trend at $\alpha< 0.1$ level of significance
(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$
Where:
X: Ordinal number of year for index
Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year
R: Sen's slope (change in index per year)
I: Intercept

Appendix 6. Consolidated Results of Non-parametric Statistics (Fort McKay)

Table 16: Non-parametric statistical results for trend analysis of NO_2 (Fort McKay) (1999 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 1 ppb NO_2	5	No	92.00	4704.50
Annual hours of exceeding 3 ppb NO_2	-1	No	-2.00	3578.00
Annual hours of exceeding 5 ppb NO_2	1	No	39.00	2734.00
Annual hours of exceeding 7 ppb NO_2	7	No	102.00	1949.00
Annual hours of exceeding 12 ppb NO_2	3	No	25.33	1215.17
Annual hours of exceeding 16 ppb NO_2	3	No	23.00	716.50
NO_2 Concentration(ppb) (50% Percentile)	2	No	0.00	3.00
NO_2 Concentration(ppb) (65% Percentile)	3	No	0.00	5.00
NO_2 Concentration(ppb) (75% Percentile)	7	No	0.50	7.00
NO_2 Concentration(ppb) (80% Percentile)	7	No	0.33	9.17
NO_2 Concentration(ppb) (90% Percentile)	7	No	0.33	15.17
NO_2 Concentration(ppb) (95% Percentile)	9	No	1.00	17.50
NO_2 Concentration(ppb) (98% Percentile)	12	*	1.00	20.00

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance

**: There exists the trend at $\alpha=0.01$ level of significance

***: There exists the trend at $\alpha=0.001$ level of significance

+: There exists the trend at $\alpha=0.1$ level of significance

No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where: X: Ordinal number of year for index

Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year

R: Sen's slope (change in index per year)

I: Intercept

Table 17: Non-parametric statistical results for trend analysis of O_3 (Fort McKay) (1999 to 2004)

	Mann-Kendall trend		Sen's slope estimate	
Index	Test S	Significant	R	I
Annual hours of exceeding 20 ppb O_3	5	No	119.00	3912.50
Annual hours of exceeding 25 ppb O_3	7	No	155.25	2649.13
Annual hours of exceeding 28 ppb O_3	5	No	184.00	1851.00
Annual hours of exceeding 30 ppb O_3	5	No	133.00	1560.00
Annual hours of exceeding 37 ppb O_3	3	No	22.00	787.00
Annual hours of exceeding 42 ppb O_3	1	No	25.00	250.00
O_3 Concentration(ppb) (50% Percentile)	7	No	1.00	18.00
O_3 Concentration(ppb) (65% Percentile)	5	No	1.00	23.00
O_3 Concentration(ppb) (75% Percentile)	6	No	0.67	27.67
O_3 Concentration(ppb) (80% Percentile)	6	No	0.67	29.67
O_3 Concentration(ppb) (90% Percentile)	4	No	0.50	36.25
O_3 Concentration(ppb) (95% Percentile)	0	No	0.00	41.50
O3 Concentration(ppb) (98% Percentile)	2	No	0.50	42.25

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance

**: There exists the trend at $\alpha=0.01$ level of significance

***: There exists the trend at $\alpha=0.001$ level of significance

+: There exists the trend at $\alpha=0.1$ level of significance

No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index

Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year

R: Sen's slope (change in index per year)

I: Intercept

Table 18: Non-parametric statistical results for trend analysis of $PM_{2.5}$ (Fort McKay) (1999 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 4.8 $\mu g/m^3$ $PM_{2.5}$	-7	No	-450.33	4750.00
Annual hours of exceeding 6 $\mu g/m^3$ $PM_{2.5}$	-7	No	-266.67	3355.00
Annual hours of exceeding 7.3 $\mu g/m^3$ $PM_{2.5}$	-7	No	-142.33	2311.50
Annual hours of exceeding 8.2 $\mu g/m^3$ $PM_{2.5}$	-7	No	-104.00	1889.00
Annual hours of exceeding 10.9 $\mu g/m^3$ $PM_{2.5}$	-5	No	-31.33	1052.17
Annual hours of exceeding 13.9 $\mu g/m^3$ $PM_{2.5}$	3	No	10.50	512.25
$PM_{2.5}$ Concentration ($\mu g/m^3$) (50% Percentile)	-7	No	-0.60	5.35
$PM_{2.5}$ Concentration ($\mu g/m^3$) (65% Percentile)	-7	No	-0.44	6.37
$PM_{2.5}$ Concentration ($\mu g/m^3$) (75% Percentile)	-7	No	-0.38	7.76
$PM_{2.5}$ Concentration ($\mu g/m^3$) (80% Percentile)	-7	No	-0.34	8.83
$PM_{2.5}$ Concentration ($\mu g/m^3$) (90% Percentile)	-3	No	-0.16	11.97
$PM_{2.5}$ Concentration ($\mu g/m^3$) (95% Percentile)	4	No	0.20	14.85
$PM_{2.5}$ Concentration ($\mu g/m^3$) (98% Percentile)	13	*	1.13	16.20

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance
**: There exists the trend at $\alpha=0.01$ level of significance
***: There exists the trend at $\alpha=0.001$ level of significance
+: There exists the trend at $\alpha=0.1$ level of significance
No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index
Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year
R: Sen's slope (change in index per year)
I: Intercept

Table 19: Non-parametric statistical results for trend analysis of THC (Fort McKay) (1999 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 1900 ppb THC	-5	No	-11.67	2097.67
Annual hours of exceeding 2000 ppb THC	-7	No	-96.50	1722.00
Annual hours of exceeding 2100 ppb THC	-9	No	-88.00	1297.00
Annual hours of exceeding 2300 ppb THC	-9	No	-81.75	813.38
Annual hours of exceeding 2400 ppb THC	-5	No	-21.75	390.38
THC Concentration (ppb) (50% Percentile)	-5	No	0.00	1800.00
THC Concentration (ppb) (65% Percentile)	-3	No	0.00	1900.00
THC Concentration (ppb) (75% Percentile)	-9	No	-33.33	2033.33
THC Concentration (ppb) (80% Percentile)	-5	No	0.00	2000.00
THC Concentration (ppb) (90% Percentile)	-8	No	-20.00	2290.00
THC Concentration (ppb) (95% Percentile)	-3	No	0.00	2400.00
THC Concentration (ppb) (98% Percentile)	1	No	0.00	2600.00

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance

**: There exists the trend at $\alpha=0.01$ level of significance

***: There exists the trend at $\alpha=0.001$ level of significance

+: There exists the trend at $\alpha=0.1$ level of significance

No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index

Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year

R: Sen's slope (change in index per year)

I: Intercept

Table 20: Non-parametric statistical results for trend analysis of SO_2 (Fort McKay) (1999 to 2004)

	Mann-Kendall trend		Sen's slope	
Index	Test S	Significant	R	I
Annual hours of exceeding 1 ppb SO_2	-11	*	-65.50	1414.75
Annual hours of exceeding 3 ppb SO_2	-3	No	-13.67	650.33
Annual hours of exceeding 6 ppb SO_2	-3	No	-8.33	368.67
SO_2 Concentration(ppb) (50% Percentile)	-5	No	0.00	0.00
SO_2 Concentration(ppb) (65% Percentile)	-8	No	-0.20	0.90
SO_2 Concentration(ppb) (75% Percentile)	0	No	0.00	1.00
SO_2 Concentration(ppb) (80% Percentile)	0	No	0.00	1.00
SO_2 Concentration(ppb) (90% Percentile)	-2	No	0.00	2.00
SO_2 Concentration(ppb) (95% Percentile)	1	No	0.00	5.00
SO2 Concentration(ppb) (98% Percentile)	5	No	0.25	10.38

Note:

(1).*: There exists the trend at $\alpha=0.05$ level of significance

**: There exists the trend at $\alpha=0.01$ level of significance

***: There exists the trend at $\alpha=0.001$ level of significance

+: There exists the trend at $\alpha=0.1$ level of significance

No: There does not exist the trend at $\alpha< 0.1$ level of significance

(2).Equation of trend line of Sen's estimation: $Y(X) = R*(X-1) + I$

Where:

X: Ordinal number of year for index

Y: Index (Annual hours of exceeding a certain concentration (Benchmark), or concentration corresponding to a certain percentile) at X^{th} year

R: Sen's slope (change in index per year)

I: Intercept

Appendix 7. Population and Traffic Historical Data of Edmonton City

	1997	1998	1999	2000	2001	2002	2003	2004
Population	625450	636100	648284	657500	666104	676300	697657	707271
Private Vehicle	329822	339397	349575	356679	365232	376157	380475	381456

(Source: Transportation and Streets, The City of Edmonton, 2005, Motor Vehicle Collisions 2004)

	1997	1998	1999	2000	2001	2002	2003	2004
Population	626500	636100	648284	658400	666104	677430	688940	700660

(Source: Planning and Development, The City of Edmonton, 2005, City of Edmonton population, historical)