A Quantitative Analysis of the Cairclip O₃/NO₂ Sensor

by

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ABSTRACT

Ozone (O₃) and nitrogen dioxide (NO₂) are two criteria pollutants that can result in adverse outcomes that effect both natural environments and human health. As these outcomes have a significant impact on people and their environments, it is necessary to closely monitor the levels of these gases in the ambient air. Currently, air quality monitoring in Edmonton is reported through the Air Quality Health Index (AQHI) as determined from measurements acquired from the four centralized ambient monitoring stations across the city. While the air quality data collected at the centralized monitoring stations provides the public with a generalized idea of the air quality for the day, they are unable to measure real time concentrations of near-field sources of pollutants based on an individual's daily activity patterns. These unique activity patterns are specific to an individual and differ from one person to the next.

The Cairclip sensor is representative of new technology in personal exposure monitors as they are small, lightweight and highly portable. In order to gain further understanding in the operational capacities and limitations of these sensors, the Cairclip $O_3 + NO_2$ sensor was tested in a two phase study. In phase one, the Cairclip was deployed at the Edmonton south monitoring station in order to determine their accuracy against the centralized monitor, as well as the level of precision between paired sensors. In phase two, the sensors were tested in various scenarios measuring near-field concentration exposures of $O_3 + NO_2$ at the personal level as well as at the subject's residence.

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The findings of phase one precision resulted in a percent relative deviation (%RSD) for one hour averaged concentrations with outliers removed that ranged from +/-20% to +/-11%. Phase one accuracy was calculated using mean absolute percent difference (MAPD) for data sets screened for outliers and based on one hour averaged concentrations of O_3 + NO₂, these values ranged from +/-40% to +/-29%, respectively. In phase two, the Cairclips responded in a highly varied pattern when challenged during personal exposure monitoring in various settings where pollutant concentrations originated from near field sources.

In conclusion, phase one determined that the level of accuracy of the Cairclips in contrast to the Edmonton south centralized station was poor. Personal exposure monitoring in various scenarios in phase two showed that the most significant findings were found in environments that are in close proximity to vehicular traffic and where sources of O₃ and NO₂ are prevalent due to gas-fired appliances. The specific settings were determined by the data collected in restaurants located close to high volumes of traffic and on public transit routes.

Prior to use in further research, it is recommended that the accuracy and precision of the sensors be retested. In addition, further research in air monitoring of levels O₃ and NO₂ in closed, built environments and on various public transportation routes using the Cairclip may be warranted.

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LIST OF SYMBOLS, ABBREVIATIONS AND ACRONYMS

AAADMS	Alberta ambient air data management
AQG	Air Quality Guide
AQHI	Air Quality Health Index
AQI	Air Quality Index
AWMA	Air and Waste Management Association
CAAQS	Canadian Ambient Air quality Standards
CASA	Clean Air Strategic Alliance
CC	Cairclip
СО	Carbon monoxide
CO_2	Carbon dioxide
DPAS	Directional passive air sampler
DQO	Data Quality Objective
ECHA	Edmonton Clinic Health Academy
ECSM	Edmonton central station monitor
EPHT	Environmental Public Tracking
FCAA	Federal clean air act
H_2S	Hydrogen Sulfide
HAPS	Hazardous air pollutants
НС	Hydrocarbons
HDDM- CMAQ	Highorder Decoupled Direct Method-Community Multiscale Air Quality
JRC	Joint Research Center
LOD	Level of detection
LV	Limit values
MAL	Maximum accepted level
MAPD	Mean absolute percent difference
MDL	Maximum desirable level
MTL	Maximum tolerated level
NAAQS	National Ambient Air quality Standards
NAPS	National Air Pollution Surveillance

NH ₃	Ammonia
NO	Nitrogen oxide
NO ₂	Nitrogen dioxide
NO _x	Total concentration of NO and NO ₂
NRC	National Research Council
O ₃	Ozone
PEM	Personal exposure monitoring
PPB	Parts per billion
PSD	Prevention of significant deterioration
S-R	Source-receptor relationship
SD	Standard deviation
SGS	Southgate Station
SO_2	Sulfur dioxide
SO_2	Sulfur dioxide
TAD	Time activity diary
Ug/mg ³	Micrograms per cubic meter
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile organic compounds
WEM	West Edmonton Mall
WHO	World Health Organization

1 INTRODUCTION

The term environmental health encompasses a range of external factors, which may directly or indirectly affect an individual or an identified source population. These extrinsic factors may be biological, chemical or physical in nature and all have the potential to affect the health and well-being of all living organisms both positively and negatively.

Ambient air pollution may be defined as a combination of gases that are constantly present within an environment whether urban, suburban or rural. Often these gases are man-made through industrial, agricultural and commuting practices. Subsequently, potential exposures exist due to the activities of people in their homes and the household products used, which often contribute to concentrations of pollutants in a built environment where people spend significant amounts of time.

With this in mind, air quality plays a significant role in both human and environmental health. In a world experiencing continued, exponential growth in population and industrial activities, air pollution has the potential to be an everincreasing environmental and human health issue. In order to address the human and environmental impact associated with air pollution, it is important to define which are the "criteria air pollutants" of concern; through what activities are they formed; how these pollutants interact with others in an environment; and what are the potential byproducts of theses interactions. Importantly, this information aims to provide an understanding of the intricate interaction between living organisms

in both built and ambient environments to air pollutants in order to set standards and promote optimal health.

In order to facilitate knowledge for science, policy and public purposes we must gain a more in-depth understanding of the degree of human health effects associated with exposure to air pollution based on duration, location and concentration of exposure. Personal exposure monitors may have the potential not only to provide for identification of geographically problematic areas but also to promote an individual's awareness to make conscientious choices and inspire a prevention-based attitude to improving their air quality.

Lifestyle choices like taking public transportation and making conscientious decisions when purchasing certain consumable household products can help to reduce the negative impact on the natural environment. Improving air quality and environmental health is not solely the responsibility of the government; people must do their part in changing the things that we can at the individual level.

For the purposes of this study the focus is on air quality and the effects of two specific criteria pollutants, ground level ozone (O₃) and nitrogen dioxide (NO₂). These gases are commonly present in indoor and outdoor environments as a result of anthropogenic activities, interactions with other air contaminants and certain events of nature. The human health effects of high concentrations of these gases is linked to respiratory ailments, particularly for vulnerable members of the population. The advent of personal exposure monitoring devices used in conjunction with time activity records/diaries show promise for a new paradigm in air quality monitoring. Understanding the spatiotemporal difference between

ambient and personal exposure to air pollutants may be key to providing education, improve programing and development of policy standards that act more proactively to protect both human and environmental health.

This dissertation will provide a background discussion of the formation of O_3 and NO_2 , the current regulatory standards, the effects they have on environmental and human health and components of exposure science in effectively measuring human exposure. Following the background section, details of this thesis research using the Cairclip O_3/NO_2 sensor to study personal air quality will be discussed in the methodology, results and conclusions sections, respectively.

1.1 Objective of Study

The objective of this study was to compare and test the efficacy and unique capabilities of new technology in personal monitors, the Cairclip, in measuring concentration exposures to $O_3 + NO_2$. This objective was achieved by measuring the Cairclip's level of accuracy and precision; and to assess its ability in personal exposure monitoring. Through testing these new personal air monitoring devices in various capacities and scenarios, this research aims to be useful in determining if these sensors can provide valuable insight about near-field sources of pollutants in indoor and outdoor environments that may indicate risk potential.

In the following research, the findings aim to provide insight and promote further research into the future of air quality monitoring of pollutants in growing urban environments where people live and interact closely with expanding industrial operations and vehicular traffic. Importantly, it is critical for the public to understand the effects that poor ventilation and certain human activities have

on the air quality within indoor environments. Finally, the research and findings of this study aims to provide some information that may bridge the gap between current standards of air monitoring based on ambient centralized station monitoring and personal monitoring of air pollution.

1.2 Problem Statement

Past and current trends in studying human and environmental exposure to air pollutants have been focused on measuring far-field concentrations at the ambient level. In reality, science has shown that true human exposure to air pollution may be better represented by measuring exposure to air pollutants on a near-field, real time basis at the receptor level, known as personal exposure monitoring. Currently, a gap in scientific knowledge exists in understanding to what degree personal exposure monitoring differs from that of ambient fixed site monitoring.

1.3 Hypothesis

Personal exposure monitoring of near-field sources of pollution are more representative of actual human or environmental exposure and potential risk than that of fixed-site, centralized monitoring of far-field sources.

2 BACKGROUND

Air quality monitoring of enclosed spaces dates back to 1851 where workers' exposures to concentrations of carbon dioxide (CO₂), O₃ and hazardous airborne dust in coal mines were tested in order to evaluate possible adverse health outcomes (Fenske, 2010). While in the 1970's, the emergence of personal monitors for measuring environmental pollutants showed promising potential in the field of air quality, continued research and development was warranted (Wallace, 1982). Since this time, the trend towards designing personal monitoring devices that are accurate, precise, affordable and simple to use has been a focus for many researchers working in the field of exposure analysis (Wallace, 1982). Even though studies have shown that exposure to air pollution has measureable, detrimental effects on human and environmental health, scientists have yet to draw a direct causal link between certain specific pollutants and illness (Labelle, 1998).

2.1 Environmental Pollutants of Interest

Throughout the years, environmental monitoring of air quality has been an important contributory factor in determining and forecasting disease patterns in human and environmental health. The concentration of pollutants in ambient air has been a cause of concern for many decades. Organizations such as the World Health Organization (WHO), the United States Environmental Protection Agency (US EPA) and Environment Canada are actively involved in monitoring and evaluating changes in pollutant concentrations in ambient air. This information is then used to revise air quality standards where needed to protect the both the

public and the natural environment (WHO, 2005a; US EPA, 2014a; Environment Canada, 2013).

 O_3 and NO_2 have an intricate relationship as they are both found to be respiratory irritants. Studies have conclusively linked tropospheric O_3 to respiratory ailments, but have been somewhat inconclusive as to the degree of health effects associated with exposure to NO_2 . Generally in environments, when NO_2 levels are low O_3 levels will be high; and, if NO_2 levels are high then concentrations of O_3 are low. NO_2 is mainly formed due to anthropogenic activities involving combustion processes, which include vehicular engines, as well as industrial and agricultural processes. NO_2 plays a critical role in the formation of tropospheric O_3 (US EPA, 2014a; Environment Canada, 2013b).

2.1.1 Nitrogen Dioxide

 NO_2 is one of the two most common nitrogen oxides (NO_X) gases. The chemical structure of NO_2 is a nitrogen (N) atom bonded with two oxygen (O) atoms. The chemical symbol NO_x represents the combination of nitric oxide (NO) and NO_2 ; literature commonly refers to this when discussing nitrogen gases (National Library of Medicine, 2013). Other elements in the NO_x family of gases are nitrous acid and nitric acid (US EPA, 2014b). NO_x (NO_2) are formed as byproducts of the combustion process associated to vehicular engines that burn coal, oil and diesel fuel; industrial activities such as welding, electroplating, engraving and dynamite blasting; and the expansion of agricultural process which has become a major contributor to increased concentrations of NO_2 in the ambient air (Sandell, 1998; National Library of Medicine, 2013). Certain in-home activities

such as cigarette smoking and the use of kerosene or gas stoves may have the potential to promote adverse human health effects due to production of high levels of NO_x in enclosed spaces (National Library of Medicine, 2013).

 NO_x , a colorless gas, reacts with O_3 in the atmosphere where it is converted to NO_2 , which is a yellowish or reddish brown colored gas (Sandell, 1998; Koehler et al., 2013). NO_2 engages in a complex chain of both chemical and photochemical reactions with NO, O_3 and other gases. Ambient air concentrations of NO_2 are generally highest in fall and winter months when weather conditions are stable, with concentrations dissipating as the distance from source increases (Gilbert et al., 2003; WHO, 2005a).

NO_x, along with carbon monoxide (CO) and volatile organic compounds (VOC's) are O₃ precursors. When these gases react in the presence of sunlight, the by-product formed is tropospheric or ground level O₃ (Kindzierski, et al., 2007). The type of interaction that takes place is a photochemical reaction, which occurs as a result of oxidation-reduction reactions induced by ultraviolet light. Ground level O₃ quickly reacts with NO_x in the environment to form NO₂ (National Library of Medicine, 2013).

Future global emissions of NO_x have been predicted to increase as developing countries continue to evolve and grow in many economic sectors. Economic development often correlates with an increase in overall standards for quality of life. The effects of economic growth often correspond to increased ownership and use of personal vehicles, which in-turn contributes to emission load and degradation of air quality. This is a problem in developing countries with lax

governmental regulations and poor compliance of industry in adhering to air quality standards (Bradley and Jones, 2002).

In a study conducted by Bradley and Jones (2002), the researcher evaluated power generation and transportation technologies that produce less NO_X than conventional practices. The aim of this research was to find alternatives to conventional technologies for power generation and transportation technologies that produce fewer NO_x emissions in developing countries. The researchers concluded that the concept of a technology leap may be a possible solution for developing countries to counter-balance the projected increase in NO_x emission (Bradley and Jones, 2002).

As discussed outdoor ambient production of NO₂ is a source of human and environmental exposure. This said, indoor concentrations of NO₂ in built environments has shown to be a significant source of human exposure. As reported by the National Academy of Science (NAS) (1991), studies spanning over several years show indoor levels of NO₂ tend to be of greater concern than outdoor levels. Concentrations of the pollutant, NO₂, in built environments have been shown to be consistently and significantly higher than that measured outdoors. Elevated levels of indoor concentrations of NO₂ are in part due to an increase in popularity and use of gas fired cooking appliances, home heating systems such as fireplaces and inadequate indoor ventilation or air exchange systems (National Research Council (NRC), 1991; National Library of Medicine, 2013).

In Canada in 2005 the main emission sources of NO_X originated from the transportation sector, contributing 53% of the ambient air concentration (Kindzierski, et al., 2007). The remaining contributors were upstream oil and gas industry at 19% with various other sources accounting for 18% (Kindzierski, et al. 2007). Similar to Canada's statistics, Alberta's air emissions for NO_X gas was primarily attributed to upstream oil and gas operations with smaller contributions associated to natural gas, oil sands and other industries (Kindzierski, et al., 2007).

Although the full impact of health effects associated with exposure to NO₂ are not yet certain, air quality monitoring of NO₂ is important. From a human health perspective, when exposure duration is long enough and concentration is high enough, NO₂ may have adverse effects on vulnerable populations and ecosystems (WHO, 2003b). Exposures to concentrations of NO₂, have been associated to induce or exacerbate problems with the human respiratory system. These respiratory responses may include a number of conditions such as bronchitis, pneumonia and increased susceptibility to viral infections (Sandell, 1998).

Similarly, Yoshida and Kasama (1987) concluded that inhaled concentrations of NO/NO₂ had the potential to adversely react with human tissues of the respiratory system cell membranes, contribute to peroxidation of lipids in cell membranes, increase the risk of cancer and promote premature aging (Yoshida and Kasama, 1987).

Day to day fluctuations of NO_2 has been reported to increase risk of ischemic stroke during summer months (Johnson et al., 2013). In a study conducted in Edmonton, Alberta by researchers Johnson et al., (2013), the scientists measured

the relationship between highly spatially resolved estimates of NO₂ and emergency room visits for those people suffering strokes. Unlike short term, fluctuating levels, medium and long-term human exposure to ambient air pollution was found to be less likely to increase risk of stroke (Johnson et al., 2013).

In the environment, NO₂ contributes to the formation of ground level ozone, as well as the destruction of stratospheric ozone and delicate ecosystems (USEPA, 2014b; NRC, 1991). Ambient air containing NO₂ is capable of damaging and preventing optimum plant growth. The pollutant may damage the leaves of plants, inhibit photosynthesis and impede growth of vegetation (US EPA, 2014b). When NO₂ is deposited on land, in estuaries, lakes and streams, acidification and excess fertilization can occur. Although the extent of harm that NO₂ has on ecosystems is not thoroughly understood, effects such as alterations in biodiversity, water quality, mutation or extinction of fish and possibly wildlife have found to be linked to exposure of this pollutant (US EPA, 2014b; WHO, 2000c).

2.1.2 Ozone

The chemical structure of O_3 is comprised of three oxygen atoms, a configuration that makes it extremely reactive with a potential to decompose explosively in the environment. As a result of O_3 's powerful oxidative action, the chemical has been used in several industrial and consumer processes that are associated with oxidation. The molecular weight of O_3 is 48g mol⁻¹ and is it is described as a pale blue gas with a pungent odor (US EPA, 2014b).

O₃ formation occurs in the atmosphere as a result of photochemical reactions in the presence of sunlight as well as in the presence of precursor pollutant gases such as NO₂ and VOC's (WHO, 2005a). O₃ levels are generally highest in the summer due to warmer temperatures and more hours of daylight resulting in higher levels and longer duration of ultraviolet light (UV). In rare situations, according to past findings by the US EPA (2014b), high O₃ levels have been recorded in elevated regions of the western states during fall and winter months where temperatures were at or below the freezing point. This was attributed to the high ambient air concentrations of VOC's and NOx emissions in this geographical area (US EPA, 2014b).

O₃ is classified as either stratospheric or tropospheric. The stratosphere is the second major atmospheric layer and lies directly above the troposphere. The altitude of the stratosphere extends in a range from 8 to 30 miles high. Within this part of the atmosphere lies the ozone layer, which is most often contained in the lower portion of the stratosphere. The O₃ concentration within the ozone layer is extremely important to life on earth as it absorbs biologically harmful ultraviolet radiation (US EPA, 2014b).

Conversely, O_3 can leak from the stratosphere to ground level in response to weather systems. When in the troposphere, O_3 is highly reactive, extremely mobile and can easily be transported from urban and industrial settings to downwind, off site rural environments (Alberta Environment 2014a). Concentration levels of O_3 are generally higher in rural areas than in cities and towns (Alberta Environment, 2014a).

Rural areas generally measure higher concentrations of O_3 due to the following: 1) the transport of NO_x and VOCs from upwind urban centers and industrial operations, 2) the natural infiltration of stratospheric O_3 to the ground level and 3) as a result of natural processes produce VOCs (Alberta Environment, 2014a).

Tropospheric or ground level O₃ is not released directly into the air and is considered a secondary pollutant. Concentrations of ground level O₃ are present from two sources: 1) as a product of a reactions of precursor gases and UV light, and 2) the leaching of stratospheric O₃ through the stratospheric barrier into the troposphere. Tropospheric O₃ is a highly reactive pollutant and a major constituent of smog (Fort Air Partnership, 2014; US EPA, 2014b; Kindzierski, et al., 2007).

On ground level, O₃ has been proven to adversely affect human health, particularly in vulnerable and highly sensitive populations. People with preexisting lung conditions, children, those in advanced age groups and individuals that spend a significant portion of their lives active in the outdoors are considered to be the most intensely and, possibly, the most adversely effected by high levels of O₃ (US EPA, 2014b).

2.2 Global, National and Local Standards for Air Quality

2.2.1 Global

Air pollution poses a significant concern to health, as it is linked to increased morbidity and mortality rates of those exposed to high concentrations of pollutants from both indoor and outdoor sources (WHO, 2005a). Initially, the WHO published an air quality guideline (AQG) for air pollutants in 1987 with a

revision released as the second edition 1997. Since the completion of Europe's second edition guidelines, further research has provided evidence that those living in countries of low and middle incomes are at the greatest risk to the effects of air pollution. The rationale for this is that air pollution levels are rapidly increasing as these countries develop (WHO, 2005a). In many situations this problem is confounded by the lack of regulatory standards or poor enforcement of industry to abide by standards (WHO, 2005a).

In 2005, the WHO responded to the global concern of air pollution by releasing the Global Update Risk Assessment document (WHO, 2005a). These guidelines were developed in response to a real and global public health threat that air pollution presents. The guidelines were designed to provide guidance in reducing health effects of air pollution worldwide but were not standards or legally binding criteria (WHO, 2005a). Instead the WHO (2005) formulated these guidelines to provide scientific knowledge and information to various geographical regions with diverse air quality conditions that lack the necessary scientific framework and resources to conduct their own assessments.

At this time air quality standards are determined by the individual countries. The impetus of these air quality standards set by the nation is to be directed towards protection of the public health of its residents (WHO, 2005a). Each country's air quality standards are compiled as components to national risk management and environmental policies. Because each country sets their own air quality standards, a wide range of diversity exists between nations. Every country has their diverse circumstances and priorities, which may be dictated by factors

such as resources, economics, and political and social parameters. Some or all of these factors play a large role in influence a country's leaders to set and enforce preventative air quality management standards (WHO, 2005a).

As touched on above, the impact of O_3 and its' precursor gases, NO and NO_2 , in developing countries has become an increasing area of concern not only to human health but also to that of the environment. Concerns with the rapid deterioration of air quality have become a challenge for those living in countries such as China and India due in part to the increase volume and use of automobiles.

Two studies, one by Chan et al. (2003) in Asia and by Prabamroong et al. (2012) in Thailand, addressed the impact of rapid growth of industry and economic development on countries in Asia. In Hong Kong, Chan et al. (2003) researched changing levels of ground level O₃ and precursor gases in Asia using long-term data collected from early 1980's to 2000. Sharp increases in ground level O₃ over the span of fifteen years were related to regional O₃ buildup. These regions were areas where the data trends showed pollutant emissions were rising due to rapid urban and industrial development (Chen et al., 2003). In Thailand, Prabamroong et al. (2012) achieved similar findings supporting air quality deterioration correlated to unprecedented industrial and economic growth of developing countries.

The information in Table 1, gives reference values of global standards for NO₂ based on one hour and annual mean concentrations, which were set by the WHO (2005a) to protect human and environmental health in both the short and long-

term perspectives. Short term (one hour) standards for NO₂ were determined by the WHO not to exceed 200 ug/m³ or 106 ppb based on results from experimental studies that indicate a potential for significant health effects when exposure to concentration reached beyond this level (WHO, 2000c). The need for annual mean standards for NO₂ were determined based on evidence from animal toxicological studies. These particular studies suggested that long-term (annual) exposure to concentrations of NO₂ above the ambient standard had the potential of exerting adverse health effects in animals, thereby rationalizing the need for annual limits (WHO, 2005a). The health implications associated with NO₂ are not provided in Table 1 due to a level of uncertainty that exists with correlating the degree and type of human health effects with exposure to various levels of NO₂ (WHO, 2005a; WHO, 2000c).

Additionally, Table 1 provides the WHO's global standards for eight hour limits of concentrations O_3 for high levels, interim target (IT) levels and the Air Quality Guideline (AQG) (WHO, 2005a). The standards for all three of these categories were set based on the severity of health related outcomes of exposure to an eight hour mean concentrations of O_3 . At this time the evidence of outcomes related to long-term (annual) exposure were inconclusive and not sufficient enough to indicate a need for an annual guideline for O_3 (WHO, 2005a).

NO ₂	Concentrations	Health Implication
Annual mean	21 ppb	Public protection
One hour mean	106 ppb	Protects vulnerable
		populations
O3	Daily Max. :	
	8hr mean ppb	
High levels	120 ppb	Significant health effects in
		vulnerable populations
Interim target-1 (IT-1)	80 ppb	Inadequate public health
		protection
Air Quality Guideline (AQG)	50 ppb	Adequate public health
		protection

Table 1. Global standards for O₃ and NO₂ (WHO, 2005a).

Globally, each country plays a role in contributing to national risk management and the development of environmental policies by setting air quality standards that protect the public health of its people (WHO, 2005a). These standards set by individual countries are influenced by their level of development on a global scale, economic affluence, technological circumstance, public awareness, and various other political and social factors (WHO, 2005a).

2.2.2 National Standards: United States

In the United States (US), the National Ambient Air Quality Standards (NAAQS) sets regulatory standards on allowable emission rates of criteria pollutants released from stationary sources, i.e. industry (Berman et al., 2012; US EPA, 2014c). In 1977, the Prevention of Significant Deterioration (PSD) permit program was established by the United States Congress as a way of ensuring those countries meeting NAAQS guidelines were also continuously maintaining the standard (Berman et al., 2012). The Federal Clean Air Act (FCAA) plays a role by creating and maintaining partnerships between federal and state governments to achieve targeted goals for air quality (Berman et al., 2012). The current NAAQS values for O₃ and NO₂ are listed in Table 2 (US EPA, 2014c).

Pollutant	Averaging Time	Concentration
NO ₂	1hour	100 ppb
	Annual	53 ppb
03	8 hour	75 ppb

Table 2. NAAQS of O₃ and NO₂ for the United States (US, EPA, 2014c).

On the North American stage, the US and Canada have partnered to create the Canada – US Border Air Quality Strategy with the key players being Environment Canada along with Health Canada and the US EPA (Environment Canada, 2014a). The goal of this allegiance was to develop a Border Air Quality Strategy to identify and reduce trans-border air pollution through the design of specific pilot projects in an attempt to reduce air pollution between countries (Environment Canada, 2014a).

2.2.3 National Standards: Canada

Within the boundaries of Canada, Environment Canada is responsible for overseeing air quality monitoring. As a governing body, Environment Canada has produced programs and regulatory frameworks such as the Canada Environmental Protection Act. The act is an important part of Canada's federal environmental legislation aimed at preventing pollution and protecting the health of both the environment and humans (Environment Canada, 2005b). Canada-Wide Standards are designed to set restrictions on ambient air concentrations, closely monitor these
standards, and make changes in accordance with newly gained knowledge in order to protect and promote the health of human and environmental life (Environment Canada, 2005b).

The federal and provincial governments set standards for air pollutant concentrations; these concentration standards are set with strict expectations of adherence (Environment Canada, 2005b). These standards are set with the expectation that source-based industry and governmental regulatory bodies will strictly adhere to these air pollution protocols in order to protect the health of the natural environment, workers and the public (Environment Canada, 2005b).

The National Air Pollution Surveillance Program (NAPS) in Canada is committed to a goal to provide long term, accurate and uniform air quality data spanning across the nation (Environment Canada, 2013c). The NAPS program was established in 1969 with two purposes of monitoring and accessing the quality of ambient (outdoor) air in areas of Canada populated by people (Environment Canada, 2013c). The National Air Pollution Surveillance Network monitors air for specific pollutants such as gases SO₂, NO₂, O₃ and CO, as well as fine particulate matter (PM_{2.5}). This data collected can be used provincially to report the local Air Quality Index (AQI) and by Environment Canada for the Air Quality Health Index (AQHI) (Environment Canada, 2013c).

The data bank complied by NAPS enables comparisons of current and past data results in order to determine if any improvements or deterioration of air quality have been recorded. The information is also used by NAPS to promote reduction strategies for air emissions such as the Canada-Wide Standards for

Particulate Matter and Ozone and the Canada-US Air Quality initiative (Alberta Environment, 2014a).

The Canadian Ambient Air Quality Standards (CAAQS) and the National Ambient Air Quality Standards (NAAQS) are health based air quality objectives for regulating pollutant concentrations in outdoor air. In Canada, for purposes of promoting health, the CAAQS aims to improve air quality by continuously evaluating levels of ambient pollutants (Environment Canada, 2013c). Under the Canadian standards the NAAQO sets parameters on pollutant concentrations based on three exposure levels: the maximum tolerated level (MTL), the maximum accepted level (MAL) and the maximum desirable level (MDL) (Environment Canada, 2013c).

In response to the expansion of industry, a growing population and increase in vehicular emissions Canada has recently announced changes to the Canadian Ambient Air Quality Standards (CAAQS) for O₃ based on an 8-hour exposure duration time. Currently the existing standards is set at 65 ppb; in 2015 the projected standard is set to be reduced to 63 ppb with a long-range goal of 62 ppb by 2020 (Environment Canada, 2013c). The new air quality standards are needed in order to further protect the health of Canadian people and their natural environments. Due to various anthropogenic activities, people living in various regions of the country may be exposed to levels of air pollutants that exceed the national average. As Canadians, people are privileged to enjoy a good level of air quality, these improved standards for O₃ will act to further protect human health, especially for vulnerable sectors of the population such as children and the

elderly. Additionally, the new objectives or standards will ensure that bad air quality will be improved, while good air quality will be maintained (Environment Canada, 2013c).

Provided in Table 3 is a list of the current standards for both Canada and Alberta for two criteria pollutants, NO₂ (NOx) and O₃, for one hour and eight hour concentrations. Trigger values are those time-averaged values for O₃ based on an eight hour average concentration adopted from the Canada-Wide standard and applied at the provincial level (Alberta Environment, 2014a; Environment Canada, 2014a).

Parameter	Average Time	Alberta Ambient	Canada-wide
		Air Quality Objective	Standard
NO _x (NO ₂)	1 hour	300 ug/m ³ or 159 ppb	*MAL 213 ppb
. ,			*MTL 532 ppb
NO _x (NO ₂)	Annual	$45 \text{ ug/m}^3 \text{ or } 24 \text{ ppb}$	*MDL 32 ppb
			*MAL 53 ppb
O 3	1 hour	160 ug/m ³ or 82 ppb	*MDL 50 ppb
			*MAL 80 ppb
O ₃	8 hour average	128 ug/m ³ or *65 ppb	*65 ppb or 128 ug/m ³

Table 3. Canadian and Alberta AQG for O₃ and NO₂ (NOx)

Note:*denotes trigger values; MAL: Maximum allowable level; MDL: Maximum desirable level; MTL: Maximum tolerated level (Alberta Environment, 2014; Environment Canada, 2014).

2.2.4 Local Standards: Alberta and Edmonton

The air quality guidelines for Alberta are also provided along with the Canadian standards in Table 3. Alberta has 48 air quality monitoring stations throughout the province that operate to continuously measure levels of air pollutants such as CO, NO_x , O_3 , sulfur dioxide (SO₂), hydrogen sulfide (H₂S),

total reduced sulfur, PM_{2.5} and PM₁₀, dust and smoke, hydrocarbons (HC) and ammonia (NH₃) (CASA, 2014). The data retrieved from the air quality monitoring stations are stored in a central repository for ambient air, the Alberta Ambient Air Data Management System (AAADMS) or more commonly referred to as the Clean Air Strategic Alliance (CASA) Data Warehouse. The CASA Data Warehouse stores and archives time averaged hourly concentrations of air pollutants, including specific gases and particulate matter, which are measured at various urban and rural locations throughout Alberta via the Airshed monitoring (CASA, 2014).

In the city of Edmonton, ambient air quality is monitored through a joint effort that exists between the Alberta provincial government and various industrial groups (City of Edmonton, 2014). Within and bordering Edmonton's city limits there are four ambient air-monitoring station, as well as one station designed solely to measure particulate matter. All of these centralized monitors are operated by Alberta Environment (City of Edmonton, 2014). Edmonton participates with the Alberta Capital Airshed, a multi-stake holder which is a nonprofit organization that plays an essential role in air quality management and monitoring. The Alberta Capital Airshed also acts as a portal for public information on air quality (Alberta Capital Airshed, 2014).

Alberta Environment, Environment Canada, the City of Edmonton and interested community members have worked cooperatively to create a network to monitor ambient air quality and regulate industrial emissions (Alberta Environment, 2009b). The non-profit group CASA.org collaborates with the

above key players to manage, provide guidance and address concerns regarding air quality issues in local regions throughout the province (CASA, 2014).

In addition to centralized monitoring through the Alberta Airshed, there are a few other methods and techniques used for monitoring air quality in Alberta (Alberta Environment, 2013c). Other methods used for air quality monitoring include intermittent monitoring and passive sampling. Intermittent air quality monitoring is a system that monitors air pollutants as a 24-hour integrated concentration on a six-day interval. Passive sampler air quality monitoring is conducted by gathering air pollution samples from various locations on a monthly basis, which are collected and analyzed for pollutant concentrations (CASA, 2014).

Air quality plays an important role in determining the health of the environment. As literature reveals, the impact of industrialization, commercialization and personal vehicular use has the potential to compromise ambient air quality by increasing levels of NO_2 (NO_x) and O_3 . The air quality standards that are set globally, nationally and provincially are applied by various organizations, which strive to support optimum air quality. The objective of these various organizations is to work collaboratively to provide preventative air quality measures that are proactive in responding to the environmental impact of continuous population and economic growth in urban and suburban environments.

2.3 Human Exposures to Pollutants

When considering human exposure to air contaminants in the outdoor/ambient environment, certain factors must be considered prior to designing a human

exposure assessment. The factors which must be considered in accessing a possible human exposure to air pollution in outdoor environments are: 1) meteorological conditions 2) degree of mobility of contaminants in the atmosphere 3) source type, emission density and rate, and 4) distance/location of an individual in relation to the generating source of pollution (NRC, 1991).

The National Academy of Sciences (1991) has determined that the concentration of air pollutants in a given environment are generally dependent upon a combination of factors in relation to types of activities operating within a geographical location of interest. These environments of interest can be either indoor or outdoor venues. The activities within these environments may be those indoors as related to the types of household products used, or poorly ventilated living spaces; and outdoors as related to high volumes of vehicular traffic or industrial operations. The researchers concluded that the presence of air contaminants within any environment is often the result of a series of multiple, interactive and interrelated factors (NRC, 1991).

Concentrations of air contaminants within non-industrial indoor environments, for example homes, may be dictated by the following factors: 1) the quantity, physical location and characteristics of the sources, 2) the diverse characteristics of the specific built environment, including ventilation and infiltration rates, 3) air mixing and penetration of outdoor contamination, 4) meteorological conditions and 5) human and animal activity within the indoor environment (NRC, 1991).

Further research conducted on exposure analysis by Ott (2007) describes the concept of the full risk model as a tool to reduce the risk of adverse health outcomes as a result of exposure to environmental pollutants. The full risk model, as described by Ott (2007), has five foundational components that must be considered when conducting an exposure analysis. The components include: source of pollution, movement of pollutants, duration of exposure, dose concentration of exposure, and the subsequent effect of the exposure. The main emphasis of the science of exposure analysis is placed on the middle three components: the movement of pollutants, to the exposure, to the dose (Ott, 2007a). A relationship between the source of environmental pollutants and their effects on humans must be established. In this model pollutions sources are considered to be either traditional or non-traditional in origin (Ott, 2007a).

Traditional sources are those that are obvious such as smoke stacks and plumes exiting industrial operations and seen as directly entering the ambient air. The public may associate pollution with the sight and smell of these stacks and plumes and correlate these with a potential or current adverse health outcome for those living and/or working in the area (Ott, 2007a).

Conversely, non-traditional pollutants are those that are not obvious to human senses and are attributed to poorly-ventilated indoor environments or the use of products such as household cleaning products, personal care items, and indoor building products (Ott, 2007a). In comparison to traditional sources of air pollution, these non-traditional sources of pollution may not be well regulated or their environmental impact measured. These non-traditional sources may contain

highly reactive chemicals and when used in a closed environment, produce byproducts that can be more reactive than their predecessors. Human exposure to non-traditional sources of air pollutants is the premise of the receptor-based approach, known as exposure science (Ott, 2007a).

2.3.1 Exposure Science

Researcher and scientist, Wayne Ott (2007) stated that, in the past, environmental policy on air quality was determined using traditional methods that trace pollutants from the source to the human; the source oriented approach. According to Ott (1985), determining an exposure/outcome at the human level is extremely difficult, if not impossible, to trace using the source oriented approach. Exposure science has provided a fundamental understanding of exposure by narrowing its focus to the following components: the individual exposed, the ways the pollutants reach these individuals and the potential adverse effects that may result at the individual level (Ott, 2007a). Exposure science is a receptorbased approach, a concept that is designed to trace exposure retrospectively from the target to the source (Ott, 1985b).

Zhang et al. (2012) described the fundamental importance of collecting air pollutant exposure data at the personal human level in order to set regulatory and preventative risk assessment guidelines. Studies by several researchers have indicated that people are more highly exposed to pollutants indoors in places such as their homes, work and automobiles than in the ambient, outdoor settings (Ott, 2007a; Zhang et al., 2012).

Understanding the causal link between pollutant exposure and the effects at the target is necessary in linking air pollutions sources with human health impact. Exposure science is based on measuring human exposure to pollutants at the personal level as related to the surrounding environment.

2.3.2 Source Based and Receptor Based Exposure

Tracing the cause and effect of pollution on the target organism can be conducted in two ways: the concentration of pollutants can be measured at the source and traced forward to the target (source based) or the concentrations of pollutants can be measured at the target and traced backwards to source (receptor based). The first looks at the source while the second focuses on the receptor.

The phrase ambient air quality refers to the quality of outdoor air in the environment, pollutants can be measured based on their proximity to a source also known as source-based exposure monitoring (NRC, 1991; Fenske, 2010). These sources of emission are generally anthropogenic in nature and are often related to areas of large volumes traffic and industrial operations (NRC, 1991; Fenske, 2010).

Receptor-based exposure refers to the concentration of pollutants that an individual is exposed to in confined spaces and built environments such as workplaces, homes and schools (Ott, 2007a). Indoors, air pollutants can be released into the environment via store bought household cleaning products, synthetic building material and inadequate ventilation of the built environment (Lioy, 2010). Air quality indoors can be further compromised when the chemicals from these sources combine to produce other by-products (Lioy, 2010). Many of

these near-field sources of pollutants can be found in the average home and can be potentially harmful to the health of its occupants, especially small children, those with respiratory ailments and the elderly.

Figure 1 provides an example of some of the common and potentially harmful household toxins people may be exposed to within their homes. The combinations of various chemicals to form other chemicals is not easy to access as this process of air mixing can be rapid and spontaneous. While there are current standards set for maximum concentrations of the criteria pollutants, it is very difficult to measure the effects of air mixing and moment to moment concentrations of other harmful chemicals created by this process (Lioy, 2010).



Figure 1. Diagram of potential household pollutants and their sources.

Note: 1) chemicals released from building materials; 2) outdoor ambient air pollutants; 3) mold and bacteria; 4) chemicals released from modern furniture; 5) personal care products; 6) combustion gases from fireplaces and wood-burning stoves; 7) improperly or non-ventilated cooktops (gas); 8) vehicular emissions, paint, solvents, herbicides and pesticides; 9) detergent, fabric softeners, aerosol spray cleaners; 10) cigarette smoking and candles burning; and 11) soil vapor (adapted from Harris, 2013).

2.3.3 Direct Versus Indirect Approach to Measuring Human Exposure

In past history, the indirect and direct approaches to measuring air pollution concentrations at the personal level have differed greatly. A new paradigm in air monitoring has evolved due to the need to better understand the connection between human exposure and pollution. This evolution in exposure concepts has resulted in blending and integrating elements of both the direct and indirect approaches in order to better measure human effects. A brief description of both methods along with an outline of the benefits and limitations will be provided in the following section.

Indirect methods of air quality monitoring involves the use of either passive or active samplers to measure concentrations of pollutants in an environment of interest (Zhang and Lioy, 2002). A time activity diary supplements the data collected by the monitors and records artifacts as related to the specific monitoring period. The time activity records or journals are used as a means of recording circumstantial details during monitoring times based on the subjects' activities patterns given time and space (Zhang and Lioy, 2002). Limitations of the indirect method pertain to the questionable reliability of the sensors in collecting accurate concentration levels of pollutants; and inconsistency and inaccuracy in documentation by the subject of time activity information (Zhang and Lioy, 2002).

The indirect approach is considered a modeling approach. A greater level of uncertainty lies within the indirect method due to the inherent presence of confounding factors and measures of bias. Research that employs indirect

approaches such as environmental monitoring, questionnaires, diaries and models (i.e. fugacity or Monte Carlo method) does not provide data that either accurately nor realistically represents actual personal exposure (Kindzierski, 2013).

In the past, the direct approach to measuring human exposure to air pollution used either biological markers or personal air quality monitors to record pollutant concentrations (NRC, 1991). Historically, personal exposure monitoring devices were expensive, somewhat obtrusive, and limited in which pollutants they could measure (NRC, 1991). New developments have produced small, light-weight, inexpensive personal exposure monitors. These devices are highly technical with the capabilities to measure a larger variety of pollutants (US EPA, 2012c).

Recent air quality research has incorporated the use of personal exposure monitors with time activity diaries, a method that incorporates facets of both indirect and direct approaches. As reported by Zhang and Lioy (2002) and Ott (2007), time activity diaries have been designed and used as a way of recording details pertaining to time, space, duration and conditions related to the activities of the individual during monitoring periods. From these time activity diaries and the quantitative data collected by the sensors, inferences can be drawn from a sample of people as being representative of that area, and therefore, applied to a larger population.

The direct approach of measuring human exposure to pollutants through use of personal exposure monitoring has been found to be valuable. The rationale for this can be explained in that personal monitoring provides for a realistic measurement of exposure to near-field sources of pollutants based varied time activity patterns

of an individual or across a population of interest (Ott, 2007a). The approach was also found to be valuable in providing quantitative measurements of ingestion through food, water and dermal contact (Ott, 2007a). The direct approach is receptor based and is often referred to as personal exposure monitoring (PEM) (Kindzierski, 2013).

2.4 Types of Air Monitoring Methods

Studies across the world have delved into various techniques for measuring air pollution levels from ambient air concentrations to near-field exposures at the personal or individual level. While both centralized and personal exposure monitors aim to measure concentrations of air pollutants, one is far-field source based while the other is near-field source based.

In Houston, Carzola et al. (2012) tested ambient air ozone levels using a new direct measurement technique labeled Measurement of Ozone Production Sensor (MOPS). The MOPS was compared with two ambient air estimation methods for measuring ozone, the calculated $P(O_3)$ and the modeled $P(O_3)$. The quantitative comparison of the three methods showed that the measured and calculated O_3 were similarly dependent on NO, whereas the modeled O_3 was half that of the measured O_3 . The researchers found that although the MOPS technique requires more testing, the model shows potential to contribute to the understanding of the chemistry required to produce O_3 and, thereby impacting future air quality regulatory actions (Carzola, et al. 2012).

East Asian countries have become increasingly concerned by atmospheric pollutant concentrations in the ambient air due to growth of industry and vehicular use.

Itahashi, et al., (2013) studied episodic pollutant activities using the High Order Decoupled Direct Method and Community Multiscale Air Quality Model (HDDM-CMAQ) to clarify the source-receptor relationship (S-R relationship) of O₃ concentrations to NO_x and VOC in regions of East Asia. The study determined that far-field sources of NOx presented as the foundational precursor to increased O₃ levels in spring, summer and fall.

Due to a resurgence of interest in the need for further development of personal air monitoring systems, the US EPA took action in the spring of 2009 (Gwinn et al., 2011). This sparked a workshop gathering of parties which then led to the formation of a mission with the mandate of estimating the benefits of reducing hazardous air pollutants. From this, a list of hazardous air pollutants (HAPS) was produced as a part of the Clean Air Act Amendments of 1990 as facilitated by the US EPA (Gwinn et al., 2011).

The report by Gwinn et al. (2011) concluded that estimating benefits of reducing air toxins is a multifactorial, complex process which required special consideration and alternative methods of evaluation. Gaps in toxicological data, uncertainties in dose/response extrapolation for high dose animal studies to low dose human exposure, and limited ambient and personal monitoring data are issues that required further clarification in order to fully understand the mechanism of action and to enable effective regulation of HAPS (Gwinn et al, 2011).

In 2012, the US EPA held an Apps and Sensors for Air Pollution Monitoring Workshop to facilitate collaboration between US EPA scientists and developers of

air monitoring sensors (US EPA, 2012d). The sensor developers came from various parts of the United States and Europe in order to seek guidance from US EPA scientists on issues pertaining to air monitoring. The emphasis was placed on the development of effective personal air quality monitors that were sensitive, accurate and easily calibrated. The goal of this collaboration was to promote communication between the US EPA scientists and agencies dedicated to exposure assessment sensors in order to improve technology, accuracy and functionality (US EPA, 2012d).

Geyh et al. (1997) developed a small active O_3 sampler, the Harvard Active Ozone Sampler. The Harvard Active Ozone Sampler demonstrated a high level of accuracy when compared with UV photometric measurements. Quantitatively, the study found that the Harvard active ozone sampler/UV photometer showed an accuracy of 0.94 to 1.00 and a level of precision equal to \pm 4.1 to 6.5%. Additionally, Geyh et al. (1997) concurred that this sampler performed equally as well as the Time Exposure Diffusion Sampler, the only other O₃ monitor of its kind at the time (Geyh et al., 1997).

The studies discussed above provide evidence that centralized fixed-site station monitoring and personal exposure monitoring have their respective roles in air quality monitoring. While fixed-site monitoring provides for information on general geographical air quality conditions; personal exposure monitoring provides insight into exposures incurred at the receptor level, which vary greatly from one person to the next. In order to correlate an adverse health outcome with an exposure to air pollutants with any certainty, the fundamentals of exposure

science must be met. Personal exposure monitoring may provide the exposure/dose information necessary to ascertain if and where a true health risk exists.

2.4.1 Station Monitoring Versus Personal Monitoring

Studies have shown that centralized fixed-site monitoring may not be the most representative of true exposure and that personal exposure monitoring of air pollution may be the better solution. Personal monitoring incorporates elements of exposure to air pollutants relating to activity and behavior patterns that are unique to the individual which may not be well represented by fixed site measurements.

The following three factors are of interest when studying human exposure patterns to air pollutants: ambient concentrations of pollutants, the combined and cumulative effect of various indoor sources of air pollutants, and human time activity patterns (Demokritou, et al., 2001). Centralized fixed-site monitoring has been shown in the past to provide essential information and a general evaluation of the air quality to provide evidence to support the development of regulatory policy for promotion of environmental and public health.

In addition to addressing pollution levels in ambient air, the US EPA and Environment Canada have also recognized the need to better understand the short and long term effects of exposure to O₃ and NO₂ on a personal, individual level as humans go about their daily lives (US EPA, 2012d; Environment Canada, 2013b). The development of active, personal, real time monitors has improved vastly in the last decade with devices constructed to be small, lightweight, cost effective and easily powered (US EPA, 2012d).

In past studies, researchers in the United Kingdom studies the limitations of fixed-site air quality monitoring. Sherwood and Greenhalgh (1960) discussed the restrictions associated with fixed-site or static air sampling methods when monitoring at occupational sites. The researchers explained their concerns in this following statement: "it is sometimes necessary to determine the exposure of workers who are engaged in a number of operations of working in a variety of places. Under these conditions, air sampling at fixed points can give little indication of exposure" (Sherwood and Greenhalgh, 1960, p. 127).

The National Academy of Science (1991) supported the need for receptorbased monitoring of pollutants in their study by concluding that measuring air pollutant concentrations was a fundamental part of predicting problems and taking action in protecting both environmental and human exposures to pollutants. The researchers concluded that air quality measurements must be conducted in both an effective and accurate manner in order to optimize resources and provide representative data for devising regulatory protocols that are reflective of realtime activity exposures (NRC, 1991).

Nejadkoorki et al. (2011) addressed the issue of optimizing locations of sampling station. In their research, a spatiotemporal approach was used to measure actual human exposure to air pollutants. In fast-growing urban centers such as Yzad, Iran, air pollution monitoring practices have focused on locating monitors at several pollution 'hot spots'. While these locations are acceptable for determining maximum exposures and for estimating the degree of health risk, the researchers questioned whether this type of monitoring practice was indicative of

actual, real-time daily exposure at the individual level (Nejadkoorki et al., 2011). After comparing results from the spatiotemporal approach to 'hot spot' monitoring, researchers concluded that monitors when strategically placed in areas most representative of urban exposure provided cost-effective and time saving solutions in real-time air quality monitoring (Nejadkooki et al., 2001).

In existing epidemiological studies, the relationship between human health and air pollutants has been researched by using centralized fixed-site monitoring as the standard for quantifying exposure (Ozkaynak et al., 2013). Unfortunately, due to variation in human activity patterns, station monitoring does not have the capacity to account for the multifactorial nature of human exposure to air pollutants (Ozkaynak et al., 2013).

Often air pollutants that are spatially heterogeneous, such as vehicular emissions, are easily misclassified based on values reported at fixed-site monitors (Ozkaynak et al., 2013). Station site monitoring data generally lacks information based on spatial and temporal boundaries, providing an unclear picture of true human exposure (Ozkaynak et al., 2013). In the study conducted by Ozkaynak (2013) and similarly by Stienle (2013), the findings of both concluded that human exposure to air pollutants was best represented through personal monitoring in various geographical locations during different times of day.

A study by Spaeth (2002) reported that, traditionally, the practice of setting regulations for air pollutants has been based on emissions rather than exposure (Spaeth, 2002). In Spaeth's (2002) report, the researcher states that air quality assessment and regulatory bodies currently discount or completely disregard

human exposure as a major factor in setting standards. Human exposure levels to toxic amounts of pollutants at a continuous rate have not been well represented.

As commonly reported in studies, Speath (2002) reconfirms that the average person spends approximately 90% of time in indoor environments. With regulatory standards for air quality being set based on ambient data, indoor exposure which best represents personal exposure, has been entirely discounted. Because of this, air quality standards are set with data that is based on real-time concentrations of far-field ambient pollutants and not personal exposure to near-field sources of pollutants (Spaeth, 2002).

Busy urban centers are thought to be focal areas for air quality monitoring; these are presumed to be spots where human exposure to near-field, ambient air pollutants may be significantly high. The Boston Personal Monitoring study conducted in Boston by Ryan et al. (1986) tested human exposure to NO₂ by using personal exposure monitoring of a selected group of study subjects. The premise of the study was to measure peoples' exposure to NO₂ based on unique time activity patterns. Data collection involved the use of NO₂ monitors, time activity diaries and took into consideration the unique design of the home being monitored.

The study by Ryan et al. (1986) concluded that people living within indoor environments with gas ranges experienced a higher exposure (11 ppb) to NO_2 in comparison to those with electric ranges. Subsequently, the type of furnace fuels used for heating the home, whether the home was single or multi-family and if there was a microwave on-site had an impact on the level of indoor concentrations

of $O_3 + NO_2$ (Ryan, et al., 1986). The researchers did caution that these results may be unique to this geographical setting and specific circumstances, stating that findings may not be applicable to other similar exposure scenarios.

These studies discussed provide insight into some of the research that has been conducted comparing far-field, source-based monitoring to near-field, receptor-based monitoring. While these technologies have the capacity to measure similar parameters their sources are different. Fixed-site monitoring provides for a guide as to the air quality for a geographical area; while personal exposure monitoring offers an insight into exposures incurred in areas where people spend their time. At this time both monitoring approaches are necessary in assessing and preventing potential environmental and human health risks in various settings.

2.4.2 Passive Monitors

Passive samplers (Figure 2) are commonly used in remote locations and wilderness areas where there is no access to electricity. Passive samplers operate without needing a power source. Subsequently, passive samplers are advantageous because they are inexpensive, small and easy to use. They are limited in that they may be effected by elements such as wind velocity, temperature and relative humidity which may result in inaccurate measurements of cumulative exposures in comparison to those collected by a continuous monitor or an active sampler (Krupa and Legge, 2000).



Figure 2. Diagram of a passive sampler.

Note: The components of the passive sampler in Figure 2 are as follows: 1) front cap; 2) diffusion membrane; 3) spacer; 4) collection filter; 5) carbon filter; and 6) badge body (adapted from: Krupa and Legge, 2000).

A study conducted in Alberta by the Wood Buffalo Environmental Association (WBEA) in 2008 used passive air samplers and time activity diaries to record air quality data in a community. The research findings concluded that ambient monitoring of far-field sources of pollutants was not a reliable predictor of real time personal exposure to air pollutants. This conclusion was justified by findings showing that indoor built environments are often found to be where air pollutant exposures are at the highest of levels due to human activities and structural details of the specific built environment (WBEA, 2008). Similar studies in other areas of Alberta over the last decade have concluded similar results. These studies were

conducted by the Wabamum and Area Community Association, the Fort Saskatchewan and Area Community Association and the Grande Prairie and Area Community Association due to their close proximity to industrial operations of oil, gas and mining (WBEA, 2008).

Passive samplers work best at collecting concentrations of air pollutants when conditions allow for free-flow, rapid air movement over a vast spatial area (Gaga et al., 2012). The technology does not require active air movement through a pump, rather airborne gases are collected through means of a physical process such as diffusion or permeation through a membrane (Gaga et al., 2012).

A study conducted by Krupa and Legge (2000) found that passive samplers are incapable of identifying short-term pollutant exposures or levels which exceed regulated standards. Although statistical methods have been established to effectively correct for these limitations of passive sampling, development of this technology was ongoing. (Krupa and Legge, 2000). The authors conclude that the use of co-located passive samplers was advantageous in studies focused on regional level air quality and ecological risk assessments.

Yu et al. (2008) reviewed the development of passive samplers for detecting NO₂ levels in air, the sampling features of those currently available, and their ability to monitor indoor/outdoor ambient as well as personal exposure to this pollutant. The purpose of Yu et al.'s (2008) study was to aid researchers and risk assessors in designing and streamlining field sampling strategies that are representative of actual indoor/outdoor and personal exposures to air pollutants (NO₂).

In the United Kingdom, Lin et al. (2010) introduced a new directional passive air sampler (DPAS) as a way of conducting continuous sampling of ambient air for NO₂ concentrations. The DPAS responded to directional wind changes and velocities, showing potential of providing qualitative data. Diffuse passive sampling is less expensive and requires fewer resources when compared with a chemiluminescent analyzer (Lin et al., 2010). With the advent of some design changes, the DPAS was found to be capable of sampling for air pollutants beyond NO₂. The researchers conclude that further testing and field trials of the DPAS were supported.

2.4.3 Active Monitors

Research has demonstrated that active sampling is thought to be the method of choice for use in measuring personal exposure to air pollutants. The technology and usability of these devises has improved vastly, due to reduced size and advanced capacities to store data, retrieve data and download data for future analysis. Figure 3 provides for an example of just one of the new designs in active samplers.



Figure 3. Diagram of a Cairclip O₃ + NO₂ monitor (adapted from Cairpol, 2014).

Note: The components are as follows: 1) highly sensitive electronics; 2) microelectronic with data-logger; 3) lithium-ion battery; 4) electrochemical sensor; 5) micro-fan; 6) patented buffer; and 7) assembled sensor (Cairpol, 2014).

The active sampling devices use a pump to pull air borne contaminants through a collection device (NRC, 1991). Active sampling is often used in monitoring for concentrations of gases and vapors in air. In comparison to the passive sampling technology, active sampling is not affected by wind speed and is equipped with a backup section which enables quality and reliability checks to be executed (NRC, 1991). New research and developments in technology for active sampling in measuring various air pollutants has evolved in recent years. Small, lightweight active samplers have been marketed for use in personal monitoring to measure real-time exposure to pollutants in various settings. These setting may include areas such as the workplace and/or residential environments (US EPA, 2012d).

An important aspect of this evolving technology has been to create monitors that are easy for people to wear, simple to use and provide instant warnings when exposures are high. These particular design features aim to engage people and create awareness of issues pertaining to their exposure to pollutants in the local environment with which they spend the majority of their time (US EPA, 2012d). By engaging the public through the use of these active air quality samplers, the public are able to develop an awareness of air pollution as it pertains to the health of their immediate environments (US EPA, 2012d).

In particular, recent developments by Cairpol have resulted in the production of small, personal active air monitors that measure a sum of the continuous concentrations of O_3 and NO_2 on a real-time capacity (Cairpol, 2013). In a technical report conducted by the Joint Research Center (JRC) in Europe, the sensors were evaluated for functionality in comparison to other similar sensors, as well as performance in laboratory and field settings. After a series of tests, the researchers determined that the Cairclip $O_3 + NO_2$ was found to have met the Data Quality Objective (DQO) of indicative method of the European Directive (JRC, 2013). A more in-depth discussion on the Cairclip $O_3 + NO_2$ sensors will be provided in Chapter 3.

2.4.4 Personal Monitors

Currently, the three most common methods of personal exposure monitoring are: personal air monitoring, personal dietary monitoring and reconstruction of exposure based on findings from biomarkers (Kindzierski, 2013). Personal exposure monitoring is considered the 'Gold Standard' and the most reliable method of attaining accuracy in the concentrations of a pollutant(s) received by the human in order to ascertain if a risk exists (Kindzierski, 2013).

Personal air monitors use either passive or active technology, depending upon the instruments design, to measure pollutant concentrations at the receptor level. As described briefly, new designs of personal exposure monitors, such as the Cairclip, have resulted in the emergence of small, highly sensitive, low powered, cost effective and portable devices worn by a person at or around the breathing zone (NRC, 1991).

Initially, the focus on air quality was placed on developing national outdoor monitoring systems for criteria pollutants with little interest focused on personal exposure monitoring (US EPA, 2012d). Regardless of the beliefs of some that felt that centralized monitoring was the best option, researchers continued to study and gain knowledge on personal exposure monitoring.

The result of research conducted in the 1970's by Granger Morgan and Leonard Hamilton showed that the efficacy of personal monitors was found to be feasible due to improvements in technology (Morgan and Morris, 1976). These findings set the stage for further testing and development of sensors that were designed to better measure near-field exposure to pollutants (Morgan and Morris, 1976).

Simultaneously, the National Academy of Science (NAS) (1977), upon the request of the United States Congress, reviewed the scientific methods of the US EPA. Findings in their nine volume report contained a section titled 'Environmental Monitoring' (NAS, 1977). The report confirmed that the organization was not participating in further development of personal air quality monitors. In response to the US EPA's stance on further development of personal monitoring technologies, Wallace (1982) vocalized his concern. Wallace (1982) aimed to inspire further research and developmental strategies for improving personal air monitoring devices by making this statement: "the Agency is not currently developing personal air quality monitors. By equipping a controlled sample of people with these portable sampling devices, the concentration of the pollutants to which they are exposed could be measured. There is evidence to challenge a common objection that personal monitors are technologically impracticable. Prototypes have been developed to detect several air pollutants at levels near ambient concentrations" (Wallace and Ott, 1982).

The above words written by Wallace were intended to promote development and improve the technology of personal active air monitoring devices to enhance reliability of air quality data and to act as an adjunctive tool exposure assessments. Upon these recommendations, the US EPA responded by sponsoring a symposium and allocating funding in order to instigate development of personal air quality monitors (Wallace, 2007b).

As a result of forward thinking on the part of the NAS and the support of the US EPA, developmental advances of personal monitoring devices have evolved to

a point where air quality issues can be pinpointed with far greater accuracy (Wallace, 2007b). Personal monitoring has determined that the main sources of exposure of humans to pollution are those that are close to the person (near-field sources) that are incurred during various activities as a person moves about their day.

Cairpol, the manufacturer of a new technology in personal exposure monitoring, is one of many companies engaged in further, advanced development in air quality monitoring. The European based company has produced active samplers that are designed to measure personal level exposure to various gases including one that measures a sum of $O_3 + NO_2$, named the Cairclip $O_3 + NO_2$ (Cairpol, 2014).

Currently, limited research has been conducted that tests the accuracy and reliability of these sensors in both field and laboratory settings. The study released from Europe and conducted by the JRC in 2013 tested the Cairclip O₃+NO₂ to evaluate their performance and degree of measurement uncertainty in laboratory and field settings (Spinnelle et al., 2013). The sensors were evaluated in relation to the DQO, a guideline established to promote the health of humans and ecosystems, set by the European Air Quality Directive (Spinnelle et al. 2013).

The aim of the study by the JRC was to demonstrate whether or not the Cairclip sensor satisfied the DQO of 60 nmol/mol (60 ppb) for O₃ Indicative Methods at the target level limit values (LV) (Spinnelle, et al., 2013). The DQO defines target level for O₃ as a fixed level that is aimed at avoiding long-term harmful effects on human health and/or the environment as a whole. The term LV

is defined by the DQO as a concentration limit is set based on scientific findings, aimed at avoiding, preventing or reducing the harmful effects on human health and/or environment as a whole. These LVs for pollutants pertain to concentrations reached within a set period of time and once reached are not be exceeded (European Commission, 2014a). In reference to a LV value of 60 ppb, the research found the Cairclip $O_3 + NO_2$ sensor satisfied the DQO Objective of indicative method of the European Directive. Field testing, which challenged the Cairclip $O_3 + NO_2$ sensor against the centralized monitors in France, showed a relative expanded uncertainty of 20%, a value very similar to the manufacturer determined value of 19% (Cairpol, 2014).

A fundamental part of the European Commission's study involving the Cairclips was to challenge the integrity and accuracy of the sensors given different environmental settings and conditions. The Cairclips were tested in both a laboratory and a field setting for their efficacy in measuring levels of O₃ and NO₂. In the field, researchers tested the sensors for O₃ monitoring in suburban/rural settings. The sampling sites for NO₂ were selected to represent high density urban areas, characterized by large volumes of traffic and population density (Spinnelle et al., 2013).

In order to determine the Cairclip's integrity to collect concentrations of O_3 and NO_2 equally, researchers placed the sensors in settings that were favorable for collection of the individual gases. By doing this, the researchers were able to conclude that in both laboratory and field settings the Cairclip showed a heightened sensitivity or affinity to concentrations of NO_2 over O_3 . Because of

this, the researchers determined that the sensors would act to underestimate levels of O_3 when monitoring in areas where both gases are equally and simultaneously high (Spinnelle et al., 2013).

In addition to the findings discussed above, the JRC found that on average the response time of one and a half minutes, the fall time of less than one minute and the rise time of approximately two minutes of the Cairclip $O_3 + NO_2$ sensor were congruent with that originally reported by the manufacturer. The sensor did not experience short or long term drift, were not sensitive to temperature changes and did not report extreme effects when concentrations of O_3 changed (Spinnelle et al., 2013).

Limitations of the sensors were found to be that the Cairclip had the potential to become desensitized or deconditioned post-calibration if not exposed to similar concentrations in a new setting. Deconditioning of the Cairclip was thought to occur when the sensor was placed in new environmental conditions with lower concentrations of O₃ and NO₂ or if the battery charge was lost (Spinnelle, et al., 2013). The researchers also believed the sensors to be overly sensitive to concentrations of NO₂ affecting its reliability in measuring accurate O₃ levels (Spinelle, et al., 2013).

Different methods, such as fixed-site monitors, stationary microenvironment monitors and personal monitors, may be used to measure concentrations of air pollutants. When these methods are compared and rated in terms of accuracy, personal monitoring has been found to be, by far, the most effective and realistic method for attaining individual exposure information (Steinle et al., 2013). This

said, current policy on air quality remains set based on centralized fixed-site monitoring, suggesting that the technology of personal monitoring has not quite reached a consistently reliable level in order to replace station monitoring. Better yet, as the personal exposure technology improves these have the potential to be an essential adjunct to centralized monitoring.

2.5 Components of Personal Exposure Monitoring

Humans have a unique way of interacting within their environments. Because on this, exposure to pollutants varies from person to person based on the variety of activities people engaging in and the areas with which they spend time. Statistically, humans are found to spend 90 percent of their day in a variety of indoor environments, be it at work, home, school or other public establishments. A person's ethnic background, social connection, environment and socioeconomics are key elements the social determinants of health. Often these factors dictate the quality of one's health and are predictors of lifestyle habits and daily activity patterns.

Personal exposure monitoring as reported by Spengler and Soczek (1984) is best represented by the use of a combination of personal exposure sampling supplemented with individual time activity diaries. When human health is of interest, the focus of monitoring is to test the environments which people spend the majority of their time. By monitoring indoor environments of a person or a group of persons, researchers are collecting air quality data most representative of actual exposure (Spengler and Soczek, 1984).

Although this research does not expand in detail with regards to the social determinants of health, it is important to make the connection that various lifestyle choices and habits of people may be predetermined by socioeconomic status and social conditioning. These lifestyle habits, such as cigarette smoking, can inadvertently result in exposures to higher levels of indoor air pollutants on an everyday basis; and potentially impact the quality of an individual's health in the long term. As reported in a study by O'Neill et al. (2003), the researchers reaffirmed that exposure to levels of air pollution varies based on socioeconomic circumstances. Socioeconomic status and air pollution are found to be confounding factors to increased rates of morbidity and mortality from respiratory ailments (O'Neill et al., 2003).

2.5.1 Real Time Monitoring and Time Activity Diaries

Time activity may be defined as the spatial and temporal boundaries, which define how people spend their time throughout the day (Steinle et al., 2003). For purposes of studying human exposure to air pollutants, knowing where people spend their time, and the activities they engaging in during this time are the primary determining factors in assessing individual exposure/risk potential. In the case where pollution is sufficiently high and duration of human exposure is long, an exposure will occur (Kindzierski, 2013).

In order to obtain data on activities patterns of people; tools such as timeactivity diaries (TADs) and questionnaires have become essential to information gathering (Lioy, 2010). When managed with continuity and detail, data received

from TADs and questionnaires can be a critical tool used to correlate exposure to specific locations, times and activities (Steinle et al., 2013).

Real-time air monitoring devices are those that record pollutant concentrations as they occur at the receptor of interest. Research conducted by Adam et al. (2009) tested a high resolution, spatio-temporal sampling method for assessment of personal exposure to particulate matter. The researchers conducting the study concluded that this method was effective and applicable to measuring real-time personal exposure all contaminants, including particulate matter.

The future of real-time, near-field source exposure monitoring shows potential for providing a better understanding of personal exposure. The advent of new technology and design features that encourage personal compliance will assist in establishing where exposure to pollution may be high based on time and location of the individual.

2.5.2 Microenvironments

Microenvironments may be described as any physical space where people spend time engaging in certain activities at various frequencies and for certain durations of time (Steinle, et al., 2013). Measuring air quality within certain microenvironments where people spend time is beneficial to identifying exposure to pollutants in certain built environments (Steinle, et al., 2013). Although air monitoring of indoor or contained microenvironments may not be as effective as personal exposure monitoring, it has been shown to be more representative of individual exposure that that of outdoor monitoring (NRC, 1991). A condition known as 'sick building syndrome' has become a health concern for people living and working in indoor environments with compromised air quality (Wallace, 1997b). The condition can be related to structural issues of the built environment such as inadequate or poorly designed ventilation, off-gasing of synthetic materials used in carpets and furnishings, and interruption in air flow created by room dividers (NRC, 1991; Wallace, 1997b).

A study by Carvalho et al. (2009) tested air quality on public transportation due to the high number of commuters using this form of transportation in busy urban centers. In the study, the researchers introduced a mobile air monitoring station that was attached to mass transport vehicles such as buses and trains as a way of measuring air pollutant concentrations in various urban areas at various times. The mobile monitor was developed as a way of informing commuters of their level and duration of exposure to pollutants in various areas of a busy metropolitan setting. Researchers concluded that the mobile station design was advantageous over fixed site air monitoring as it allowed for real-time air monitoring in specific microenvironments close to pollutant source (Carvalho et al., 2009).

2.6 Summary

The information in Chapter 2 aimed to provide for a background discussion and overview of the air pollutants O₃ and NO₂, current and past monitoring trends and tools, details of exposure science and components of air quality monitoring. The purpose of the research presented in this study is to address the level of accuracy and precision of the Cairclip sensors in the city of Edmonton in

reference to the Edmonton south centralized station; and to test the variation in exposure to pollutants that exists between monitoring near-field sources at the receptor and far-field sources as recorded by centralized monitoring.

The study intends to test new technology in active sampling by challenging its ability to measure pollutants at a personal, real-time capacity given diverse exposure scenarios. The information may be beneficial in determining which urban environments the Cairclip sensor functions best and determining areas that may be considered 'hot spots' of pollutants, which may pose potential health risks to humans and diverse ecosystems.
3 METHODOLOGY

3.1 Basis of Study

Monitoring of air pollutants in Edmonton, Alberta is conducted through the Alberta Airshed's four fixed-site monitoring stations located throughout the city. These monitoring stations assess air concentration of criteria pollutants and particulate matter hourly. The daily Air Quality Health Index (AQHI) is set based on data collected at fixed-site monitoring stations and is available for public access. While measurements of ambient air pollutants by means of centralized monitoring is beneficial for providing a generalized rating for daily air quality and setting policy, studies have shown that this type of monitoring does not well represent air pollutant exposure at the personal or individual level.

In this study, conducted from July 2013 to January 2014, new technology in personal air quality monitoring devices was tested in a two-phase model design. Phase one of the study tested: 1) the Cairclips', a personal exposure monitor (PEM), level of accuracy in measuring continuous concentrations of O₃ and NO₂ in ambient air in comparison to the Alberta Airsheds fixed site monitor at Edmonton's south station, and, 2) to compare the level of precision between the PEM's when used in a field setting. Phase two of the study measured near-field sources of pollution at a personal level also referred to receptor based exposure. As part of phase two, the person's residence was monitored in both indoor and outdoor capacities for comparison.

The following sections provide a description of the air monitoring devices used in the study, details regarding the design of the two phases of the study, the type

of data collected, procedures for determining precision and accuracy of devices and data inclusion and exclusion criteria based on critical analysis of the data collected (Alberta Environment, 2006e). The data collected in this study is intended to evaluate the efficacy and reliability of new, innovative designs of active sampling air quality monitors as a future means of enhancing reliability in measuring human exposure to air pollution.

3.2 Description of Monitors

The US EPA (2012d) reported that the ongoing development of personal monitoring devices shows a promising future in providing alternatives to current air monitoring practices that may: 1) reduce costs and decrease the demand for manpower, and 2) promote public engagement and involvement in issues of air quality that may affect both human and environmental health (US EPA, 2012d).

New technology in active air samplers, as exemplified by the Cairclip, aim to provide data on exposures to near-field sources of pollutants measured at the human level. This may prove advantageous as a means of engaging people in understanding the importance of air quality in order to alter behavior that may further contribute to pollution levels. Also because indoor air quality poses the largest threat to human health, personal monitoring of these spaces aims to provide a real view of true risk.

Several companies have produced personal exposure monitoring devices that are targeted at measuring near-field pollution at the receptor level and are designed to measure various types of air pollutants. The Cairclip was designed and manufactured by Cairpol, a company in Mejannes-les-Ales, France (Cairpol,

2014). The unobtrusive, small, lightweight design of the Cairclip active sampler makes them more compatible for use on a personal level than that of past personal air monitoring devices. Traditionally, personal active samplers have been quite large and too cumbersome to be worn for long periods of time.

The Cairclip is designed with a LCD screen that provides time of day, battery life, as well as instant readouts and warnings based on detection levels of air pollutants by concentration and exposure time (Cairpol, 2014). The Cairclip is capable of providing four different warning levels depending upon the concentration of pollutants detected. The battery is lithium-ion with an integrity of up to 24 hours. The device can be easily recharged using a computer via a USB or an electrical outlet with an adapter, which is supplied by the company.

In order to ensure longevity and safety of the sensors, the operating guidelines as devised by the Cairpol manufacturer were adhered to strictly (Appendix A). For the entire duration of phase one and two, the monitoring was conducted on days that met these climatic conditions: 1) the temperature range of -20 to +40 degrees Celsius, 2) a relative humidity ranging between 10 to 90%, and 3) an atmospheric pressure of between 0.10 and 2.00 MPa. This information is provided in a copy of the Cairclip technical data sheet compiled by Cairpol in Appendix A.

The Cairclip sensor has the capacity to save data for up to 20 days postmonitoring. Once the data sampling time was complete, the data was downloaded from the Cairclip sensor directly onto a PC laptop computer via a program called Cairsoft. The Cairsoft software is currently compatible for use with PC computers and is a uniquely designed computer program, specifically used for data retrieval

from the sensors. The Cairclip settings can be altered through the Cairsoft program provided the sensor is connected to the computer via a USB cord. The Cairclip has the capacity to measure pollutants on a continuous, real time basis at either one or fifteen minute intervals in units of either ppb or ug/m³ (Cairpol, 2014). For purposes of this study, the one-minute data collection interval option was chosen. Downloading of data from Cairclip into excel worksheets was achieved through Cairsoft program (Cairpol, 2014). The diagram in Figure 4 shows an example of the type of Cairclip sensor that was used in the study.



Figure 4. Example of the Cairclip sensor O₃/NO₂ used in the study (adapted from Cairpol, 2014).

3.3 Phase One: Purpose and Design

The purpose of phase one of this study was to determine the degree of uncertainty of the Cairclip sensors in relation to the Edmonton fixed-site station monitors. The accuracy of the Cairclip sensors was tested in comparison to that of the Edmonton south station monitor. The precision was determined by comparing the sensors against one another. The goal was to establish a comparative baseline of data to determine the degree to which the sensors performed in comparison to the ambient station (accuracy) as well as how well each sensor performed in comparison to one another (precision).

3.3.1 Location and Deployment of Cairclip Sensors for Phase One

Phase one of the study involved co-locating the Cairclips with Alberta Environments' NAPS station monitor located in south Edmonton. The Edmonton South Station monitors for several types of pollutants such as carbon monoxide (CO), sulphur dioxide (SO₂), nitric oxide (NO), total oxides of nitrogen (NO_x), NO₂, O₃, total hydrocarbons, non-methane hydrocarbons, as well as PM_{2.5} and PM₁₀ (CASAdata.org, 2014).

The Edmonton South Station monitor was chosen because of its close proximity to the University of Alberta. It is presumed to represent air quality in residential areas of the city. The geographical coordinates for the site are as follows: latitude: 53.500139, longitude: 113.526056, elevation: 681.0 (CASAdata.org, 2014). The monitoring station is located at 6240-113 Street, Edmonton, Alberta, between the Alberta School for the Deaf and the south extension of the light rail transit (LRT) lines. The geographical location of the station monitor in relation to the University of Albert farm and the South Campus LRT station are displayed in Figure 5. The photograph in Figure 6 was taken to provide a visual perspective of the design of the fixed station, as well as to give a visual illustration of the surrounding environment. Arrangements were made with Shelley Morris of Alberta Environment to acquire a key for access to the NAPS station monitor compound.



Figure 5. The location of the Edmonton South Station monitor.



Figure 6. Photograph of the Edmonton South Station monitor.

The shelter for the Cairclip sensors consisted of a circular hood with a circumference of 56.5 centimeters (cm) in order to provide the sensors sufficient protection from wind and rain. The hood was attached to a long metal pole, measuring 123 cm in length. Directly beneath the hood was a structure that was comprised of four arms enabling attachment of four sensors, one on each arm with all components attached at the top with a screw. The assembled shelter was then fastened to a corner of the wood railings on top of the Edmonton south station monitor. A variety of clamps, brackets and screws were used to firmly secure the apparatus against inclement winds, and adverse weather conditions (Figure 7).



Figure 7. Hardware used to secure the shelter for the Cairclips.

The shelter was set at a height equal to that of the station monitor intake and placed in a corner in order to securely attach the mechanism to the wood railing, Figure 8 and 9. The location for the shelter was selected based on proximity to the station monitor intake for ambient gases, O₃ and NO₂. The photograph displayed in Figure 10 shows the shelter housing the Cairclip sensors in the left hand corner with the station monitor intake pictured on the right.



Figure 8. Set-up of the shelter at the station monitor.



Figure 9. Cairclip sensors secured under the shelter at the station monitor.



Figure 10. The shelter set-up in relation to the air intake of the station monitor.

3.3.2 Time of Day and Duration of Data Collection for Phase One

Deployment times for collection of air quality samples were determined by reviewing previous data collected for air monitoring sites across Alberta and within Edmonton city limits. A study discussing ambient air trends conducted by McCullum et al. (2004) provided temporal data on daily concentration levels of O₃ and NO₂. The study showed peaks and valleys of concentrations for all days of the week and for several areas in Edmonton and across Alberta. As the Cairclips were capable of collecting data for 24 hours, time frames for data collection were eight to twelve hours in length in order to cover peak times of concentrations of O₃ and NO₂ as related to rush hour traffic and in consideration of climatic conditions (McCullum et al., 2004; Alberta Environment, 2012d). Once the monitoring was completed, the sensors were removed, data was downloaded onto a laptop computer and the sensors were recharged overnight. Twenty-five days of data were collected during the course of Phase one of this study.

3.3.3 Quality Control and Quality Assurance Experiments

In order to validate study results and safeguard against inconsistencies between sensors, elements of quality assurance and control were essential in all areas throughout the duration of the research project. This involved downloading of data software; the development of a charging station to ensure optimal battery life during monitoring times; the numbering of the sensors from 1 to 4 for tracking purposes; and, fabrication and set up of an outdoor shelter to safeguard against damage due to wind and rain. Log sheets were developed in order to record entry and exit times into the Edmonton south station compound. Additionally, the log

sheets were used to record climatic condition and activities that may have had an impact on air quality for the day. A template of the log sheet used for this study is provided in the Appendix B.

Precision and accuracy are critical parts of research design (Montgomery, 2009; Mendenhal and Sincich, 1995). In this study, the precision was evaluated in the field by comparing Cairclip 1, 2, 3 and 4 against each other based on identical data sets that were collected on identical days and time periods. The accuracy of the Cairclip sensors was evaluated in the field by testing their performance against the Edmonton South station, by comparing concentrations measured by Cairclips to that of the fixed-site monitor based on identical sampling dates and times.

3.3.4 Determining Field Precision: Cairclip to Cairclip

In order to determine measurement precision between Cairclips 1, 2, 3 and 4, data collected throughout phase one was used to compare and contrast independent sensor sensitivity to O₃ + NO₂. Findings by Mukerjee et al. (2004), Curran et al. (2012) and Ray, (2001) demonstrate that precision calculations can be characterized by applying the percent relative standard deviation (%RSD). % RSD is a measure of accuracy that enables comparison of the standard deviations of different measurements (Alberta Environment, 2006).

The standard deviation (SD) is the square root of variance, a measure of spread or variability if data. %RSD was calculated by comparing paired data between Cairclips collected on identical sampling dates, and at 15, 30 and one-hour time intervals. The equation used for determining inter sensor precision of the Cairclips is provided in the following equations:

% RSD =
$$\left(\frac{\text{SD}}{\bar{x}}\right)$$
 * 100%; and SD = $\sqrt{\frac{\sum x' - x''}{2 * n}}$ (Eq.1) & (Eq.2)

where, SD is the standard deviation from paired Cairclip data and \overline{x} = the arithmetic average of x'.

3.3.5 Determining Field Accuracy: Cairclips to NAPS Station Monitor

To date, there has been one published study conducted in Europe by the JRC where the Cairclip sensors have been challenged for accuracy and precision in a similar capacity to this study (Spinelle et al., 2013). Due to the limited amount of knowledge about the Cairclip sensors, it was an imperative part of this study to test their accuracy against a reference point that was representative of the air quality in Edmonton. Although the station monitors record concentrations of $O_3 + NO_2$ from a fixed-site and are limited to measuring far-field sources, they were considered to be the best reference for air quality data.

Upon completion of phase one, data collected was assessed for accuracy by comparing each Cairclip with the Edmonton south station monitor data based on identical times and dates. Alberta Environment provided one, ten and sixty minute data for specific dates throughout the period from July 29 to November 1, 2013. The analysis for phase one using data collected at one minute time intervals to calculate 15 and 30 minute, and one hour time average concentrations of the sum of O₃ and NO₂.

For purposes of this study and in accordance with literature, accuracy was calculated using the mean absolute percent difference (MAPD) (Curran et al., 2012; Ray, 2001) using the following equation:

$$MAPD = \left[\frac{\left(\frac{P-C}{P}\right)}{n}\right] * 100$$
(Eq.3)

where, P is the combined concentrations of $O_3 + NO_2$ measured in ppb from the NAPS Edmonton South station monitor; C is the reported time weighted concentration of $O_3 + NO_2$ measured in ppb by the Cairclips; and n is the sample size or number of paired data.

3.3.6 Data Selection Criteria

All of the data gathered from the Cairclip sensors was screened and analyzed in order to determine which data sets met inclusion or exclusion criteria. As noted above, accuracy was determined by comparing the Cairclip data to that of the station monitor, while precision was determined through comparison of paired Cairclip data. The following selection criteria were applied to the data:

- The active sampler data had to have been collected by the Cairclip and recorded at one minute, continuous time intervals.
- The date, time and length of monitoring times for all four of the Cairclip sensors was consistent with that of the Edmonton South station monitor.
- Incomplete data from station monitor, due to power outages or maintenance, during monitoring times with co-deployment with Cairclips resulted in removal of those time-weighted values from data sets.
- Reference data for phase one of the study from station monitor was restricted to that recorded at the NAPS Edmonton South station.

3.3.7 Datasets Group One, Two and Three for Comparison

Upon completion of screening data on the specified criteria, the data sets were evaluated for presence of outliers. In phase one, accuracy data and precision data were graphed showing Cairclip vs. Edmonton south station monitor or Cairclip vs Cairclip, respectively. In both accuracy and precision graphs, linear regression lines were adapted to the points with R² equations and calculations provided.

Upon consulting with specialists within the School of Public Health at the University of Alberta, Drs. Yutaka Yasui and Gian Jhangri (personal communication April 4, 2014), it was recommended to remove any data points that were visually spurious when analyzed in linear regression. The removal of outliers was a carefully thought out process that aimed to capture quantitative comparisons of the Cairclip that were reflective of its capacity to measure concentrations of far-field sources of $O_3 + NO_2$ in comparison to the station monitor.

Subsequently, a second outliers test was applied using calculated standardized residual data to determine any data points that lay beyond ± 2 SD of the mean. Any data points beyond this were considered outliers and removed from the data sets (Currie et al., 1994; Curran et al., 2012). The accuracy and precision results of: 1) all screened data, 2) screened data with visual outliers removed and 3) screened data with outliers removed beyond m ± 2 SD, are presented for comparison in Chapter 4.

3.4 Phase Two: Purpose and Design

Phase two of the study was designed to measure selected outdoor geographical locations and indoor environments throughout the city of Edmonton. Firstly, the purpose of monitoring in certain locations was to determine if areas with high volumes of traffic, which coexist with human activity, may be potential areas of high exposures to $O_3 + NO_2$. This involved monitoring outdoors at intersections in core urban areas of Edmonton and while commuting on public transit. Secondly, to monitor indoor environments located in close proximity to intersections with high volumes of traffic that were equipped with gas ranges and fireplaces, etc. to measure the levels of $O_3 + NO_2$ in these locations.

The sensors were assigned to a specific scenario: indoor, outdoor or personal and remained assigned to the same setting for the duration of the study. The sensors were assigned as follows: 1) Cairclip 2 was placed inside the home, 2) Cairclip 3 was placed in the backyard of the home using the same protective shelter used in phase one, and 3) Cairclip 1 and 4 were assigned to be worn by a person.

Monitoring times for phase two varied somewhat in accordance with changing time activity patterns from day to day. The monitoring times ranged from 8 hours to a maximum of 12-hours to safeguard sufficient battery life and to ensure the provision of the best possible measurement accuracy of the sensors. Outdoor and indoor monitors were deployed daily at the same time as the personal monitor to be worn by the individual. A time activity diary was carried with the person and records identifying geographical location along with duration of time spent in the

specific area were recorded. Any other artifacts of interest that were thought to potentially affect data collections were also noted.

As mentioned, the focus of phase two of the research study aimed to measure exposure to air pollutants, O₃ and NO₂, during daily life activities. For this reason, the selection of exposure scenarios were done with the intent to reflect changing exposures to pollutants as an individual's activity and location of those activities changed. Data collection intervals aimed to capture diurnal patterns such as times of peak traffic flow when vehicular emissions are high. The timeline for phase two extended from September, 2013 to January, 2014.

The scenarios selected for the personal exposure monitoring were chosen to be representative of daily life patterns. The scenarios were selected to reflect a person's diurnal patterns and incorporated monitoring activities when: 1) commuting by foot in core areas of the city; 2) commuting by train and bus; and 3) inside public indoor environments adjacent to high volume vehicular traffic. Figure 11 highlights the areas of monitoring as related to the above scenarios throughout the city of Edmonton.

Once data collection was completed, the results were compared to data from the Edmonton South and Edmonton Central station monitors. The location of the Edmonton Central station monitor is in the downtown core at 10255 – 104th Street with co-ordinates of 53.54449, -113.49893; this station is designed to be representative of measurements of pollutant concentrations in a densely populated urban environment of the city (Environment Canada, 2013c). Pedestrian counts, where available, were used to determine the volumes of people in close proximity

of these monitoring locations. With the exception of monitoring during commuting via bus and LRT, traffic counts were used to provide a correlation of concentrations of O_3 and NO_2 to time of day during peak and non-peak times of traffic flow.

In summary, the goal of phase two was to measure concentrations of $O_3 + NO_2$ in a variety of indoor and outdoor environments in order to determine which areas may be considered to be of high exposure given diurnal circumstances and duration of exposure.



Figure 11. Map of approximate location of monitoring sites in phase two.

3.5 Indoor and Outdoor Residential Monitoring

The indoor and outdoor residential monitoring took place at an urban, intercity home in Old Strathcona. The residential setting was situated within close proximity to a major roadway, 99th Street and 88th Avenue, with high volumes of vehicular traffic; densely populated with people and businesses close by.

Monitoring of the residential area was designed in order to compare indoor concentrations to outdoor concentrations of $O_3 + NO_2$ in the study subject's residential area during the day. Sensors were placed inside the home and in the backyard at this location. The data collected from these scenarios was used to calculate ratios as a means of comparing concentrations of $O_3 + NO_2$ indoor to those outdoor. Calculating concentration ratios of indoor versus outdoor enabled for analysis and determination of which environment contained the highest concentration during times of monitoring.

Cairclip 2 was placed indoors, attached to an inside wall, within range of the kitchen and placed at breathing zone height, (Figure 12). A plastic zip tie was used to attach the sensor to a wall hanging between the kitchen and dining areas, free of obstruction to air flow. The outdoor sensor was placed in the middle of the backyard of the home at the breathing zone height (Figure 13). The shelter that was used for phase one was used to protect the sensors from rain, snow and wind. Zip ties were used to secure the sensor in place (Figure 14).



Figure 12. Photograph showing the indoor residential placement of the Cairclip.



Figure 13. Photograph of outdoor residential placement of Cairclip.



Figure 14. Photograph of Cairclip attached under shelter in backyard setting.

3.6 Personal Exposure Monitoring

The personal exposure monitoring portion of this study is designed with the premise of the fundamentals of exposure science as described by Ott (2007a). The premise of this portion of the study was to evaluate the level of exposure to near-field sources of environmental pollutants, $O_3 + NO_2$, in busy urban areas at the personal level.

Personal monitoring was conducted to represent exposure levels as an individual engages in daily activities at locations outside of the home. These indoor and outdoor locations were meant to represent an average day of a person's life. For purposes of this study, these selected locations were limited to and inclusive of monitoring in non-residential environments during times spent commuting and in public indoor places. The personal monitor was worn within the range of the human breathing zone; an area that lies with 10 inches in any direction of the mouth and nose (Ojima, 2012; Zhang & Lioy, 2002). Therefore, the monitor was attached to the upper arm just below the shoulder with a Velcro strap for security during activities. Figures 15 and 16, demonstrate the placement and apparatus used to secure the sensor for personal exposure monitoring. A time activity diary was used to supplement the Cairclip sensors. The time activity diary was a tool used to provide for recording of pertinent information relating to location, duration and any other circumstances related to daily activities patterns of the individual (Ott, 2007a).



Figure 15. Photograph of Cairclip placement for personal monitoring.





3.6.1 Outdoor Monitoring at Jasper Avenue and 109th Street

This scenario involved monitoring at two downtown intersections in the urban core of Edmonton: 109th Street and Jasper Avenue, and 97th Avenue and 109th Street, Figures 17. The Jasper Avenue and 109th Street monitoring site was selected as the area was composed of a combination of high volume vehicular traffic with residential dwellings, businesses and people. Monitoring was conducted at 15-minute time intervals at the northwest corner of the 109th Street and Jasper Avenue and the northeast corner of the 109th Street and 97th Avenue intersections, respectively.



Figure 17. Diagram of the Jasper Ave. /109th St. & 97th Ave. /109th St. monitoring locations.

Note: The star symbol indicates the stationary location of monitoring for the above specified time intervals at the specific intersections of interest.

3.6.2 Outdoor Monitoring at 97th Avenue and 109th Street

The intersection of 97th Avenue and 109th Street (Figure 17) was chosen due to high volumes of vehicular traffic in relation to human activity. The High-Level Bridge lies in close proximity and acts as a common passageway for cyclists and walkers. For these reasons, monitoring in this area was a viable choice to measure levels of real-time concentrations of $O_3 + NO_2$ as related to commuting by foot.

3.6.3 Outdoor Monitoring of Whyte Avenue to 109th Street

In order to measure pollutant exposure in relation to vehicular traffic and pedestrian flow similar to that of the above described downtown locations, a second comparable location on and around Whyte Avenue was chosen. The Whyte Avenue area contains a variety of aspects of interest to air quality monitoring in relation to human exposure. This is exemplified in that the area has a number of residential dwellings, several retail businesses, with many restaurants and bars interspersed. Whyte Avenue also acts as a major vehicular thoroughfare that provides access from the Anthony Henday through to the University of Alberta and to core areas of the city.

Air quality monitoring of Whyte Avenue to 109th Street was conducted over 30 minute intervals of time. The route extended from the northwest corner of Whyte Avenue and 99th Street and continued westbound on the north sidewalk to 109th Street, (Figure 18).



Figure 18. Diagram of the 99th Street/Whyte Ave. and Whyte Ave. /109th Street monitoring locations.

Note: The star symbol upper left indicates the location of monitoring for the 99th Street to Whyte Ave. Symbol on lower left indicates location of monitoring from the northwest corner of Whyte Ave. and 99th Street to 109th Street.

3.6.4 Outdoor Monitoring of 99th Street to Whyte Avenue

The second area monitored in the Whyte Avenue area was on 99th Street

starting at 88th Avenue southbound to Whyte Avenue (Figure 18). Similar to

Whyte Avenue, 99th Street acts as a major thoroughfare for vehicular traffic and passes through areas of high density residential communities. As with the Whyte Avenue to 109th Street route, monitoring was intended to capture personal exposure to O₃ and NO₂ as a commuter travelling on foot in close proximity to vehicular traffic.

The route encompassed travelling southbound on the east side of 99th Street from 88th Avenue to Whyte Avenue, remaining at the intersection of Whyte Avenue and 99th for a period of time and then returning by walking northbound on the west side of 99th from Whyte Avenue to 89th Avenue. Monitoring times for this exposure setting were also 30 minutes in duration.

3.7 Commuter Monitoring On Public Transportation

Commuter monitoring on public transportation involved traveling by bus and by LRT. Monitoring in this scenario included travel time and wait times at selected transit stations. The specific LRT and bus routes were selected to capture routes that were used regularly by large volumes of commuters. Figure 19 illustrates the LRT and city bus route used for exposure monitoring during this study.



Figure 19. Map of bus and LRT routes monitored in phase two.

3.8 Indoor Monitoring at High Volume Traffic Areas

The monitoring areas for this scenario were chosen to capture personal indoor exposure to O_3 and NO_2 outside of the home. The locations were chosen based on: the numbers of people present, the type of appliances and design of the indoor environment, and the proximity to high volumes of traffic. The indoor environments selected for this exposure scenario were mainly coffee shops and eateries. The specific establishments chosen were popular destinations for people located at busy intersection and roadways with relatively high levels of traffic continuously throughout the day.

Three locations were selected for this air monitoring scenario, they are as follows: northwest corner of 99th Street and 89th Avenue; southwest corner of 109th Street and 88th Avenue; northwest corner of 104th Street and 82nd Avenue (Figures 20, 21 and 22). As mentioned, these locations were selected because they attract a large number of people and were situated in close proximity to high volume traffic.

The concentration levels of $O_3 + NO_2$ detected in the air of these indoor environments may be a result of a combination of factors due to the reactive nature of these gases. As demonstrated in the literature, O_3 and NO_2 are both highly reactive gases and combine rapidly with other criteria pollutants that may be residual and present in an indoor environment (WHO, 2003b). Because of this the concentration levels of $O_3 + NO_2$ measured by the Cairclip can be high or low dependent upon the types of residual parameter within these indoor environments (WHO, 2003b).

3.8.1 Indoor Monitoring at 109th Street and 88th Avenue

The business monitored at the intersection of 109th and 88th Avenue was selected because of both its popularity and location. The establishment services a high volume of people per day. The building is of old construction and houses a

number of other business including a bike shop. The business is located close to a residential area and immediately adjacent to a very busy intersection.

The indoor environment was located on the northwest corner of 109th Street and 88th Avenue at the top of the High Level Bridge. The entrance to the establishment is located on the 88th Avenue side (Figure 20). A small space equipped with a commercial grade kitchen and cooking appliances, it acts as a popular destination for people.



Figure 20. Diagram of the 109th St. & 88th Ave. indoor monitoring site.

Note: The star symbol indicates the stationary location of monitoring for the above specified time intervals at the specific non-residential, indoor exposure scenarios of interest.

3.8.2 Indoor Monitoring at 99th Street and 89th Avenue

The second indoor environment chosen for monitoring was in a restaurant located on the northwest corner of 99th Street and 89th Avenue (Figure 21). The front door of the establishment was situated approximately 1.5 meters from the intersections of 99th Street and 89th Avenue. A secondary entrance was located along 89th Avenue. Traffic volumes at this intersection were observed to be consistently heavy throughout the day. This site was a chosen for air monitoring because of: its close proximity to 99th Street, its location being within a core residential area, its interior design and cooking facilities, and the volume of people that it attracted.



Figure 21. Diagram of the 99th St. & 89th Ave. monitoring site.

Note: The star symbol indicates the stationary location of monitoring for the above specified time intervals at the specific non-residential, indoor exposure scenarios of interest.

3.8.3 Indoor Monitoring at 104th Avenue and Whyte Avenue

The public location selected for monitoring in this case was an indoor environment that provided services to a large quantity of people (Figure 22). The business was situated on a very busy intersection which handled a high volume of continuous vehicular traffic throughout the day. The business was not equipped with a commercial grade kitchen or gas cook tops. However, a fair number of patrons would smoke just outside the establishments entrance/exit points. This public, indoor location was selected based on: its' close proximity to vehicular traffic, the number of patrons visiting the establishment and because people smoked within close range of its entrance.



Figure 22. Diagram of the 104th St. & Whyte Ave. indoor monitoring site.

The methodology for this study was designed in order to test the Cairclip in the field through co-deployment with the Edmonton south station monitor. In actuality, this was testing the Cairclip's ability to measure far-field sources of pollutants. The second part of the study was designed to test the sensors in areas that are impossible for the station monitors to measure with accuracy because their structural limitations and non-portability. The Cairclips were challenged to test their capabilities in measuring near-field sources of $O_3 + NO_2$ at the personal level in various settings in the city of Edmonton.

Note: The star symbol indicates the stationary location of monitoring for the above specified time intervals at the specific non-residential, indoor exposure scenarios of interest.

4 RESULTS AND DISCUSSION

4.1 Phase One Replicate Monitoring and Field Precision of Cairclips

According to the manufacturer's technical data sheet found in Appendix A, the degree of uncertainty of the sensors has been established as < 30% (Cairpol, 2014). The Cairpol company has acquired this value of uncertainty for the Cairclip O₃/NO₂ sensor based on the DQO set by the European Commission in 2008 (European Commission, 2008b). This value encompasses uncertainty percentages defined for various measurements of which include fixed measurements and indicative measurements. The uncertainty value of < 30% is expressed at a 95% confidence interval of the individual measurements averaged over the period of the limit value for NO₂ and the target value for O₃ (European Commission, 2008b).

Tables 4 to 15, provide a summary of the quantitative parameter precision analysis and the linear regression results of three data set groupings; including screened data, data with visual outliers removed and remaining data after all points beyond ± 2 SD were removed. The data analyzed here was collected during active monitoring of O₃ and NO₂ when Cairclip sensors were deployed on location at the NAPS Edmonton south station. The summarized precision findings of paired Cairclips for the time averaged concentrations of one hour, 30 and 15 minute ranged from: ± 11 to 34%; ± 12 to 39%; and ± 14 to 37%.

The precision data was compared at three time weighted concentration intervals of one hour, 30 and 15 minute time frames. For the purposes of this document, the one hour precision results are displayed for each pairing of the

Cairclip sensors 1 to 4 in the following text. Both the 30 and 15 minute time weighted concentration precision results are provided in Appendix C. In each table, group one are all screened data, group two are data sets with visual outliers removed and group three are data with outliers removed based on ± 2 SD from the mean value. The acronym CC is used in all the precision tables to represent the Cairclip sensor while SM represents the Edmonton South station monitor.

Results of the linear regression are also displayed in tables and allow comparison of the data before and after outlying data points were removed. All values in the linear regression tables are rounded to two significant values. The linear regression graphs and tables for one hour time weighted precision results are discussed in the following text. Graphs and tables of linear regression results for 30 and 15 minute time weighted averages are provided in Appendix C.

Figure 23 is provided as an example showing all the paired screened precision data for Cairclip 1 vs. Cairclip 2 with lines showing ± 2 SD in relation to the fitted linear regression line. Although, this relationship is only presented in the text in Figure 23, the same quantitative process was applied to all other precision data sets.

4.1.1 Precision Results Cairclip 1 to Cairclip 2

A summary of the precision results for paired sensors, Cairclip 1 and 2 is provided in Table 4. For the paired Cairclips 1 and 2, the percent relative standard deviation (%RSD) was 34% (n=100), 20% (n=94) and 20% (n=94) for group 1, 2 and 3, respectively. The %RSD decreased from 34% (all screened data) to 20% when visual outliers were removed; the %RSD remained the same after the

m±2SD outlier test was applied as all points remained within the 95%; no

additional points were considered to be outliers.

During phase one, the mean ambient concentration value detected by Cairclip 1 ranged from 17 to 18 ppb, a value below the limit of detection (LOD) of 20 ppb as set by the manufacturer. Cairclip 2 measured a mean concentration of 20 ppb, and concurrent with the LOD.

Parameters for Precision Analysis	Group 1 (all screened data)		Group 2 (screened data with visual outliers removed)		Group 3 (screened data with outliers removed beyond m±2SD)	
	CC1	CC2	CC1	CC2	CC1	CC2
Ν	100		94		94	
Mean (ppb)	17.3	20	18	20	18	20
Median (ppb)	17	19	17	19	17	19
Mode (ppb)	17	26	17	26	17	26
Min (ppb)	4	5	4	5	4	5
Max (ppb)	32	40	32	40	32	40
%RSD	34%		20%		20%	

Table 4. Field precision parameter results of Cairclip 1 to Cairclip 2.

The graph of the precision data paired Cairlelips 1 to 2 is shown in Figure 23, followed by a summary of the linear regression results for the one hour averaged concentrations of $O_3 + NO_2$ (Table 5). As mentioned, Figure 23 represents all screened data (group 1) plotted in relation to lines showing data exclusion once the ±2SD outliers test was applied (group 3). A one to one line is shown to illustrate an ideal slope as well as he best fit linear regression line is shown on the graphs as applied to the remaining data after the ±2SD testing (group 3). This graph is provided in this fashion in order to illustrate which paired data points were quantitatively removed for all precision data of paired Cairclips. This detailed information is provided exclusively in this

graph and exemplifies the manner of which all the paired Cairclip precision data was analyzed.

In explanation, an R^2 value that is close to one indicates that the model fits the data better and quantifies goodness of fit, which provides evidence of a positive linear relationship (Minitab Inc., 2010). Table 5 shows that the R^2 values increased with the removal of spurious data points with values increasing from 0.23 to 0.57. Although low R^2 values are not sole predictors of the level of precision, the results show a marginally positive linear relations. The slope (Table 5) also improved from 0.54 to 0.82 with the removal of outliers. Initially, the slope of 0.54 was marginally significant whereas a slope of 0.82 produce more meaningful results as this value is > 0.70 and to 1.



Figure 23. Graph comparing precision data of Cairclip 1 to Cairclip 2.

Linear Regression Results							
Group	Ν	R ²	Slope	Intercept			
1 (screened data)	100	0.23	0.54	10.95			
2 (screened data with visual outliers removed)	94	0.57	0.82	4.87			
3 (screened data with outliers removed beyond m±2SD)	94	0.57	0.82	4.87			

Table 5. Linear regression results for field precision Cairclip 1 to Cairclip 2.

4.1.2 Precision Results Cairclip 1 to Cairclip 3

Values for precision for Cairclip 1 to Cairclip 3 based on one hour time weighted averages calculated from one minute continuous data collection are presented in Table 6. %RSD for the paired sensors was 32% (n=100) for group 1, and 14% (n=93) for both groups 2 and 3. %RSD of the screened data decreased from 32% to 14% with the visual outliers removed beyond which all data points remained within mean ± 2 SD; therefore no further data points were removed from the data set.

The time weighted average of one hour resulted in mean concentrations measured for Cairclips 1 and 3 that ranged from 17 to 18 ppb and 21 to 22 ppb, respectively. Based on these findings, mean concentrations for Cairclip 1 were below the LOD of 20 ppb.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data with visual outliers removed)		Group 3 (screened data with outliers removed beyond m±2SD)	
	CC1	CC3	CC1	CC3	CC1	CC3
Ν	100		93		93	
Mean (ppb)	17	22	18	21	18	21
Median (ppb)	17	21	17	20	17	20
Mode (ppb)	17	21	17	20	17	20
Min (ppb)	4	5	4	5	4	5
Max (ppb)	32	38	32	38	32	3
%RSD	32%		14%		14%	

Table 6. Field precision parameter results of Cairclip 1 to Cairclip 3.

The graph of the screened data sets with outliers removed for Cairclip 1 to 3 is shown in Figure 24, followed by a summary of the linear regression result for the one hour averaged concentrations of $O_3 + NO_2$ (Table 7). The R² values increased and approached the value of one with the removal of spurious data points. The R² values increased from 0.31 to 0.85, indicating a stronger and positive linear relationship. The slope improved from 0.61 to 0.95 meaning that, with the removal of outlying data points, the results improved significantly as it approached 1.


Figure 24. Graph comparing precision data of Cairclip 1 to Cairclip 3.

Linear Regression Results									
Group	Ν	R ²	Slope	Intercept					
1 (screened data)	100	0.31	0.61	10.94					
2 (screened data with	93	0.85	0.95	3.43					
visual outliers removed)									
3 (screened data with	93	0.85	0.95	3.43					
outliers removed beyond									
m±2SD)									

Table 7. Linear regression results for field precision of Cairclip 1 to Cairclip 3.

4.1.3 Precision Results Cairclip 1 to Cairclip 4

Precision results for Cairclip1 to Cairclip 4 are summarized in Table 9. The identical sensors, co-located at the Edmonton south monitoring station showed a %RSD of 33% (n=100) for group one including all screened data and 20% (n=94) for both group 2 and 3. %RSD decreased from 33% to 20% after visual outliers were removed, beyond which the remaining data fell within ± 2 SD of the mean; therefore no further points were considered to be outliers. The time weighted average of one hour resulted in mean concentrations measured for Cairclips 1 and

4 that ranged from at 17 to 18 ppb and 17 to 22 ppb, respectively. Based on this finding, mean concentrations for Cairclip 1 were significantly below the LOD of 20 ppb.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened visual out removed)	data with tliers	Group 3 (screened data with outliers removed beyond m±2SD)	
	CC1	CC4	CC1	CC4	CC1	CC4
Ν	100		94		94	
Mean (ppb)	17	17	18	22	18	22
Median (ppb)	17	22	17	22	17	22
Mode (ppb)	17	23	17	23	17	23
Min (ppb)	4	8	4	8	4	8
Max (ppb)	32	36	32	36	32	36
%RSD	3	3%	20%		20%	

Table 8. Field precision parameter results of Cairclip 1 to Cairclip 4.

The graph of the screened data sets with outliers removed for Cairclip 1 to 4 is shown in Figure 25, followed by a summary of the linear regression result for the one hour averaged concentrations of $O_3 + NO_2$, Table 9. The R² values increased with the removal of spurious data points with values increasing from 0.27 to 0.53 showing a marginally positive linear relationship as the value moved closer to 1. The slope values improved from being marginal (<0.70) with application of outliers testing. The slope changed from 0.49 to 0.71, which was meaningful as it approached 1 and a positive linear relationship.



Figure 25. Graph comparing precision data of Cairclip 1 to Cairclip 4.

Linear Regression Results									
Group	Ν	\mathbf{R}^2	Slope	Intercept					
1 (screened data)	100	0.27	0.49	13.11					
2 (screened data with visual Outliers removed)	94	0.53	0.71	9.40					
3 (screened data with outliers removed beyond m±2SD)	94	0.53	0.71	9.40					

 Table 9. Linear regression results for field precision Cairclip 1 to 4.

4.1.4 Precision Results Cairclip 2 to Cairclip 3

Precision results for Cairclip 2 to Cairclip 3 based on one hour time weighted data for phase one are summarized in Table 10. %RSD was 16% (n=100), 16% (n=98) and 11% (n=93) for Groups 1, 2 and 3. %RSD value of all screened data decreased from that of 16% to 11% upon application of m±2SD outliers test. The first outliers test saw the removal of two data sets with no change to the initial %RSD. The time weighted average of one hour resulted in mean concentrations measured for Cairclips 2 and 3 that ranged from at 20 to 21 ppb and 22 to 21 ppb,

respectively. These mean values for the Cairclips 2 and 3 were slightly above the

20 ppb LOD values of the sensors.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened visual out removed)	data with tliers	Group 3 (screened data with outliers removed beyond m±2SD)		
	CC2	CC3	CC2	CC3	CC2	CC3	
Ν	100		98		93		
Mean (ppb)	20	22	20	21	21	21	
Median (ppb)	20	22	20	20	20	20	
Mode (ppb)	26	20	26	20	26	20	
Min (ppb)	5	5	5	5	5	5	
Max (ppb)	40 38		40	38	40	38	
%RSD	1	6%	1	16%		11%	

Table 10. Field precision parameter results of Cairclip 2 to Cairclip 3.

The graph of the screened data sets with outliers removed for Cairclip 2 to 3 is shown in Figure 26, followed by a summary of the linear regression result for the one hour averaged concentrations of $O_3 + NO_2$, Table 10. The R² values increased with the removal of spurious data points with values increasing from 0.70 to 0.85, which provided evidence of a positive linear relationship. The slope improved from 0.81 to 0.86 with the application of the outlier tests, which increased the significance of the results.



Figure 26. Graph comparing precision data of Cairclip 2 to Cairclip 3.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	100	0.70	0.81	5.02					
2 (screened data with	98	0.75	0.80	4.85					
visual outliers removed)									
3 (screened data with	93	0.85	0.86	3.15					
outliers removed beyond									
m±2SD)									

Table 11. Linear regression results for field precision of Cairclip 2 to Cairclip 3.

4.1.5 Precision Results Cairclip 2 to Cairclip 4

A summary of the precision results for the active sampling of $O_3 + NO_2$ by sensors Cairclip 2 and 4 are provided in Table 12. For the paired data sets, Cairclip 2 and 4, %RSD was 22% (n=100), 18% (n=96) and lastly 16% (n=91) for Groups 1, 2 and 3, respectively.

%RSD of the screened data decreased from 22% to 18% with visual outliers removed with a further decrease to 16% with the application of the m±2SD outliers test. The mean concentration of $O_3 + NO_2$ for the one hour time weighted averages for Cairclip 2 ranged from 20 to 20 ppb while Cairclip 4 ranged from 22 to 21 ppb;

both fell within range of the LOD.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened visual out removed)	data with liers	Group 3 (screened data with outliers removed beyond m±2SD)	
	CC2	CC4	CC2	CC4	CC2	CC4
Ν	100		96		91	
Mean (ppb)	20	22	20	22	20	21
Median (ppb)	20	22	19.5	22	19	21
Mode (ppb)	26	23	26	23	26	23
Min (ppb)	5	8	5	8	5	8
Max (ppb)	40	36	40	36	40	33
%RSD	2	2%	18%		16%	

Table 12. Field precision results of Cairclip 2 to Cairclip 4.

The graph of the screened data sets with outliers removed for Cairclip 2 to 4 is presented in Figure 27, followed by a summary of the linear regression result for the one hour averaged concentrations of $O_3 + NO_2$, Table 13. The R² values increased with the removal of spurious data points with values increasing from 0.40 to 0.69, which showed slightly stronger evidence towards a positive linear relationship as the value approached 1. The slope improved slightly from 0.54 to 0.62, these results remained <0.70 and were less meaningful.



Figure 27. Graph comparing precision of Cairclip 2 to Cairclip 4.

Linear Regression Results									
Group	Ν	R ²	Slope	Intercept					
1 (screened data)	100	0.40	0.54	10.66					
2 (screened data with visual outliers removed)	96	0.59	0.64	8.96					
3 (screened data with outliers removed beyond m±2SD)	91	0.69	0.62	8.75					

Table 13. Linear regression results for field precision of Cairclip 2 to Cairclip 4.

4.1.6 Precision Results Cairclip 3 to Cairclip 4

A summary of precision results for active sampling of $O_3 + NO_2$ by sensors Cairclip 3 and 4 are provided in table 14. For the paired data sets, Cairclip 3 and Cairclip 4, the percent relative standard deviation (%RSD) was 18% (n=100), 13% (n=96) and lastly 16% (n=94) for groups 1, 2 and 3, consecutively.

%RSD of the screened data decreased from 18% to 14% with visual outliers removed with a further decrease to 13% with the application of the m±2SD outliers test. The mean concentration of $O_3 + NO_2$ for the one hour time weighted averages for Cairclip 3 ranged from 22 to 21 ppb while Cairclip 4 values remained at value of 22 ppb. The mean concentrations for both Cairclip 3 and 4

remained above the 20 ppb LOD.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened visual out removed)	data with tliers	Group 3 (screened data with outliers removed beyond m±2SD)	
	CC 3	CC4	CC3	CC4	CC3	CC4
Ν	1	00	96		94	
Mean (ppb)	22	22	21	22	21	22
Median (ppb)	20.5	22	20	22	20	22
Mode (ppb)	20	23	20	23	20	23
Min (ppb)	5	8	5	8	5	8
Max (ppb)	38	36	38	36	38	36
%RSD	1	8%	14%		13%	

Table 14. Field precision results for Cairclip 3 to Cairclip 4.

The graph of the screened data sets with outliers removed for Cairclip 3 to 4 is shown in Figure 28, followed by a summary of the linear regression result for the one hour averaged concentrations of $O_3 + NO_2$, Table 15. The R² values increased with the removal of spurious data points with values increasing from 0.52 to 0.73. As the R² value approached 1, stronger evidence was provided towards a positive linear relationship for the data. The slope values changed from 0.63 to 0.74, which increased the significance and meaningfulness of the results as it approached 1 showing a positive linear relationship.



Figure 28. Graph comparing precision of Cairclip 3 to Cairclip 4.

Table 15. Linear regression results for field precision of Cairclip 3 to Cairclip 4.

Linear Regression Results									
Group	Ν	R ²	Slope	Intercept					
1 (screened data)	100	0.52	0.63	8.04					
2 (screened data with visual outliers removed)	96	0.72	0.75	6.29					
3 (screened data with outliers removed beyond m±2SD)	94	0.73	0.74	6.30					

In comparison to the findings from 30 and 15 minute concentration averages, %RSD as presented in the above tables was best represented by the one hour time weighted concentrations. In summary, % RSD for 30 and 15 minute averaged concentrations ranged from ± 12 to 39% and ± 14 to 37%. In comparison, % RSD for the one hour averaged concentrations ranged from ± 11 to 34%.

4.2 Monitoring at Edmonton South Station and Field Accuracy

Similar to the precision results above, field accuracy results were calculated based on concentrations of $O_3 + NO_2$ measured in ppb at one hour, 30 and 15

minute time averaged intervals. The MAPD calculations for the above three time intervals were compared in order to determine which provided the highest level of accuracy between the Cairclip sensors and the reference station monitor. For simplicity reasons, the symbol CC and SM are used in the data tables to represent the Cairclips and station monitor, respectively.

From the time weighted calculations, the one hour averaged concentrations showed the best comparative accuracy results; therefore this data is provided to for discussion in the following section. Detailed quantitative accuracy data and graphs for 30 and 15 minute MAPD results and linear regression summaries for all Cairclips is provided in Appendix D.

Based on graphed comparison of hourly averages between the reference station monitor and the Cairclips, a few data points appeared spurious and were considered outliers in all data sets. These data points were compared with dates and times of monitoring. The dates were determined to be August 27 and 28 from 4 to 5 pm. These data points were low and spurious in comparison to the next hourly averages for the Cairclips, which measured in closer range to the station monitor. As applied to the precision data, outliers were removed according to the following criteria: 1) visual outliers were removed first and, 2) any points that lay beyond ± 2 SD of the mean were also removed (Curran et al., 2012; Currie et. al., 1994).

Once outlier tests were applied, remaining data was graphed and linear regression lines applied to the data points to provide a visual picture of the linear relationship between each Cairclip sensor and the reference NAPS station

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monitor. The best fit linear regression line graph is provided for each data set followed by a table summarizing the results of three classifications of data as follows: all screened data, data with visual outliers removed and remaining data after the SD outliers test was applied.

The data sets used for the following graphs are representative of group 3 with ± 2 SD outlier test applied for one hour averaged concentrations of the Cairclip sensor vs station monitor for monitoring from July to November, 2013.

Phase one findings are highlighted in Figure 29, the graph provides an overview showing the performance of Cairclips 1, 2, 3 and 4 in relation to measurements recorded by the station monitor based on hourly averaged concentrations of $O_3 + NO_2$. This graph was designed to provide a general idea of how well the Cairclips performed in relation with the reference or fixed site monitor. In most cases, for the one hour average, the station monitor concentration measurements for $O_3 + NO_2$ were higher than that of the Cairclip sensor. This may be explained in that the Cairclip sensor lacks sensitivity in environments where concentrations of O_3 and NO_2 are low such as that in the city of Edmonton, Alberta.



Figure 29. Comparison of accuracy results of Cairclips to station monitor.

4.2.1 Accuracy Results Cairclip 1 to Station Monitor

A summary of the accuracy results for the active monitoring of $O_3 + NO_2$ is given in the Table 16. Table 16 summarizes the accuracy parameters as well as variation in mean absolute percent difference (MAPD) values upon the application of outliers testing. The MAPD for Cairclip 1 to station monitor was 43% (n=91), 40% (n=80) and 40% (n=76) for groups 1, 2 and 3 during the 4 month period of monitoring in the field. The MAPD decreased slightly from 43%, in screened data, to 40% when the visual outlier test was employed. Even though the parameter values changed slightly there was no decrease in the MAPD with the application of the m±2SD outliers test.

Parameters	Group							
for accuracy	One		Two		Three	Three		
analysis	(screen	ed data)	(screened	l data with	(screened	l data with		
			visual ou	tliers	outliers removed			
		removed)		beyond m±2SD)				
	CC 1	SM	CC1	SM	CC 1	SM		
Ν	91		80		76			
Mean (ppb)	17	31	18	30	18	30		
Median (ppb)	15	32	18	31	17	31		
Mode (ppb)	17	35	17	31	17	35		
Minimum (ppb)	4	9	4	12	4	12		
Maximum (ppb)	32	53	32	53	31	53		
Mean Abs % Diff	4	3%	40%		41%			

Table 16. Field accuracy parameter results of Cairclip 1 to station monitor.

The accuracy graph, displayed in Figure 30, provides for a comparison of Cairclip 1 to the NAPS station monitor and is inclusive of all screened data (group one); the graph also illustrates the application of ± 2 SD (group 3) outliers testing parameters as well as the respective linear regression values and sample size. A one to one line is provide to illustrate an ideal slope as well as the best fit linear regression line is shown as applied to the group 3 data set. While the same procedure was applied to all Cairclip vs. station monitor pairings, Figure 30 exclusively presents all of this information to exemplify the manner of which the data was analyzed.

A summary of linear regression results for data sets groups one, two and three are provided in Table 17. The R^2 value approaches the value of one as outliers are removed from the data set. The value improved from 0.43 to 0.77 when any data points beyond ±2SD of the mean are removed and indicates a positive linear relationship. The linear regression results show that the slope ranged from 0.49 to 0.62 with application of the ± 2 SD outliers testing. Even though the slope was closer to 1, the value was below 0.70 and not highly significant.



Figure 30. Graph of accuracy results of Cairclip 1 to the station monitor.

Table 17. Linear regression results for field accuracy of Cairclip 1 to station monitor.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	91	0.43	0.49	2.38					
2 (screened data with	80	0.77	0.65	-1.36					
visual outliers removed)									
3 (screened data with	76	0.77	0.62	-0.77					
outliers removed beyond									
m±2SD)									

4.2.2 Accuracy Results Cairclip 2 to Station Monitor

A summary of the accuracy results for the active sampling of $O_3 + NO_2$ is

presented in Table 18. The MAPD for the paired monitors, Cairclip 2 versus

NAPS station monitor, was 35% (n=91), 32% (n=80) and 31% (n=77) for Groups

1, 2 and 3, respectfully. The above values indicate that comparing measurements of

 $O_3 + NO_2$ collected by Cairclip 2 to those collected by the NAPS station monitor resulted in an accuracy of 35%, 32% and 31% for Groups 1, 2 and 3 during the four month monitoring period. The MAPD of the screened data decreased for 35% to 32% when the visual outliers test was employed; while a slight decrease was incurred from 32% to 31% when the m±-2SD outlier test was applied.

Parameters	Group								
for accuracy	One		Two		Three	Three			
analysis	(screened data)		(screened	data with	(screened of	data with			
			visual outliers		outliers removed				
			removed)		beyond $m \pm 2SD$)				
	CC 2	SM	CC 2	SM	CC2	SM			
Ν	9	1	80		77				
Mean (ppb)	21	31	21	30	21	30			
Median (ppb)	20	32	20	32	20	31			
Mode (ppb)	20	35	20	35	20	35			
Minimum (ppb)	5	14	5	14	5	14			
Maximum (ppb)	40	53	40	53	40	50			
Mean Abs % Diff	3	5%	31	2%	3	1%			

Table 18. Field accuracy parameter results of Cairclip 2 to station monitor.

The accuracy graph displayed in Figure 31 shows the relationship between Cairclip 2 in relation to the station monitor. The graphed data represents those data points that fell within ± 2 SD of the mean for the data set. The values presented in Table 19, provides a summary of linear regression results data set groups one, two and three. The R² value approaches the value of one as outliers are removed from the data set, providing evidence of a positive linear relationship. In summary the R² value improved from 0.40 to 0.67 when data that lied outside ± 2 SD of the mean were removed. The slope values increased from

0.56 to 0.79 with the application of outlier testing, which positively affected the significance of the relationship.



Figure 31. Graph of accuracy results of Cairclip 2 to the station monitor.

Table 19. Linear regression results for field accuracy of Cairclip 2 to station monitor.

Linear Regression Results					
Group	n	R ²	Slope	Intercept	
1 (screened data)	91	0.40	0.56	2.82	
2 (screened data with	80	0.59	0.71	-0.40	
visual outliers removed)					
3 (screened data with	77	0.67	0.79	-2.61	
outliers removed beyond					
m±2SD)					

4.2.3 Accuracy Results for Cairclip 3 to Station Monitor

A summary of the accuracy results for the active sampling of $O_3 + NO_2$ is

presented in Table 20. The MAPD for the paired monitors, Cairclip 3 versus

NAPS station monitor, was 31% (n=91), 31% (n=89) and 32% (n=82) for Groups

1, 2 and 3, respectively. The above values indicate that comparing measurements

of $O_3 + NO_2$ collected by Cairclip 3 to those collected by the NAPS station monitor resulted in an accuracy of 31%, 31% and 32% for Groups 1, 2 and 3 during the four month monitoring period. The MAPD of the screened data remained the same at 31% after the visual outliers test was applied to the data, while a slight increase from 31% to 32% was observed when the m±2SD outlier test was applied.

Parameters			Group			
for accuracy	One		Two		Three	
analysis	(screened data)		(screened data with		(screened data with	
			visual outl	iers	outliers ren	noved
			removed)		beyond m±	: 2SD)
	CC 3	SM	CC 3	SM	CC 3	SM
Ν	9	1	8	9	8	32
Median (ppb)	30	31	22	30	21	30
Median (ppb)	32	32	21	32	20	32
Mode (ppb)	35	35	11	35	11	35
Minimum (ppb)	5	14	5	14	5	14
Maximum (ppb)	38	53	38	53	38	50
Mean Abs % Diff		31%	3	1%	3	2%

Table 20. Field accuracy results of Cairclip 3 to station monitor

The accuracy graph for Cairclip 3 to the station monitor, which represents the remaining data points that fell within ± 2 SD of the mean for the data set, is displayed in Figure 32. The linear regression results in Table 21 show that the R² value approaches the value of one as outliers are removed from the data set. The R² value improved from 0.49 to 0.77 when all data points beyond ± 2 SD of the mean were removed from the data set, indicating a more positive linear relationship. The slope values changed from 0.59 to 0.75 with outliers removed, which improved the significance of the relationship as it moved towards a value of 1 showing a positive linear relationship.



Figure 32. Graph of accuracy results of Cairclip 3 to station monitor.

Linear Regression Results					
Group	n	R ²	Slope	Intercept	
1 (screened data)	91	0.49	0.59	3.33	
2 (screened data with visual outliers removed)	89	0.64	0.73	-0.58	
3 (screened data with outliers removed beyond m±2SD)	82	0.77	0.75	-1.82	

Table 21. Linear regression results for field accuracy of Cairclip 3 to station monitor.

4.2.4 Accuracy Results for Cairclip 4 to Station Monitor

A summary of the accuracy results for the active sampling of $O_3 + NO_2$ is presented in Table 22. The MAPD for the paired monitors, Cairclip 4 versus NAPS station monitor, at one hour averaged concentration over the four month monitoring period was 31% (n=91), 29% (n=85) and 29% (n=83) for Groups 1, 2 and 3, respectively. The MAPD of the screened data decreased from 31% to 29% after the visual outliers test was employed; subsequently, the MAPD remained constant at 29% following the application of the m±2SD outlier test. According to the MAPD values for all paired Cairclips to station monitor data sets, the Cairclip 4 showed the best performance of all four sensors when challenged against the station monitor.

Parameters	Group						
for accuracy	One	One		Two		Three	
analysis	(screen data)		(screened data with visual outliers removed)		(screened data with outliers removed beyond m±2SD)		
	CC 4	SM	CC 4	SM	CC 4	SM	
Ν	91		85		83		
Mean (ppb)	21	31	21	30	21	30	
Median (ppb)	21	32	21	32	21	31	
Mode (ppb)	23	35	23	35	23	35	
Minimum (ppb)	8	9	8	14	8	14	
Maximum (ppb)	36	53	36	53	35	53	
Mean Abs % Diff	31%		29%		29%		

Table 22. Field accuracy	results of	Cairclip 4	4 to	station	monitor
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The accuracy graph displayed in Figure 33 shows the relationship between Cairclip 4 in relation to the station monitor. The graphed data represents those data points that fell within ± 2 SD of the mean for the data set. Table 23 provides for a summary of the linear regression results data set groups one, two and three. The R² value approaches the value of one as outliers are removed from the data set. The value improved from 0.22 to 0.43 when all data points beyond ± 2 SD of the mean were removed from the data set. As the R² was favorable to the value of -1, this provided strong evidence of a negative relationship between the variables. Of all the pairings, Cairclip 4 showed the poorest linear relationship (R² value) to the station monitor but had the highest MAPD in group 3 at a level of 29%, indicating that R² values are not solely predictive of the degree of accuracy between variables (Minitab Inc., 2010). The slope ranged from 0.34 to 0.50 and are less significant results that show a marginal relationship when compared to a value of >0.70, which is indicative and representative of a meaningful and positive linear relationship between the variables.



Figure 33. Graph of accuracy results Cairclip 4 to station monitor.

Table 23. Linear regression results for field accuracy of Cairclip 4 to station monitor.

Linear Regression Results					
Group	n	R ²	Slope	Intercept	
1 (screened data)	91	0.22	0.34	10.62	
2 (screened data with visual outliers removed)	85	0.39	0.49	7.03	
3 (screened data with outliers removed beyond m±2SD)	83	0.43	0.50	6.56	

The directive for phase one of this study was to determine an accuracy baseline that was representative of Edmonton's field sampling conditions; therefore the most reliable air quality data to use for comparison was the NAPS monitoring station measurements that recorded concentrations (ppb) of $O_3 + NO_2$. The one hour averaged concentrations with outliers removed shows slightly better accuracy values than those of the 30 and 15 minute averaged concentrations, Appendix E. The range of accuracy results for all Cairclip to station monitor pairing for group one, two, and three data sets for the one hour, 30 and 15 minute averaged concentrations are summarized as follows: ± 29 to 43%; ± 31 to 48%; and, ± 32 to 48%, respectively. When used for monitoring in this study, all Cairclips with the exception of Cairclip 4 exceed the manufactures determined uncertainty value of <30%, a point of reference that has been previously explained at the beginning of this chapter. These results indicate that the overall performance of the Cairclips in the urban Edmonton environment was not as accurate as suggested by the manufacturers of the sensors (Cairpol, 2014).

Importantly, the Cairclip sensors are designed to measure near-field sources of pollutants on a real-time capacity. Furthermore, the Cairclip differs from the centralized station monitors in measuring pollutants because they: 1) are portable, 2) do not require electricity for monitoring in the field, 3) have different response times, 4) different travel times from inlet to sensors, and 5) different inlet locations.

4.3 Phase Two: Indoor and Outdoor Residential Monitoring

As described previously in the Chapter 3, concentrations of $O_3 + NO_2$ collected by Cairclip 2, which represented indoor residential monitoring, were compared to concentrations of $O_3 + NO_2$ data collected by Cairclip 3, which represented the outdoor/ backyard monitoring at the same residence. The residential location was

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in a core neighborhood in Edmonton located at 88th Avenue and 98th Street and is shown on the map provided in Figure 34.



Figure 34. Map showing approximate location of residential monitoring.

Monthly and hourly intervals were established in order to compare concentrations for 6 to 9 am, 10 am to 1 pm, 2 to 5 pm and finally 6 to 7 pm, Table 25. The graph provided in Figure 37, compares the ratios of the data from Cairclip 2 to Cairclip 3 in relation to hourly ranges as indicated in Table 24.

An arbitrary value of 1 was set to distinguish outdoor from indoor, with ratios less than 1 (<1) meaning outdoor concentrations measured in ppb of $O_3 + NO_2$ were higher than that of the indoor concentrations. In general, it was observed that the residential outdoor near-field concentrations were higher than indoor nearfield concentrations for most of the phase two monitoring period at this

designated location.

Time Period	Mean of Ratios	Ν
6-9 am	.41	3898
10am – 1pm	.32	6507
2-5pm	.29	6338
6 –7pm	.36	1076
Total	.33	17819

Table 24. Descriptive statistics of concentration ratios Cairclip 2 to Cairclip 3.



Figure 35. Graph of mean ratio results of indoor (CC2) vs outdoor (CC3) concentrations.

As the Cairclip sensors measured the sum of O₃ and NO₂, knowing the independent concentrations of each gas indoors and outdoors the residence was

not possible. This said, inferences can be made based on aspects and qualities of the indoor and outdoor environment in question. Characteristics of the house such as the style, age, location, types of heating systems and level of human activity can provide valuable information in understanding why indoor concentrations of $O_3 + NO_2$ were lower than outdoor residential concentrations.

The home used for monitoring in this study was a 1940's bungalow that was not highly insulated or sealed; therefore this may have influenced the concentration levels of $O_3 + NO_2$ present indoors. These structural elements inherent in the home may have encouraged air flow and mixing of ambient outdoor air into the indoor environment. The main reason for low concentrations of O_3 and NO_2 was due to the scavenging process and because there was low production of these gases in the home.

The outdoor air that infiltrates to the indoor environment may affect indoor air quality particularly when attempting to measure highly reactive gases, such as O_3 and NO_2 . This is explained as NO_2 can undergo photolysis, which transforms it into NO and O_2 . The O_2 atoms rapidly react with molecular oxygen to form O_3 . Simultaneously, NO quickly scavenges for O_3 resulting in the formation of NO_2 and O_2 (US EPA, 2014e). O_3 is a powerful oxidizing agent, its capacity to react quickly with other chemicals in the air acts to create other by-products. Because of the high capacity of this air mixing phenomenon with other residual parameters within the indoor environment, concentrations of $O_3 + NO_2$ once present are quickly changed. Because of the highly reactive and scavenging character of these

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gases, the Cairclip may not have been capable of measuring concentrations as they were already transformed into other chemical compounds (WHO, 2003b).

4.4 Phase Two: Personal Exposure Monitoring

In the personal exposure portion of the study, Cairclip sensors 1 and 4 were used to measure exposure to $O_3 + NO_2$ as an individual carried out their various daily activities. The objective of this part of the study was to select scenario locations that captured near-field exposure to the pollutants, O_3 and NO_2 , representative of the average person's daily routine in an urban environment.

The Cairclips are designed to measure exposure to concentrations of $O_3 + NO_2$ in relation to time-activity patterns that represent the unique behaviors' of an individual in the microenvironments with which they interact. Whereas, the fixedsite centralized monitors such as the Edmonton south station monitor (ESSM) and the Edmonton central station monitor(ECSM), provide concentration measurements of criteria pollutants based on their localized ambient area (Nejadkooki et al., 2011; Ott, 2007a). Both monitoring technologies are designed to measure ambient concentrations of $O_3 + NO_2$, the source of pollution differs. The centralized stations measure far-field sources while the Cairclip is designed to measure near-field sources at the receptor, in this case a person (Ott, 2007a; Cairpol, 2014).

Through monitoring with the Cairclips, the personal exposure portion of the study aimed to show the degree of variation between concentrations of pollutants measured at the individual level based on varied spatio-temporal conditions with that of concentrations measured by centralized monitoring. Consideration of the

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degree and duration of exposure to concentration to $O_3 + NO_2$ were instrumental to assessing the potential human exposure to these pollutants as related to certain urban locations.

For purposes of this study, the reference value for comparison used with be a sum concentration of 240 ppb which was calculated by adding the one-hour Alberta Ambient Air Quality Objectives for O_3 at 80 ppb and NO_2 at 160 ppb, respectively. The data presented in this part of phase two includes only the monitoring times that showed significant eventful concentrations, i.e. concentration spikes above those of the station monitor. In addition to this, only those monitoring events that exceed the Cairclip's limit of detection (LOD) of 20 ppb were considered relevant for discussion (Cairpol, 2014).

The ECSM located on the top of a building downtown Edmonton located on 104^{th} Avenue between 109^{th} and 110^{th} Streets and is meant to be representative of urban core exposures to concentrations of $O_3 + NO_2$ whereas, the ESSM in the southwest side of the city is meant to be representative of residential ambient air concentrations of $O_3 + NO_2$. The discussion includes findings from various settings that were monitored with Cairclips 1 and 4 which are contrasted with the centralized station monitor as a means of reference.

4.5 Monitoring of Busy Intersections and Roadways

In this environmental setting, the personal exposure scenarios pertained to monitoring outdoor sites on foot at high volume traffic areas located in urban core areas. The intersections of interest were chosen to represent a comparison of two downtown locations, as well as two locations in the Whyte Avenue vicinity. Data collected by the Cairclips is presented for the following four specified outdoor intersections/roadways: Jasper Avenue and 109th Street, 97th Avenue and 109th Street, Whyte Avenue and 99th Street and Whyte Avenue to 109th Street. The map provided in Figure 36, shows the geographical location of the four specific monitoring sites in relation to the ESSM and the ECSM.



Figure 36. Map showing the urban site outdoor sites used for personal exposure monitoring.

In summary, monitoring data at these four outdoor sites, the 97th and 109th Street location displayed a greater variation with a number of concentration spikes in comparison to the Jasper and 109th setting. While the data from Whyte Avenue and 109th Street displayed higher concentrations and more frequents spikes than levels measured at the Whyte Avenue and 99th Street location. The two intersections in the downtown core and the Whyte Avenue area were similar in that several residential and commercial dwellings were in close range of the monitored areas. As the monitoring at these intersections was outdoor and within 2 meters of high traffic areas, the near-field source of O₃ and NO₂ is mostly related to emissions from various types of vehicles.

4.5.1 Outdoor Monitoring of Jasper Avenue at 109th Street

The following discussion is based on monitoring events that reflect the Cairclip's ability to capture near field exposure at the Jasper Avenue and 109th Street location, additional graphs for this scenario can be found in Appendix E. The monitoring events presented in the graphs were those that showed concentrations higher than 20 ppb for the Cairclip and where data for both station monitors was available. Monitoring times were intended to capture mid-morning and afternoon periods.

On September 13th and 27th, 2013, respectively, the Cairclip recorded spikes in concentration above that of the centralized monitoring stations (Figures 37 and 38). The spikes coincided with high volumes of vehicular traffic flow that may be expected at the observed times of 11:33 am and 17:53 pm, which can be considered as brief segments of peak traffic periods (McCullum et al., 2004). As the ambient temperatures at this time were beginning to cool, it is most likely that in this case the Cairclip was measuring higher levels of NO₂ than O₃.



Figure 37. Comparison of Cairclip to station monitor on Sept. 13, 2013 at Jasper Ave. & 109th St.



Figure 38. Comparison of Cairclip to station monitor on Sept. 27, 2013 at Jasper Ave. & 109th St.

Traffic counts from 2013 for an average weekday for this intersections were measured and recorded at a value of 17,300 (City of Edmonton, 2013). Pedestrian count data was limited to data collected at Jasper Avenue and 104th Street, five blocks to the east of where monitoring for this study was conducted. For purposes

of this study, the pedestrian counts at a mid-day peak of 292 was assumed as a reference value to representative of pedestrian activity in this area (Gresiuk, 2013). It was observed and recorded in the time activity diary that, for this location, pedestrian volumes varied from light to moderate dependent upon the time of day.

The findings at the Jasper Avenue and 109^{th} Street location showed that while both the centralized monitoring stations measured concentrations of $O_3 + NO_2$ at a relatively stable and consistent level, the Cairclips showed greater variability. Although the Cairclips recorded spikes in concentrations of $O_3 + NO_2$, there were no events that exceeded the reference value of 240 ppb. Furthermore, the concentration spikes that were observed were limited to one to three minutes in durations.

4.5.2 Outdoor Monitoring at 97th Avenue and 109th Street

Findings at the 97th Avenue and 109th Street location are discussed in the following. Weekday traffic counts at this intersection have been measured at 33,300 (City of Edmonton, 2013). Although pedestrian counts have not yet been measured, it was observed that a high number of commuters travelled this area by bicycle and foot to and from the downtown core. This location is centered in the hub of the city, close to government buildings and residential developments. Throughout the duration of monitoring at this location there was a one-time event recorded on October 10, 2013 at 10:00 am where Cairclip 1 recorded a short term concentration of 255 ppb, a level that exceeded the reference value of 240 ppb (Figure 39).

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Graphs represent one-minute monitoring events are presented that highlight the Cairclip's capacity to measure pollutants close to source. Monitoring periods that showed significant spikes in concentration are included for discussion, additional graphs are provided in Appendix E. The graphs display measured concentrations of $O_3 + NO_2$ by Cairclip 1 and 4 are compared to those measured by the ESSM and the ECSM. Finding are characterized by a highly variable patterning of one-minute concentrations measured in relation to the station monitors, Figures 39, 40 and 41. During these monitoring times, short term peaks in $O_3 + NO_2$ concentrations ranged from 200 ppb on October 10, 2013 to 90 ppb on October 11, 2013, Figures 39 and 40. Whereas, on these same dates, the station monitors recorded concentrations of $O_3 + NO_2$ in a more consistent manner with concentrations remaining quite level.

These comparative observations between the Cairclips and the station monitor show a high degree of variability in one-minute concentration levels that existed between near-field and far-field measurements of pollutants. The near-field measurements by the Cairclip showed short durations spikes in concentrations. These finding were consistently observed throughout the study.



Figure 39. Graph of comparison of Cairclip to station monitor on Oct. 10, 2013 at 97th Ave. and 109th St.



Oct 11, 2013 Monitoring Time-One Minute Continuous

Figure 40. Graph of comparison of Cairclip to station monitor on Oct. 11, 2013 at 97th Ave. and 109th St.

Findings from January 9, 2014 (Figure 41) show spikes in concentrations of $O_3 + NO_2$ at 8:47 and 8:59 am, respectively. The first spike remains constant for approximately 4 minutes before it begins to fall. The second spike reached its

highest point then immediately fell below the LOD within a minute. Given the high number of vehicles and the time of day being a peak travel time, these spikes recorded by the Cairclip were most likely related to changing of vehicular emissions as traffic moved through the intersection.



Figure 41. Graph of comparison of Cairclip to station monitor on Jan 9, 2014 at 97th Ave. and 109th St.

While short term spikes in concentrations are recorded by the Cairclip, the sensors show a high degree of variation in measuring one minute concentrations of $O_3 + NO_2$ over a specific period of time in relation to the station monitor data. Traffic counts for this area have been measured at 33,300, rating this area as having the second highest volume of vehicular traffic of all scenarios monitored in this study (City of Edmonton, 2013). Due to the volume of traffic in this area, any spikes in concentrations of $O_3 + NO_2$ measured at the receptor can be correlated to vehicular emissions (US EPA, 2014e).

4.5.3 Outdoor Monitoring of Whyte Avenue to 109th Street

Traffic count data collected for Whyte Avenue in 2012 measured weekday volumes in the range of 22,000 to 24,600 and pedestrian counts ranged from approximately 320 to 2400 (Gresiuk, 2012; City of Edmonton, 2013). A time interval of thirty minutes was selected for this particular scenario.

As in previous discussions of other monitoring scenarios, the Cairclip sensors generally measured concentrations of $O_3 + NO_2$ lower than that of the station monitors. Figures 42 and 43 are provided as specific examples of the monitoring results of the Cairclips at this monitoring site, additional graphs are available in Appendix E. As displayed in Figure 42, the overall performance of Cairclip shows that exposures at the personal, real time level were much lower than concentrations recorded by the ECSM. However, on this date Cairclip 4 records a one minute spike at the end of the monitoring period at 1:59 pm with a level of 75 ppb. The concentrations measured by Cairclip 4 were climbing while the ECSM were steady. The ESSM data remaining consistent at a much lower concentration.

On December 23, 2013 the Cairclip shows a highly variable pattern based on one minute averaged concentrations which ranged from approximately 80 to 120 ppb throughout the 30 minute monitoring period (Figure 43). The time of day ranges from 17:30 to 17:59 pm which correlates with rush hour times of traffic, and subsequent higher concentrations of vehicular emissions.





Figure 42. Graph of comparison of Cairclip to station monitor on Nov. 29, 2013 at Whyte Ave. & 109th St.



Dec. 23, 2013 Montioring Time-One Minute Continuous

Figure 43. Graph of comparison of Cairclip to station monitor on Dec. 23, 2013 at Whyte Ave. & 109th St.

Similar to the results obtained when testing in the downtown locations, the spikes in concentrations recorded on Whyte Avenue by the Cairclip were of short durations of one to two minutes. Findings from the data collected by the Cairclips at this location showed concentrations that did not exceed the reference value of 240 ppb for concentrations of $O_3 + NO_2$. The intersection on average handles from 22,000 to 25,000 vehicles per day (City of Edmonton, 2013). As this area is composed of a mixture of commercial/retail and residential with no industry in close range, the near-field source of exposure can be correlated to emissions from various types of vehicles.

4.5.4 Outdoor Monitoring at 99th Street to Whyte Avenue

In this scenario there was one monitoring time where the Cairclip recorded significant data where measurements were above the sensor's LOD of 20 ppb, see Appendix B (Cairpol, 2014). Traffic count data from 2013 was measured at approximately 27,000 vehicles, which is the third highest of all the areas monitored in this study (City of Edmonton, 2013). Data on pedestrian counts for 99th Street to Whyte Avenue were not available.

On December 15, 2013 the Cairclip recorded a spike in concentrations to 105 ppb above that of the station monitors of 105 ppb (Figure 44). The time of day that this concentration was measured was mid-afternoon at 14:25 pm with the source most likely associated to emissions from various types of vehicles, i.e. city buses, commercial and passenger vehicles.


Figure 44. Graph of comparison of Cairclip to station monitor on Dec. 15, 2013 at 99th St. & Whyte Ave.

Similar to the other areas monitored in this scenario of phase two, the nearfield source of exposure measured by the Cairclip can be attributed to vehicular emissions. In consideration of the reference value of 240 ppb, the Cairclip data showed only short term spikes of concentrations of $O_3 + NO_2$ that were far below this value.

As a general observation, monitoring data from the intersections and roadways show that the ambient monitors, ESSM and ECSM, measured concentrations of $O_3 + NO_2$ in a consistent and level pattern. Conversely, the Cairclips periodically showed a high degree of variation in concentration measurements of $O_3 + NO_2$ from minute to minute throughout the course of the monitoring times. These variations in concentrations from minute to minute are characteristic of the active, personal Cairclip samplers, as they measure near-field sources of pollutants in a real time capacity.

4.6 Commuter Monitoring on Public Transit: LRT and Bus

In this study, for purposes of measuring personal exposure to $O_3 + NO_2$, monitoring using the Cairclip was conducted on both a city transit bus and on light rail transport (LRT). The rational for choosing to monitor on public transit was to determine the concentration level of potential exposures to $O_3 + NO_2$ correlated to time of day and location while commuting. The following are the important findings of monitoring on public transit: peak concentrations ranging from 60 ppb to 150 ppb were measured on the bus at various locations on route to the West Edmonton Mall (WEM) transit station and during wait times at station, both inside and outside the bus; concentration spikes measured on LRT were more commonly observed during north-bound travel from SG to Grandin and in LRT stations following train departure.

4.6.1 Monitoring on Bus Route #33: Southgate to West Edmonton Mall

The commuting scenario chosen for travelling via a city bus was route #33 from the Southgate station to the West Edmonton Mall transit station and return (Figure 19). When possible, the air monitoring was conducted from the middle section of the bus for consistency.

Some monitoring events were removed from this analysis because of missing data from the ambient station monitors due to maintenance or malfunctions which interrupted data collection. Consistent with the findings from other monitoring scenarios, the Cairclip demonstrated a high rate of variation during this

monitoring event (Figure 45). The findings on Oct 22, 2013, which shows a high variation from minute to minute, exemplify the Cairclip's response in measuring pollutants in this monitoring scenario. As observed in Figure 45, the Cairclip exceeded measured concentrations of $O_3 + NO_2$ in comparison to the station monitors. Peak concentrations ranged from 60 ppb to 150 ppb for this day. These concentrations were measured at various intervals on route to West Edmonton Mall and when waiting inside and outside the bus at the WEM transit station, respectively.

As the transit stations accommodate several buses and are located adjacent to shopping mall parking lots close to major roadways, high volumes of vehicular traffic create a source of potential exposure to pollutants, $O_3 + NO_2$. Also it is important to note that because the cooler temperatures were favorable to NO_2 formation, it is most likely the Cairclips were recording higher levels of NO_2 than O_3 (Gilbert et al., 2003). The doors of the bus were open while waiting to depart the WEM station which may have allowed for ambient concentrations of gases to infiltrate.



Figure 45. Graph of comparison of Cairclip to station monitor on bus route #33

on Oct. 22, 2013

Note: Spikes are as follows: A: Heading west on 50th Ave. at 113th Street; B: Meadowlark Road and 87th Avenue; C: WEM station; D: WEM station; E: On return trip to SG station; G: Adjacent to Mitchener Park at 50th Avenue and 122 Street; and H: 50th Avenue and 111th Street.

4.6.2 Monitoring on LRT Routes from Century Park to Grandin Station

In this study, air monitoring of LRT routes was conducted as a means to quantify potential exposure to $O_3 + NO_2$ during commuting. The results of data collection by Cairclips 1 and 4 on LRT routes are presented in the following presentations and discussion (Figures 46 to 50). The routes monitored can be found in Figure 19.

Monitoring times for this exposure scenario vary due to factors, which could not be controlled for such as slight time variations of train schedule. Much of the data presented in graphs is based on return trips. Monitoring periods on the LRT showed breaks in the time variable in order to account for data collection in other locations of interest as extensions from the LRT. For example, northbound LRT trips were used as the start point for the continuation of monitoring at two downtown intersections; while southbound trips set the stage for the continuation onto the bus monitoring to and from the West Edmonton Mall. The finding from this monitoring scenario are as follows: the Cairclip most often measured high concentration spikes during northbound travel as compared to south bound travel, the route between Southgate station and Grandin, and; spikes in concentrations were recorded at waiting areas in LRT stations.

As seen in Figures 46, 47 and 50 the spikes in concentration ranging from 50 ppb to 130 ppb were more often measured while travelling northbound from Southgate to Grandin stations. It is hypothesized that this may be a result of emissions from higher volumes of vehicular traffic associated with the urban core. In Figure 48 and 49, the highest spikes in concentrations of $O_3 + NO_2$ ranged from 150 ppb to 200 ppb and were recorded at the underground waiting area of the University and Grandin stations, respectively. Generally, these spikes were recorded shortly after arrival and departure of the trains.



Sept. 16, 2013 Monitoring Time -One Minute Continuous

Figure 46. Graph comparing Cairclip to station monitor on LRT on Sept. 16, 2013.

Note: The location of concentration spikes are noted through uppercase letters as follows: A, B and C) Century Park station; D) northbound trail between Century Park and Southgate stations; E to I) Southgate station; J to L) northbound on the train from Southgate to Health Sciences Jubilee; and M) Health Sciences Jubilee station.



Oct. 10, 2013 Monitoring Time-One Minute Continuous

Figure 47. Graph of comparison of Cairclip to station monitor on LRT on Oct.10, 2013.

Note: Locations of concentrations spikes are as follows: A) waiting at the Health Sciences Jubilee station; B to C) on the northbound train Health Sciences Jubilee to Grandin station; D) exit train at Grandin station; and E) in underground waiting area at Grandin station.



Figure 48. Graph of comparison of Cairclip to station monitor on LRT on Oct. 11, 2013

Note: Locations of concentrations spikes are as follows: A) underground at University station wait time for train; B) on train travelling north bound to Grandin station; C and D) on train travelling south bound to University station; E) inside the University station.



Figure 49. Graph of comparison of Cairclip to station monitor on LRT on Oct. 15, 2013

Note: Locations of concentrations spikes are as follows: A to C) Health Sciences Jubilee station to Grandin station, north bound; D to F) inside Grandin station underground; G) exiting Grandin station at 110th Street; H) on the train traveling south bound from Grandin to University Station, above the river valley; I & J) travelling south bound from University to Southgate station; and, K) exiting from Southgate station.



Oct. 22, 2013 Monitoring Time-One Minute Continuous

Figure 50. Graph of comparison of Cairclip to station monitor on LRT on Oct. 22, 2013

Note: Locations of concentration spikes are as follows: A) exit bus #33 at Southgate at LRT station; B to C) waiting for north bound train at Southgate station; D to E) on northbound train from Southgate to University station.

In general, the Cairclip sensors showed a high variation, up to 200 ppb, of minute to minute concentrations. These findings are similar to that seen in the other personal exposure monitoring scenarios already discussed. The Cairclip sensors measured near-field sources of $O_3 + NO_2$ based on levels present in various locations during commuting by means of the LRT. The origin of these near-field sources are most likely correlated to emissions from surrounding vehicular traffic at transit stations and concentrations that had infiltrated into the LRT cabin.

As spikes in concentrations of $O_3 + NO_2$ were measured in underground LRT stations, the source may be difficult to ascertain. A possible explanation may be that ambient levels of $O_3 + NO_2$ infiltrated into the underground waiting area. Although, there were times of short duration where Cairclip 1 recorded levels in the 200 ppb range, as recorded in Figure 48, at no time did the concentrations recorded exceed the reference value of 240 ppb.

4.7 Indoor Monitoring at High Volume Traffic Areas

The receptor-oriented approach to monitoring pollutant concentrations indoors where people spend most of their times involves measuring $O_3 + NO_2$ very close to the person (Ott, 2007a). Therefore, testing the Cairclip's integrity in selected indoor public locations was important for this study.

The locations selected were as follows: 99th Street and 89th Avenue, Whyte Avenue and 104th Street and 109th Street and 88th Avenue, see Figure 51. The monitoring times were somewhat longer in order to capture concentrations of O_3 + NO_2 over an extended period of time. The time frame for monitoring ranged from September, 2013 to January, 2014 with monitoring intervals of one hour.

The following are the important findings of monitoring non-residential locations: 1) the locations of all three monitoring sites were in close proximity to high traffic intersections where near-field sources were created from emissions; 2) the 109th Street /88th Avenue and the 99th Street /89th Avenue locations were equipped with full commercial grade kitchens with gas-fired cook tops, acting as a potential source of pollutants; and 3) the Whyte Avenue and 104th Street location often had several patrons smoking within close range of the front door, environmental tobacco smoke is a common indoor pollutant which may be considered a contributing factor affecting the air quality inside this location, and; 5) the finding from the 99th Street and 89th Avenue location were unique in that,

at times, the Cairclips measured concentrations over a sustained period of time minute suggesting the presence of a continuous source of $O_3 + NO_2$.



Figure 51. Map of indoor monitoring sites

4.7.1 Indoor Monitoring at 109th Street and 88th Avenue

Consistent with findings observed in other scenarios, Cairclip data demonstrates a highly variable pattern in $O_3 + NO_2$ concentrations over the monitoring period at this location. In the analysis of the individual monitoring times, concentration spikes of short duration measured by the Cairclips during various periods were from 2 to 8 times the concentrations recorded by the centralized station monitors. These recorded concentration spikes lasted anywhere from 1 to 3 minutes followed by a rapid drop off. Supplementary graphs of additional monitoring times at this location are available in Appendix F.

On November 28, 2013 three monitoring times of one hour were conducted consecutively from 9:30 to 12:29 pm, Figures 52, 53, and 54. Each one of these

monitoring times recorded significant short term concentrations at and above 200 ppb. On November 28, 2013 at 9:56 am (Figure 52), the Cairclip recorded a one minute concentration of 255 ppb which exceeded the 240 ppb reference value for a short time period. The spikes may have been associated to activities such as food preparation using gas fired ranges in a poorly ventilated indoor environment.



Nov. 28, 2013 Monitoring Time-One Minute Continuous

Figure 52. Graph of comparison of Cairclip to station monitor on Nov. 28, 2013 at 109th St. & 88th Ave.



Nov. 28, 2013 Montioring Time-One Minute Continuous

Figure 53. Graph of comparison of Cairclip to station monitor on Nov. 28, 2013 at 109th St. & 88th Ave.





Figure 54. Graph of comparison of Cairclip to station monitor on Nov. 28, 2013 at 109th St. & 88th Ave.

4.7.2 Indoor Monitoring at 99th Street and 89th Avenue

The main entrance to this location was situated approximately 1.5 meters from 99th Street with a secondary entrance accessed from 89th Avenue. This indoor environment had a commercial grade kitchen which was equipped with gas powered ranges and a gas fireplace just inside the 89th Avenue entrance. Pedestrian count data was not available for this location. The weekday traffic count for this intersection in 2013 was determined to be 23,700 vehicles (City of Edmonton, 2013). Traffic volumes were consistently high while monitoring in this location between the hours of 8:00 and 10:00 am.

Monitoring times on December 2, 10 and 12, 2013 (Figures 55, 56 and 57) show sharp, short duration spikes ranging from 150 to 250 ppb followed by a drop to a sustained concentration level that remained higher than the station monitor readings. This pattern displayed by the Cairclip in these three events was atypical in comparison to observation in other indoor environments in that the sensor measured a relatively high concentration for a period close to one hour in duration. Historically, in all other observations, the monitoring pattern was characterized by short term spikes with drop offs to concentrations at or below the LOD. This may have been related to near-field sources of continuous pollutants emitted from gas fired cooktops as food preparation activities increased, the onsite gas fireplace cutting in and out, and increased infiltration of outdoor pollutants due to cold outdoor ambient temperatures and high traffic volumes.



Dec. 2, 2013 Monitoring Time-One Minute Continuous

Figure 55. Graph of comparison of Cairclip to station monitor on Dec. 2, 2013 at 99th St. & 89th Ave.



Figure 56. Graph of comparison of Cairclip to station monitor on Dec. 10, 2013 at 99th St. & 89th Ave.



Dec. 12, 2013 Monitoring Time-One Minute Intervals

Figure 57. Graph of comparison of Cairclip to station monitor on Dec. 12, 2013 at 99th St. & 89th Ave.

Data collected on December 17, 2013, Figure 58, shows four significant spikes in concentrations of $O_3 + NO_2$ to 125 ppb, 100 ppb, 60 ppb and 100 ppb, respectively. These spikes occur approximately 20 minutes apart. This pattern was unique to this indoor environment and may also be linked to higher concentrations of emission from gas fired appliances or to outdoor traffic as related to higher volumes of vehicles on 99th Street. The establishment was very busy with patrons between 8:00 and 9:30 am while, outdoors, morning vehicular traffic was often quite heavy.



Dec. 17, 2013 Monitoring Time-One Minute Continuous

Figure 58. Graph of comparison of Cairclip to station monitor on Dec. 17, 2013 at 99th St & 89th Ave.

The overall performance of the sensors in this scenario showed variable patterns in measuring concentrations of $O_3 + NO_2$. In this setting, the Cairclip showed the ability to measure higher concentrations over a sustained period of time. In the previous scenarios, the Cairclip's capacity for measuring near-field exposure were characterized by rapid spikes and steep drop offs over a short period of time, 1 to 3 minutes. This observation may be indicative of steering future monitoring strategies in placement of the Cairclips in environments to which they are most suited. Notably, there were events where the concentration spikes recorded by the Cairclip were similar to the reference value of 240 ppb but they were of short duration.

4.7.3 Indoor Monitoring at Whyte Avenue and 104th Street

The site monitored was a public gathering place located on the northwest corner of the intersection of Whyte Avenue and 104th Street. The establishment

was not equipped with a commercial grade kitchen. However, the site had a commercial grade espresso machine and small appliances used for grilling foods. Indoor air monitoring at this location was conducted at a 30 minute time intervals. Additional graphs of data collected by the Cairclip at this location are provide in Appendix F.

The monitoring patterns displayed in Figures 59 and 60 show the Cairclip's short term variability in measuring $O_3 + NO_2$ concentrations. The intermittent concentration spikes during the monitoring periods coincide with morning peak traffic times, which range between 6 to 9 am (McCullum, et al., 2004). Weekday traffic counts of 21,200 were available for north of 104th Street and 81st Avenue, which was within a block of the monitoring area of interest (City of Edmonton, 2013). Pedestrian counts for this location ranged from 1400 to 2300 (Gresiuk, 2013).

In consideration of the reference value for concentrations of $O_3 + NO_2$ of 240 ppb the Cairclip recorded a short term spike of 250 ppb on January 9, 2014 at approximately 7:23 am for a duration on one minute, Figure 59. The main sources of $O_3 + NO_2$ are likely attributed vehicular emissions due to the establishment's close proximity to vehicular traffic and monitoring conducted at times of peak traffic flow. Also it was observed that a number of patrons would smoke just outside the entrance/exit point of the business. Environmental tobacco smoke is known to emit NO_2 .



Figure 59. Graph of comparison of Cairclip to station monitor on Jan. 9, 2014 at 104th St. & Whyte Ave.



Jan. 10, 2014 Monitoring Time-One Minute Continuous

Figure 60. Graph of comparison of Cairclip to station monitor on Jan. 10, 2014 at 104th St. & Whyte Ave.

According to the study conducted by the Joint Research Commission, the sensors were believed to become somewhat deconditioned after leaving the

factory where they are initially conditioned to detect O_3 (Spinelle, 2013). In the event that this deconditioning occurs, the sensitivity of the sensor decreases until which time it is exposed to sufficient levels of O_3 . For this research, there is a possibility that the sensors became deconditioned after leaving the factory and that the concentrations that the sensors were exposed to during this study were not high enough to recondition the sensors to an optimal level of sensitivity. This may provide an explanation as to the sensors low $O_3 + NO_2$ concentration levels in relation to both the NAPS station monitors and in real time scenarios where it is was assumed the readings would be high.

As noted consistently throughout the study, the Cairclip's monitoring capabilities are designed to capture receptor-based exposure from a near-field source. The Cairclip sensor is intended to represent measurements based on a real time capacity which, in this study, was characterized with fluctuations in concentrations of $O_3 + NO_2$ due to near-field sources.

5 CONCLUSIONS

The direction and focus of this research conducted using the Cairclip $O_3 + NO_2$ sensors was to provide evidence to support that air quality data recorded at centralized fixed-site monitors, may not provide the best or most representative information about individual personal exposures. While the Cairclips did not perform as well as that dictated by the manufacturer when challenged against the Edmonton south ambient monitoring station; they did provide valuable information on short term concentration spikes during personal exposure monitoring in various environments.

The Cairclips are designed to function in a similar capacity to that of the centralized ambient monitoring stations; but differ in that the origin of the pollutant sources are near-field and measured at the personal level. The centralized monitors are large, expensive, non-portable, highly technical instruments that are designed to measure pollutants on far-field source capacity.

In summary of phase one of the study, % RSD for the one hour, 30 and 15 minute averaged concentrations collected by paired Cairclips ranged from ± 11 to 34%, ± 12 to 39% and ± 14 to 37%, respectively. The one hour averaged concentrations presented the best comparative precision results, ± 11 to 34%. The summarized accuracy results for the one hour, 30 and 15 minute averaged concentrations were as follows: ± 29 to 43%; ± 31 to 48 %; and, ± 32 to 48%, respectively. Again the one hour averaged concentrations showed the best comparative accuracy results at a range between ± 29 to 43%.

In summary of phase two monitoring of a residential environment, indoor levels were consistently lower that outdoor concentrations. These findings can be related to low production of indoor sources of $O_3 + NO_2$ and the scavenging activities characteristic of these gases which lowers their concentrations (US EPA, 2014a).

Findings during phase two monitoring of outdoor intersection sites in urbancore environments demonstrated that the 97th and 109th Street location displayed a greater variation with a number of concentration spikes ranging from 70 ppb to 200 ppb in comparison to the Jasper and 109th setting where concentration spikes ranged from 40 ppb to 125 ppb, respectively. While the data from Whyte Avenue and 109th Street displayed more frequent spikes of higher concentrations ranging from 80 ppb to 120 ppb than levels measured at the Whyte Avenue and 99th Street, which reached a one-time height of concentration at 100 ppb. The intersections in the downtown core and the Whyte Avenue area were similar in that several residential and commercial dwellings were located within close proximity to vehicular traffic. As the monitoring at these intersections was outdoor and within 2 meters of high traffic areas, the near-field source of O₃ and NO₂ is mostly related to emissions from various types of vehicles.

The following are the important findings from phase two monitoring on public transit via city bus and LRT. Peak concentrations on bus route #33 ranged from 60 ppb to 150 ppb. These concentrations were measured at various intervals on route to West Edmonton Mall and when waiting inside and outside the bus at the WEM transit station, respectively. During monitoring on LRT routes,

concentration spikes over the course of the entire monitoring period ranged from 50 ppb to 200 ppb. These spikes in $O_3 + NO_2$ measured were more commonly observed during north-bound travel from Southgate to Grandin and in underground LRT stations following train departure. The origin of these near-field sources are most likely correlated to emissions from surrounding vehicular traffic at transit stations and ambient concentrations that had infiltrated underground the LRT passenger waiting areas.

Phase two findings from monitoring indoor non-residential locations displayed concentration spikes of $O_3 + NO_2$ that ranged from 125 ppb to 250 ppb. The following are the important findings from the three targeted locations are 1) the locations of all three monitoring sites were in close proximity to high traffic intersections with vehicular emission most likely the major contributor to near-field sources; 2) the 109th Street /88th Avenue and the 99th Street /89th Avenue locations were equipped with full commercial grade kitchens with gas-fired cook tops, a potential source of pollutants; and 3) the Whyte Avenue and 104th Street location often had several patrons smoking within close range of the front door, environmental tobacco smoke (ETS) is a source of NO₂, and; 4) the finding from the 99th Street and 89th Avenue location over a sustained period of time indicating a continuous source of $O_3 + NO_2$.

Based on the results of this study, the efficacy of the Cairclip $O_3 + NO_2$ sensor is questionable in environments where concentrations of O_3 and NO_2 are relatively low such as that in urban Edmonton. Consideration must be given to the fact that

the sensors are both manufactured and tested in Europe, specifically France, where geographical, climatic, and emission conditions are quite different from that of Edmonton.

Because the sensors measure a sum concentration of O_3 and NO_2 it is difficult to determine the independent levels of each gas. As the monitoring period extended from mid-September to late December, 2013 and the Cairclip is thought to have a higher sensitivity to NO_2 (Spinnelle, 2013), it is most likely that higher levels of NO_2 were recorded. Ozone is characteristically known to be more abundant in summer months when ambient temperatures are high with ample UV light exposure (Alberta Environment, 2013c). Finally, any significant spikes in concentrations of $O_3 + NO_2$ measured by the Cairclips during these monitoring times ranged from just one to three minutes with levels mostly below the reference value of 240 ppb.

As this research provides a baseline for understanding the capabilities and limitations of new technology in air monitoring, further studies in various microenvironments may be advantageous. In this study, the Cairclip sensors displayed interesting results when tested on public transit and when placed in indoor commercial environments. Further studies using the Cairclips in similar settings to these may prove to be advantageous in gaining further knowledge of receptor-based exposure of short duration to near-field sources. Prior to further monitoring in these locations, it may be advantageous to replace the micro-filter and lithium-ion battery as suggested by the manufacturers. Upon which time, the accuracy and precision of these sensors be re-tested prior to further use in personal monitoring research.

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APPENDIX A: MANUFACTURERS TECHNICAL DATA SHEET FOR CAIRCLIP O₃/NO₂ SENSOR



Range	0-250 ppb (0 - 240 ppb analog)			
Limit of detection (1,2)	20 ppb			
Repeatability at zero (1, 2)	+/- 7 ppb			
Repeatability at 40 % of range (1, 2)	+/- 15 %			
Linearity (1, 2)	< 10%			
Uncertainty	< 30% (2,3)			
Short term zero drift (1, 2, 4)	< 5 ppb/24 H			
Short term span drift (1.2.4)	<1% FS ⁽⁵⁾ /24 H			
Long term zero drift (1.2,4)	< 10 ppb/1 month			
Long term span drift (1, 2, 4)	< 2% FS ⁽⁵⁾ /1 month			
Rise time (T10-90) (1,2)	<90s (180s if large variation of RH)			
Fall time (T10-90) (1,2)	<90s (180s if large variation of RH)			
Effect of interfering species (1)	Cl ₂ : around 80% Reduced sulphur compounds : negative interference			
Temperature effect on sensitivity (2)	< 0.5 % / °C			
Temperature effect on zero (2)	+/- 50 ppb maximum under operating conditions			
Maximum exposure	50 ppm			
Annual exposure limit (1 hour average)	780 ppm			
Operating conditions	- 20°C to 40°C / 10 to 90% RH non-condensing 1013 mbar +/- 200 mbar			
Recommended storage conditions	Temperature: between 5°C and 20°C Air relative humidity: > 15% non-condensing			
Power supply (6)	5 VDC/200mA (rechargeable by USB via PC or 100V-240V/5V 0.8A-1.0A with adapter)			
Communication interface	USB, UART Analog (UART & 4-20 mA / 0-5 V converter)			
Dimensions	Diameter: 32 mm - Length: 62mm			
Weight	55g			
Protection	IP42 (according IEC60529)			
Electrical certification	Conform to UL Std. 61010-1 Interface avoid avoid to CSA Std. C22,2 N°. 61010-1			
Parameters Set up / Downloading	CairSoft			

Technical Data Sheet CairClip O₃-NO₂

Parameters Set up / Downloading

¹ According to our operating conditions during tests in laboratory: 20°C +/- 2°C / 50% RH +/- 10% / 1013 mbar +/- 5%
 ² Volues possibly effected by exposures to high gradients of concentration
 ³ In accordance with the Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe Fall scale continuous exposure

Full scale continuous expanse FS = Full Scale
* The complete discharge of a device (screen turned off) can lead to a deterioration of its performances' Any use of the sensor not complying with the conditions specified in berein, including exposures, even short ones to environments other than ambient air, to dry and / any use of the sensor not complying with the conditions specified in majority of air. even during calibration, will invalidate the warranty.
CairTobe autonomy 21 days

	CairTub: autonomy 21 days
Main options	CairNet: wireless communication & battery powered by solar panel
Alternation in the Association and	Sofiware: CairSoft, CairMap, CairWeb

Office :	CA	RP	OL.
	100 a. 100 a.	1	(

- ZAC du Capra
- 55, avenue Emile Antoine

30340 Méjannes les Alès - France

Tel: +33 (0)4 66 83 37 56 Fax: +33 (0)4 66 61 82 53 info@cairpol.com Web site: www.cairpol.com

SARL au capital de 354 200€ - Nº Siren : 492 976 253

APPENDIX B: SIGN IN SHEET FOR ENTRANCE AND EXIT INTO THE EDMONTON SOUTH STATION MONITOR

Sign in Sheet	Time in: AM or	Time Out: AM or	Conditions or
Station Monitor	PIVI	PIVI	comments
Edmonton south			
Date:			

APPENDIX C: PRECISION RESULTS FOR 30 AND 15 MINUTE AVERAGED CONCENTRATIONS OF O₃ + NO₂

Precision Results 30 Minute Averaged Concentrations

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data with visual outliers removed)		Group 3 (screened data with outliers removed beyond m±2SD)	
	CC1	CC2	CC1	CC2	CC1	CC2
Ν	182		166		166	
Mean (ppb)	17	21	18	19	18	19
Median (ppb)	17	20	18	19	18	19
Mode (ppb)	8	18	17	18	17	18
Min (ppb)	1	5	1	5	1	5
Max (ppb)	32	43	32	38	32	38
%RSD	38%		24%		24%	

Table AC-1: Precision parameter results for Cairclip 1 to Cairclip 2 data based on 30 minute averaged concentrations of $O_3 + NO_2$.



Figure AC-1: Precision of Cairclip 1 to Cairclip 2 based on 30 minute averages with all outliers removed.
Linear Regression Results									
Group	Ν	R ²	Slope	Intercept					
1 (screened data)	182	0.15	0.43	13.11					
2 (screened data with visual outliers removed)	166	0.46	0.70	6.81					
3 (screened data with outliers removed beyond m±2SD)	166	0.46	0.70	6.81					

Table AC-2: Linear regression for field precision of Cairclip 1 to Cairclip 2.

Table AC-3: Precision parameter results for Cairclip 1 to Cairclip 3 data based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data with outliers removed beyond m±2SD)	
	CC1	CC3	CC1	CC3	CC1	CC3
Ν	182		167		167	
Mean (ppb)	17	22	18	21	18	21
Median (ppb)	17	21	18	20	18	20
Mode (ppb)	8	11	17	11	17	11
Min (ppb)	1	5	4	6	4	6
Max (ppb)	32	39	32	39	32	39
%RSD		39%	2	2%	22%	



Figure AC-2: Precision of Cairclip 1 to Cairclip 3 based on 30 minute averaged concentrations with outliers removed.

Linear Regression Results									
Group	Ν	\mathbb{R}^2	Slope	Intercept					
1 (screened data)	182	0.17	0.46	13.90					
2 (screened data with visual outliers removed)	167	0.61	0.79	6.45					
3 (screened data with outliers removed beyond m±2SD)	167	0.61	0.79	6.45					

 Table AC-4: Linear regression for field precision of Cairclip 1 to Cairclip 2

Table AC-5: Precision parameter results for Cairclip 1 to 4 data based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC1	CC4	CC1	CC4	CC1	CC4
Ν	1	82	175		172	
Mean (ppb)	17	22	17	22	17	22
Median (ppb)	17	22	17	22	17	22
Mode (ppb)	8	16	8	16	8	16
Min (ppb)	1	7	1	7	1	7
Max (ppb)	32	32	32	40	32	36
%RSD	3	6%	31%		31%	



Figure AC-3: Precision data of Cairclip 1 to 4 based on 30 minute averaged concentrations with outliers removed.

Linear Regression Results									
Group	n	\mathbb{R}^2	Slope	Intercept					
1 (screened data)	182	0.24	0.47	13.73					
2 (screened data with visual outliers removed)	175	0.40	0.61	11.23					
3 (screened data with outliers removed beyond m±2SD)	172	0.43	0.63	11.01					

Table AC-6: Linear regression for field precision of Cairclip 1 to Cairclip 4.

Table AC-7: Precision parameter results for Cairclip 2 to 3 data based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group (all scro data)	Group One (all screened data)O (all v v r		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC2	CC3	CC2	CC3	CC2	CC3	
Ν	1	82	178		171		
Mean (ppb)	21	22	21	21	21	21	
Median (ppb)	20	21	20	21	20	20	
Mode (ppb)	18	11	18	11	18	11	
Min (ppb)	5	5	5	5	5	6	
Max (ppb)	43	39	43	39	43	39	
%RSD	1	6%	1	5%	12%		



Figure AC- 4: Precision of Cairclip 2 to Cairclip 3 based on 30 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	182	0.68	0.81	5.19					
2 (screened data with	178	0.75	0.84	4.20					
visual outliers removed)									
3 (screened data with outliers removed beyond m±2SD)	171	0.80	0.84	3.86					

Table AC-8: Linear regression for field precision of Cairclip 2 to Cairclip 3.

Table AC-9: Precision parameter results for Cairclip 2 to 4 data based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)		
	CC2	CC4	CC2	CC4	CC2	CC4	
Ν	1	82	177		169		
Mean (ppb)	21	22	20	22	20	21	
Median (ppb)	20	22	20	22	19	21	
Mode (ppb)	18	16	18	16	18	16	
Min (ppb)	5	7	5	7	5	7	
Max (ppb)	43	40	43	40	43	35	
%RSD	2	3%	2	20%		17%	



Figure AC-5: Precision of Cairclip 2 to Cairclip 4 based on 30 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	\mathbb{R}^2	Slope	Intercept					
1 (screened data)	182	0.42	0.48	8.28					
2 (screened data with	177	0.57	0.68	8.41					
visual outliers removed)									
3 (screened data with outliers removed beyond m±2SD)	169	0.65	0.66	8.17					

Table AC-10: Linear regression for field precision of Cairclip 2 to Cairclip 4.

Table AC-11: Precision parameter results for Cairclip 3 to 4 data based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC3	CC4	CC3	CC4	CC3	CC4
Ν	182		177		173	
Mean (ppb)	22	22	22	22	21	22
Median (ppb)	21	22	21	22	21	22
Mode (ppb)	11	16	11	16	11	16
Min (ppb)	5	7	6	7	6	7
Max (ppb)	39	40	39	40	39	36
%RSD	1	9%	1	5%	1	4%



Figure AC-6: Precision data of Cairclip 3 to Cairclip 4based on 30 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	182	0.52	0.64	7.94					
2 (screened data with visual outliers removed)	177	0.68	0.75	5.96					
3 (screened data with outliers removed beyond m±2SD)	173	0.73	0.77	5.59					

Table AC-12: Linear regression for field precision of Cairclip 3 to 4 based on 30 minute averaged concentrations of $O_3 + NO_2$.

Precision Results for Paired Cairclips 15 Minute Averaged Concentrations with Outliers Removed

Table AC-13: Precision parameter results for Cairclip 1 to 2 data based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group ((all scre data)	1 eened	Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)		
	CC1	CC2	CC1	CC2	CC1	CC2	
Ν	3	364		43	3.	42	
Mean (ppb)	17	20	18	19	18	19	
Median (ppb)	17	20	12	14	12	14	
Mode (ppb)	17	18	17	18	17	18	
Min (ppb)	0	4	0	4	0	4	
Max (ppb)	35	44	35	44	35	44	
%RSD		37%		25%	2	24%	



Figure AC-7: Precision of Cairclip 1 to Cairclip 2 based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	Ν	\mathbb{R}^2	Slope	Intercept					
1 (screened data)	364	0.21	0.51	11.58					
2 (screened data with visual outliers removed)	343	0.49	0.74	6.33					
3 (screened data with outliers removed beyond m±2SD)	342	0.51	0.75	6.22					

 Table AC-14: Linear regression for field precision of Cairclip 1 to Cairclip 2.

Table AC-15: Precision parameter results for Cairclip 1 to 3 data based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screend visual o remove	Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC1	CC3	CC1	CC3	CC1	CC3	
Ν	3	364	342			338	
Mean (ppb)	17	22	18	21	18	20	
Median (ppb)	17	21	17	20	17	20	
Mode (ppb)	17	21	17	21	17	21	
Min (ppb)	0	3	0	3	0	3	
Max (ppb)	35	40	35	40	35	40	
%RSD		37%		20%		18%	



Figure AC-8: Precision of Cairclip 1 to Cairclip 3 based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	\mathbb{R}^2	Slope	Intercept					
1 (screened data)	364	0.30	0.58	11.54					
2 (screened data with visual outliers removed)	342	0.71	0.87	5.23					
3 (screened data with outliers removed beyond m±2SD)	338	0.77	0.89	4.62					

 Table AC-16: Linear regression for field precision of Cairclip 1 to Cairclip 3.

Table AC-17: Precision parameter results for Cairclip 1 to Cairclip 4 data based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC1	CC1 CC4 (CC4	CC1	CC4
Ν	364		352		342	
Mean (ppb)	17	22	17	22	17	22
Median (ppb)	17	21	17	21	17	21
Mode (ppb)	17	22	17	22	17	22
Min (ppb)	0	0 5		5	0	5
Max (ppb)	35	35 46		41	35	39
%RSD	3	6%	33%		29%	



Figure AC-9: Precision of Cairclip 1 to Cairclip 4 based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results								
Group	n	R ²	Slope	Intercept				
1 (screened data)	364	0.27	0.50	13.06				
2 (screened data with visual outliers removed)	352	0.39	0.61	11.25				
3 (screened data with outliers removed beyond m±2SD)	342	0.48	0.68	9.83				

Table AC-18: Linear regression for field precision of Cairclip 1 to Cairclip 4.

Table AC-19: Precision parameter results for Cairclip 2 to Cairclip 3 data based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened visual out removed)	data liers	Group 3 (screened data outliers removed beyond m±2SD)		
	CC2	CC2 CC3		CC3	CC2	CC3	
Ν	36	54	357		343		
Mean (ppb)	20	22	20	21	20	21	
Median (ppb)	20	21	20	20	20	20	
Mode (ppb)	18	21	18	21	18	21	
Min (ppb)	4	4 3		3	4	3	
Max (ppb)	44 40		44	40	44	40	
%RSD	1	8%	1	17%		14%	



Figure AC-9: Precision of Cairclip 2 to Cairclip 3 based on 30 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results								
Group	n	\mathbb{R}^2	Slope	Intercept				
1 (screened data)	364	0.67	0.80	5.36				
2 (screened data with visual outliers removed)	357	0.71	0.80	5.22				
3 (screened data with outliers removed beyond m±2SD)	343	0.79	0.82	4.33				

Table AC-20: Linear regression for field precision of Cairclip 2 to Cairclip 3.

Table AC-21: Precision parameter results for Cairclip 2 to 4 data based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC2	CC4	CC2	CC4	CC2	CC4
Ν	364		353		343	
Mean (ppb)	20	22	20	22	20	21
Median (ppb)	20	21	19	21	19	21
Mode (ppb)	18	22	18	22	18	22
Min (ppb)	4	5	4	5	4	5
Max (ppb)	44	46	42	46	42	46
%RSD	25	%	2	0%	19%	



Figure AC-9: Precision of Cairclip 2 to Cairclip 4 based on 15 minute averaged concentrations of $O_3 + NO_2$ outliers removed.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	364	0.39	0.55	10.55					
2 (screened data with visual outliers removed)	353	0.58	0.69	8.05					
3 (screened data with outliers removed beyond m±2SD)	343	0.62	0.69	7.74					

Table AC-22: Linear regression for field precision of Cairclip 2 to Cairclip 4.

Table AC-23: Precision parameter results for Cairclip 3 to 4 based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters for Precision Analysis	Group One (all screened data)		Group 2 (screened data visual outliers removed)		Group 3 (screened data outliers removed beyond m±2SD)	
	CC3	CC4	CC3	CC4	CC3	CC4
Ν	3	64	353		341	
Mean (ppb)	22	22	21	22	21	22
Median (ppb)	21	21	20	21	20	21
Mode (ppb)	21	22	21	22	21	22
Min (ppb)	3	5	5	5	5	5
Max (ppb)	40	46	40	46	40	36
%RSD	2	20%	1	6%	14%	



Figure AC-10: Precision of Cairclip 3 to Cairclip 4 based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	364	0.51	0.64	7.79					
2 (screened data with visual outliers removed)	353	0.67	0.76	5.56					
3 (screened data with outliers removed beyond m±2SD)	341	0.74	0.77	5.38					

Table AC-24: Linear regression for field precision of Cairclip 3 to 4.

APPENDIX D: ACCURACY RESULTS FOR 30 AND 15 MINUTE AVERAGE CONCENTRATIONS OF O₃ + NO₂

Accuracy Results 30 Minute Averaged Concentrations

Parameters		Group							
for accuracy	One		Two		Three	Three			
analysis	(screened data)		(screened of	lata	(screened of	lata with			
			with visual	loutliers	outliers rer	noved			
			removed)		beyond m±2SD)				
	CC 1	SM	CC 1	SM	CC 1	SM			
Ν	13	82	159		151				
Mean (ppb)	17	32	18	32	18	31			
Median (ppb)	17	34	18	33	18	33			
Mode (ppb)	8	36	17	36	18	36			
Minimum (ppb)	1	13	4	13	4	14			
Maximum (ppb)	32	54	32	50	32	50			
Mean Abs % Diff	43	8%	45	5%	45	5%			

Table AD-1. Accuracy parameter results Cairclip 1 to station monitor based on 30 minute averaged concentrations of $O_3 + NO_2$.



Figure AD-1. Accuracy of Cairclip 1 to station monitor based on 30 minute averages of $O_3 + NO_2$ with outliers removed.

Linear Regression Results								
Group	n	R ²	Slope	Intercept				
1 (screened data)	182	0.31	0.48	1.44				
2 (screened data with	159	0.62	0.66	-2.95				
visual outliers removed)								
3 (screened data with	151	0.72	0.74	-5.35				
outliers removed beyond								
m m±2SD)								

Table AD-2. Linear regression results for field accuracy of Cairclip 1 to station monitor.

Table AD-3. Accuracy parameter results for Cairclip 2 to station monitor based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters		Group							
for accuracy	One		Two		Three				
analysis	(screene	ed data)	(screened	l data with	(screened	data with			
	visual outliers		visual outliers outliers removed		moved				
		removed)		beyond $m \pm 2SD$)					
	CC 2	SM	CC 2	SM	CC 2	SM			
Ν	182		159		151				
Mean (ppb)	21	33	21	32	20	31			
Median (ppb)	20	34	19	33.5	19	33			
Mode (ppb)	18	36	18	36	18	36			
Minimum (ppb)	5	13	5	13	5	13			
Maximum (ppb)	43	54	43	54	38	50			
Mean Abs % Diff	3	8%	3	36%		36%			



Figure AD-2. Accuracy of Cairclip 2 to station monitor based on 30 minute averages of $O_3 + NO_2$ with outliers removed.

Linear Regression Results								
Group	Ν	R ²	Slope	Intercept				
1 (screened data)	182	0.42	0.62	0.28				
2 (screened data with visual outliers removed)	162	0.57	0.75	-2.79				
3 (screened data with outliers removed beyond m±2SD)	155	0.64	0.78	-3.93				

Table AD-4. Linear regression results for Cairclip 2 to station monitor.

Table AD-5. Accuracy parameter results for Cairclip 3 to station monitor based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters	Group							
for accuracy	One		Two		Three			
analysis	(screened data)		(screened	data with	(screened	data with		
		visual outliers		visual outliers outliers removed		moved		
			removed)		beyond m±2SD)			
	CC3	SM	CC3	SM	CC3	SM		
Ν	182		170		169			
Mean (ppb)	22	33	22	33	22	33		
Median (ppb)	21	34	21	34	21	33		
Mode (ppb)	11	36	11	36	11	36		
Minimum (ppb)	39	54	39	50	39	50		
Maximum (ppb)	5	13	6	13	6	13		
Mean Abs % Diff	3	4%	3	35%		33%		



Figure AD-3. Accuracy of Cairclip 3 to station monitor based on 30 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	\mathbb{R}^2	Slope	Intercept					
1 (screened data)	182	0.52	0.68	-0.33					
2 (screened data with	170	0.65	0.78	-0.65					
visual outliers removed)									
3 (screened data with	169	0.74	0.81	-4.19					
outliers removed beyond									
m±2SD)									

Table AD-6: Linear regression results of Cairclip 3 to station monitor.

Table AD-7. Accuracy parameter results of Cairclip 4 to station monitor based on 30 minute averaged concentrations of $O_3 + NO_2$.

Parameters	Group						
for accuracy	One		Two		Three		
analysis	(screened data)		(screened data with visual outliers removed)		(screened data with outliers removed beyond m±2SD)		
	CC4	SM	CC4	SM	CC4	SM	
Ν	182		170		168		
Mean (ppb)	22	33	22	33	22	33	
Median (ppb)	22	34	22	33	22	33	
Mode (ppb)	16	36	16	36	16	36	
Minimum (ppb)	7	13	7	13	7	13	
Maximum (ppb)	40	54	40	54	40	54	
Mean Abs % Diff	3	2%	3	35%		35%	



Figure AD-4. Accuracy of Cairclip 4 to station monitor based on 30 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results									
Group	n	R ²	Slope	Intercept					
1 (screened data)	182	0.31	0.46	6.72					
2 (screened data with	170	0.50	0.63	1.99					
visual outliers removed)									
3 (screened data with	168	0.52	0.62	2.14					
outliers removed beyond									
m±2SD)									

Table AD-9. Linear regression results of Cairclip 4 to station monitor.

Accuracy Results for 15 Minute Averaged Concentrations

Table AD-10. Accuracy parameter results of Cairclip 1 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters	Group							
for accuracy	One		Two		Three			
analysis	(screened data) (v r		(screened data with visual outliers removed)		(screened data with outliers removed beyond m±2SD)			
	CC1	SM	CC1	SM	CC1	SM		
Ν	36	54	320		318			
Median (ppb)	17.0	32	18.2	31	18	31		
Median (ppb)	17	34	18	23	18	33		
Mode (ppb)	17	35	17	35	17	35		
Minimum (ppb)	0	13	1	13	1	13		
Maximum (ppb)	35	54	35	51	35	51		
Mean Abs % Diff	48	8%	4.	3%	4.	3%		



Figure AD-5. Precision of Cairclip 1 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results							
Group	n	R ²	Slope	Intercept			
1 (screened data)	364	0.34	0.51	0.45			
2 (screened data with visual outliers removed)	320	0.70	0.70	-3.88			
3 (screened data with outliers removed beyond m±2SD)	318	0.70	0.70	-3.85			

 Table AD-11. Linear regression results for Cairclip 1 to station monitor.

Table AD-12. Accuracy parameter results of Cairclip 2 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters	Group							
for accuracy	One		Two		Three			
analysis	(screened	(screened data)		ata with	(screened	l data with		
			visual outliers		outliers r	emoved		
			removed)		beyond m±2SD)			
	CC2	SM	CC2	SM	CC2	SM		
Ν	364		324		315			
Median (ppb)	20	32	21	31	20	31		
Median (ppb)	20	34	20	33	20	33		
Mode (ppb)	18	35	18	35	18	35		
Minimum (ppb)	4	13	4	13	4	13		
Maximum (ppb)	44	54	44	51	42	51		
Mean Abs % Diff	3	8%	3	6%	36	5%		



Figure AD-6. Accuracy of Cairclip 2 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Linear Regression Results								
Group	n	R ²	Slope	Intercept				
1 (screened data)	364	0.40	0.61	0.45				
2 (screened data with	324	0.59	0.77	-3.64				
visual outliers removed)								
3 (screened data with outliers removed beyond	315	0.61	0.76	-3.52				
m±2SD)								

Table AD-13.	Linear regression	results of C	Cairclip 2 to	station mon	itor.
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Table AD-14. Accuracy parameter results of Cairclip 3 to station monitor based
on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters	Group						
for accuracy	One		Two		Three		
analysis	(screened data)		(screened data with visual outliers removed)		(screened data with outliers removed beyond m±2SD)		
	CC3	SM	CC3	SM	CC3	SM	
n	364		356		345		
Median (ppb)	22	32	22	32	22	32	
Median (ppb)	21	34	21	34	21	33	
Mode (ppb)	21	35	21	35	21	35	
Minimum (ppb)	3	13	5	13	5	13	
Maximum (ppb)	40	54	40	51	40	51	
Mean Abs % Diff	34%		34%		34%		



Figure AD-7. Accuracy of Cairclip 3 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Table AD-15. Linear regression results for Cairclip 3 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$.

Linear Regression Results						
Group	n	R ²	Slope	Intercept		
1 (screened data)	364	0.50	0.67	0.70		
2 (screened data with	356	0.63	0.77	-3.15		
visual outliers removed)						
3 (screened data with	345	0.70	0.81	-4.05		
outliers removed beyond						
m±2SD)						

Table AD-16. Accuracy parameter results for Cairclip 4 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$.

Parameters	Group					
for accuracy	One		Two		Three	
analysis	(screened data)		(screened data with		(screened data with	
			visual outliers		outliers removed	
			removed)		beyond m±2SD)	
	CC4	SM	CC4 SM		CC4	SM
Ν	364		340		336	
Mean (ppb)	22	32	22	32	22	32
Median (ppb)	21	34	21	33	21	33
Mode (ppb)	22	35	22	35	22	35
Minimum (ppb)	5	13	5	13	5	13
Maximum (ppb)	46	54	41	51	36	51
Mean Abs % Diff	33%		35%		33%	



NAPS Station Monitor Measurements of $O_3 + NO_2$ ppb

Figure AD-8. Accuracy of Cairclip 4 to station monitor based on 15 minute averaged concentrations of $O_3 + NO_2$ with outliers removed.

Table AD-16.	Linear	regression	results	for field	accuracy	of Cairclip	4 to station
monitor.							

Linear Regression Results						
Group	n	\mathbb{R}^2	Slope	Intercept		
1 (screened data)	364	0.29	0.46	6.77		
2 (screened data with	340	0.48	0.62	2.15		
visual outliers removed)						
3 (screened data with outliers removed beyond	336	0.51	0.63	1.85		
m±2SD)						

APPENDIX E: MONITORING AT BUSY INTERSECTIONS

Pedestrian Monitoring at Jasper and 109th Street



Oct. 5, 2013 Monitoring Time-One Minute Continuous

Figure AE-1. Graph of concentrations of $O_3 + NO_2$ measured outdoors at Jasper Ave. and 109th St. on Oct. 5, 2013 with Cairclip 1 in relation to ESSM and ECSM.



Figure AE-2. Graph of concentrations of $O_3 + NO_2$ measured outdoors at Jasper Ave. and 109th St. on Oct. 11, 2013 with Cairclip 1 in relation to ESSM and ECSM.



Figure AE-3. Graph of concentrations of $O_3 + NO_2$ measured outdoors at Jasper Ave. and 109th St. on Jan 9, 2014 at 9:30 to 9:46 am with Cairclip 4 in relation to ESSM and ECSM.



Jan. 9, 2014 Monitoring Time-One Minute Continuous Figure AE-4. Graph of concentrations of $O_3 + NO_2$ measured outdoors at Jasper Ave. and 109th St. on Jan 9, 2014 10:00 to 10:14 am with Cairclip 4 in relation to ESSM and ECSM

Pedestrian Monitoring at 97th Avenue and 109th Street



Figure AE-5. Graph of concentrations of $O_3 + NO_2$ measured outdoors at 97th Ave. and 109th St. on Oct. 17, 2013 from 9:30 to 9:44am with Cairclip 1in relation to ESSM and ECSM.

Pedestrian Monitoring at Whyte Ave. and 109th Street



Figure AE-6. Graph of concentrations of O_3 + NO₂ measured outdoors at Whyte Ave. and 109th St. on Sept. 13, 2013 from 14:30 to14:59 pm with Cairclip 1 in relation to ESSM and ECSM.



Figure AE-7. Graph of concentrations of O_3 + NO₂ measured outdoors at Whyte Ave. and 109th St. on Sept. 30, 2013 from 14:30 to14:59 pm with Cairclip 1 in relation to ESSM and ECSM.



Figure AE-8. Graph of concentrations of O_3 + NO₂ measured outdoors at Whyte Ave. and 109th St. on Oct. 5, 2013 from 13:30 to 13:59 pm with Cairclip 1 in relation to ESSM and ECSM.



Figure AE-9. Graph of concentrations of O_3 + NO₂ measured outdoors at Whyte Ave. and 109th St. on Oct. 22, 2013 from 9:00 to 9:29 pm with Cairclip 4 in relation to ESSM and ECSM.



Dec. 23, 2013 Monitoring Time-One Minute Continuous

Figure AE-10. Graph of concentrations of $O_3 + NO_2$ measured outdoors at Whyte Ave. and 109th St. on Dec. 23, 2013 from 17:00 to 17:29 pm with Cairclip 4 in relation to ESSM and ECSM.

APPENDIX F: INDOOR MONITORING AT HIGH VOLUME TRAFFIC AREAS



Indoor Monitoring at 109th Street and 88th Avenue

Nov. 28, 2013 Monitoring Time-One Minute Continuous

Figure AF-1. Graph of concentrations of $O_3 + NO_2$ measured indoors at 109th St. and 88th Ave. on Nov. 28, 2013 from 12:30 to 13:29 pm with Cairclip 4 in relation to ESSM and ECSM.



Nov. 30, 2013 Monitoring Time-One Minute Continuous

Figure AF-2. Graph of concentrations of $O_3 + NO_2$ measured indoors at 109th St. and 88th Ave. on Nov. 30, 2013 from 8:00 to 8:59 am with Cairclip 4 in relation to ESSM and ECSM.



Figure AF-3. Graph of concentrations of $O_3 + NO_2$ measured indoors at 109th St. and 88th Ave. on Nov. 30, 2013 from 9:00 to 9:59 am with Cairclip 4 in relation to ESSM and ECSM.

Indoor Monitoring at 99th St. and 89th Avenue



Dec. 11, 2013 Monitoring Time-One Minute Continuous

Figure AF-4. Graph of concentrations of $O_3 + NO_2$ measured indoors at 99th St. and 89th Ave. on Dec. 11, 2013 from 8:00 to 9:59 am with Cairclip 4 in relation to ESSM and ECSM.

Indoor Monitoring at 104th Street and Whyte Avenue



Figure AF-5. Graph of concentrations of $O_3 + NO_2$ measured indoors at 104th St. and Whyte Ave. on Jan. 9, 2014 from 7:30 to 7:59 am with Cairclip 4 in relation to ESSM and ECSM.



Jan. 10, 2014 Monitoring Time-One Minute Continuous

Figure AF-6. Graph of concentrations of $O_3 + NO_2$ measured indoors at 104th St. and Whyte Ave. on Jan.10, 2013 from 18:00 to 18:29 pm with Cairclip 4 in relation to ESSM and ECSM.