ASSESSMENT OF SOURCES OF UNCERTAINTY IN PASSIVE SAMPLERS OF AMBIENT AIR QUALITY: EVALUATION LAKELAND INDUSTRY AND COMMUNITY ASSOCIATION AIRSHED 2009 – 2011

By

Gregory John Pippus

A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In

ENVIRONMENT AND MANAGEMENT

We accept this thesis as conforming to the required standard

Allan H. Legge, PhD., F.A.A.A.S. Thesis Supervisor
Biosphere Solutions

MEM Program Reviewer
School of Environment and Sustainability

Michael-Anne Noble, Director
School of Environment and Sustainability

ROYAL ROADS UNIVERSITY

February 2012

ABSTRACT

Passive samplers are subject to a myriad of sources of uncertainty, which affect their precision and accuracy. To investigate this uncertainty, an evaluation of passive sampler data for SO_2, NO_2, O_3, and H_2S was carried out in the Lakeland Industry & Community Association in east-central Alberta from 2009 – 2011. The results of this study indicate that while passive sampler data followed the same general trend as continuous monitoring data, passive sampler data were often statistically different which strongly indicates they were not always accurate. Passive samplers are further limited by only providing a time weighted average of pollutant concentrations over the sampling period, which prevents determination of when or where a pollutant has exceeded regulatory limits. While passive samplers are useful in monitoring general changes in ambient air quality at low concentrations, this work strongly suggests that passive sampler data should not be used for regulatory monitoring.

ACKNOWLEDGEMENTS

It is with great humility that I thank the many people who helped me with this work. Their assistance has meant the world to me and without that help this would not have been possible.

I have never had the pleasure of working with so gifted a mind as Dr. Allan Legge. Your contributions to the field of Air Quality are the things of myth and legend, and I find you today as much as the day we first met, an inspiration. It was an honor and a privilege to get to know you and work with you.

For giving your time selflessly and providing me with significant direction when I found myself out of my realm I thank Dr. Melissa Day. The technical assistance you provided me is greatly appreciated.

I have no words to express my thanks to Tara Dunphy for all of her help. As a cohort and peer your timely advice and tremendous assistance were invaluable. Your friendship and guidance helped significantly with this work. We arrived as classmates and depart as friends.

Finally, I would like to dedicate this work to my wife Sandra and daughter Robin Pippus. The support and understanding that I received from both of you is beyond comprehension. The long hours and weeks away were difficult, but knowing that I had your support at home lightened the load considerably. I both appreciate and respect the sacrifices you both made to see me through this and love you both endlessly.

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LIST OF ACRONYMS

AAAQO – Alberta Ambient Air Quality Objective

AENV – Alberta Environment

AEW – Alberta Environment and Water

CASA – Clean Air Strategic Alliance

EC – Environment Canada

EPA – United States Environmental Protection Agency

H_2S – Hydrogen Sulphide

LICA – Lakeland Community and Industry Association

NO_2 – Nitrogen Dioxide

O_3 – Ozone

PAH - Polycyclic Aromatic Hydrocarbons

PAI – Potential Acid Input

PM - Particulate Matter

ppb – parts per billion

QAP - Quality Assurance Plan

SO_2 – Sulphur Dioxide

THC - Total Hydrocarbons

TWA – Time Weighted Average

VOC - Volatile Organic Compounds

INTRODUCTION

Catalyst for this study

The Lakeland Industry and Community Association (LICA) is currently one of the nine airsheds in Alberta which were established by the Clean Air Strategic Alliance (CASA) for the purpose of implementing a regional approach to monitoring ambient air quality in Alberta. Located in east-central Alberta, LICA is a not-for-profit society comprised of stakeholders such as, area residents, representatives from industry, non-governmental organizations and government personnel whose main goal is a healthy and sustainable environment (Lakeland Industry and Community Association, 2009; Jacques Whitford, 2006). LICA was created in 2000 and is now in its 12th year of operation.

The LICA Airshed Zone (airshed) is approximately 17,995 square kilometres is illustrated in Figure 1. Its eastern border is the Alberta / Saskatchewan border and Township 55, Range 12, W4M to the west. The northern boundary is the Cold Lake Air Weapons range and Highway 45 to the south (Lakeland Industry and Community Association, 2009). The LICA area is comprised of three distinct ecological zones: Aspen Parkland in the south, Boreal Transition Ecoregion in the centre, and Mid-Boreal Uplands in the north (Strong & Leggat, 1981).

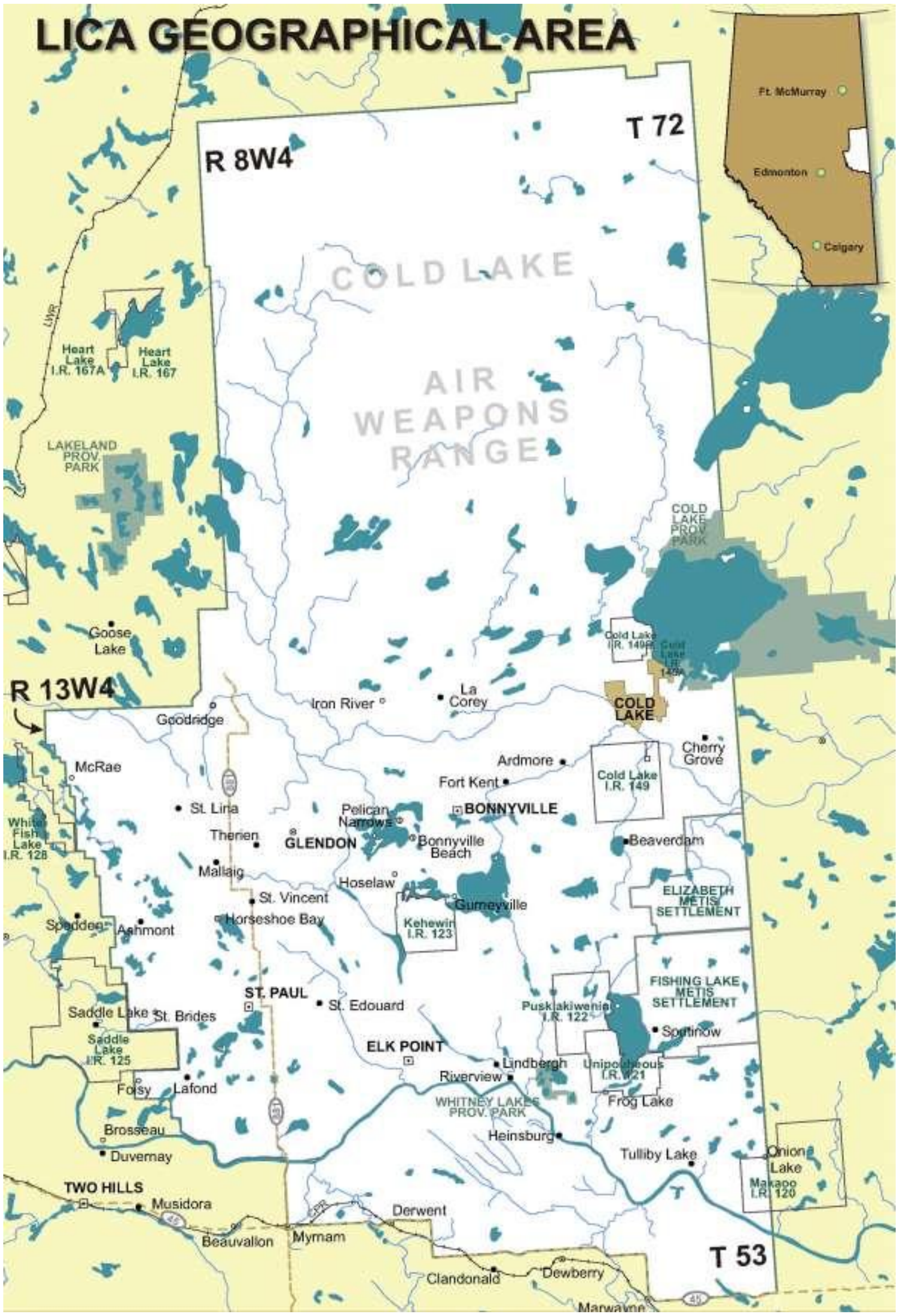

Figure 1. Map showing the boundary and areal extent of the Lakeland Industry and Community Association Airshed. The upper left hand area of figure shows the LICA airshed in relationship to the province of Alberta. From Lakeland Industry and Community Association (2009). Reprinted with permission.

The LICA passive sampling program was initially carried out to satisfy a request made by Alberta Environment to explore the accuracy and precision of the passive sampling for sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), and hydrogen sulphide (H_2S) taking place in the LICA airshed (Alberta Environment, 2009). A report from the consulting firm RWDI in 2008 during an audit of LICA's Quality Assurance Plan, also recommended that investigation of the discrepancies between continuous and passive data should take place in order to substantiate the objectives of LICA's ambient air quality monitoring program (RWDI, 2008).

This has lead to the concern that, if the results of passive sampling are not accurate or inconsistent, they may not be appropriate for making future airshed management plans. A better understanding of the data provided by passive air samplers is necessary to ensure that future sustainable development planning efforts makes use of the best available information.

Research objectives

The overarching purpose of this work is to explore if the data generated from passive samplers in the LICA airshed accurately reflect ambient air quality for selected air quality parameters and to gain a better understanding of how to interpret the data from passive samplers. Further, this work is intended to critically evaluate if the use of passive samplers in a regulatory context has merit. This is accomplished by the exploration of the following five main research questions:

1. Are there observable trends such as seasonality in the passive sampling program data?
2. What is the level of precision and accuracy in the duplicate passive samples?
3. What is the relationship between data from the passive samplers and data from collocated continuous monitors?

4. What are the potential sources of uncertainty associated with passive sampling?
5. Does the current use of passive samplers accurately predict potential cumulative impacts?

The passive sampling data are examined for evidence of trends. Examples of this would be where data supports evidence of trends such as seasonality, which has been previously demonstrated in pollutants such as ozone (Logan, 1985; Hsu et al., 2010). This would be consistent with findings from several other sources (Hsu et al., 2010; WBK & Associates, 2008; Legge & Krupa, 1990) where O_3 trends demonstrated higher values during the March through May period and lower reported values in the July to October period. If seasonality is influencing reported values, this should be taken into consideration when evaluating trends in pollutant concentration on a month-to-month basis. This natural variation is not caused from anthropogenic sources and as a result would need to be considered prior to enforcing any compliance penalties based upon regulatory exceedances. Seasonality will also affect assumptions around normal distribution of the data and therefore influence what statistical methods are appropriate for analyzing the data from this and similar studies.

Exploring the discrepancies observed in LICA's passive sampling data and determining if these discrepancies are cause for concern statistically will influence both the confidence of managers evaluating these data as well as determine what the reasonable expectation is for the end use of the data from a regulatory perspective. If passive samplers are shown to be imprecise or inaccurate it brings into question the validity of passive sampler use in certain applications such as regulatory compliance.

The performance of passive samplers is further characterized by comparing how the passive sampler data relates to continuous monitoring data concerning accuracy. Establishing this correlation will lead to a better understanding of how the time weighted average (TWA) measurement from the passive samplers compares to the data displayed by averaging monthly totals from continuous monitors. This is important because previous variation in this data set has lead to a lack of confidence in the results from passive samplers. By determining if the difference in reported values is of concern this will help assess LICA's current monitoring strategy. Further, this will help to validate the use of passive samplers for both cumulative impact assessment as well as regulatory compliance.

A list of potential sources of uncertainty within passive sampling will be generated in this thesis. This aligns with the overarching goal of the study to gain a better understanding of how to critically evaluate passive sampler data provided in the LICA network as well as make better-informed decisions based on a more full understanding of what the data exhibits (Bisaga, 2010). This thesis will create an approach that environmental managers can utilize when critically evaluating results from their passive ambient air monitoring programs.

The final goal of this work is to explore what role the passive samplers may have in the assessment of cumulative impacts. Passive sampler data may not accurately reflect the potential for cumulative impacts because of the inconsistency displayed in the passive sampler results when compared to the more highly resolved continuous data. The result of this inconsistency could mean that cumulative impacts are not being accurately estimated and LICA's cumulative impact management strategies require re-evaluation.

Passive Technology

The transfer of gaseous pollutants across the diffusion barrier in passive samplers is based on Fick’s first law of diffusion shown in:

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Figure 2. Fick’s Law, where J = the diffusion rate, D = the diffusion coefficient, A = the effective cross sectional area, x = the distance along the diffusion path, and c = the analyte concentration at distance X. The negative sign indicates that the concentration of the analyte decreases in the direction of diffusion

The passive samplers in use by LICA (as endorsed by Alberta Environment) were developed by Maxxam Analytics in the late 1990’s and are called the Passive Air Sampling System (PASS) and illustrated in Figure 3 (Tang, et al., 1997; Tang, et al., 1999; Tang & Lau, 2000; Tang, et al, 2002a; Tang, et al., 2002b). These passive samplers work by controlling the exposure of pollutants to a sampling media by the application of a diffusion barrier between the absorption media and the external environment (Tang, et al., 1997; Tang, et al., 1999; Tang & Lau, 2000; Tang, et al, 2002a; Tang, et al., 2002b). The passive samplers are deployed in a downward facing direction to avoid complications created by deposition of particulates and wetfall onto the diffusion membrane which eventually will affect diffusion barrier pore size and therefore sampling rate (Tang, et al., 1997).

The detection limit of a passive sampler is a function of the sampling rate, sampling exposure time, blank values of unexposed samplers, the sensitivity of the reactive material, reproducibility of analytical result, and the sensitivity of the column used in final analysis of the passive samplers (Namiesnik, et al., 2005). Each of these variables has their own variable components leading to a very complex inferential method in calculating concentration. This contrasts to the continuous monitor's direct measurements and finite detection limits based on instrument calibration to known standards (Huckins et al., 2006; Vallero, 2007).

Current Alberta Ambient Air Quality Objectives

In Alberta, passive samplers have been in regulatory use since only February 2011 (Alberta Environment, 2010c). Currently in Alberta, SO_2 is the only pollutant to have a passive ambient air quality objective. The reason for this delay may be a result of the uncertainty with regards to precision and accuracy and their lack of ability to be calibrated in the field (Mills, et al, 2009). Even some of the manufacturers of passive samplers have recommended against the use of passive samplers for regulatory compliance purposes unless stringent validation can be met (SKC, 2011). It has been suggested that for passive samplers to gain more acceptance in the regulatory field, better quality assurance / quality control programs and method validations will be required to gain regulatory acceptance (Zabiegala, et al., 2010).

Alberta Environment states that the purposes of Ambient Air Monitoring is to, assess the quality of the air, assess trends, determine compliance within guidelines and standards, perform modeling for approval applications and review analysis, and fulfill other environmental management functions (Alberta Environment, 2006). Since ambient air quality models rely heavily on data input from ambient air quality monitoring programs, the analytical method for determining actual ambient concentrations of air pollutants has a great bearing on model validation (Huckins, et al., 2006).

Several documents regulate Ambient Air Quality in Alberta, notably the Alberta Air Monitoring Directive 1989 (Alberta Environment, 1989), the Alberta Environmental Enhancement and Protection Act (Alberta Environment, 2010a), and The Alberta Ambient Air Quality Objectives

(Alberta Environment, 2010c). These three central documents form the basis for the majority of the compliance legislation in Alberta regarding the governance of ambient air quality.

In February 2011, Alberta Environment brought into force a new passive monitoring air quality objective for sulphur dioxide with a 30-day concentration limit of 11 ppb (Alberta Environment, 2010b). There has been a great deal of discussion about the performance of the passive samplers within the Alberta air quality monitoring community and if they are sufficiently precise and/or accurate for use as a regulatory tool (Legge, 2011; Bisaga, 2010; RWDI, 2008).

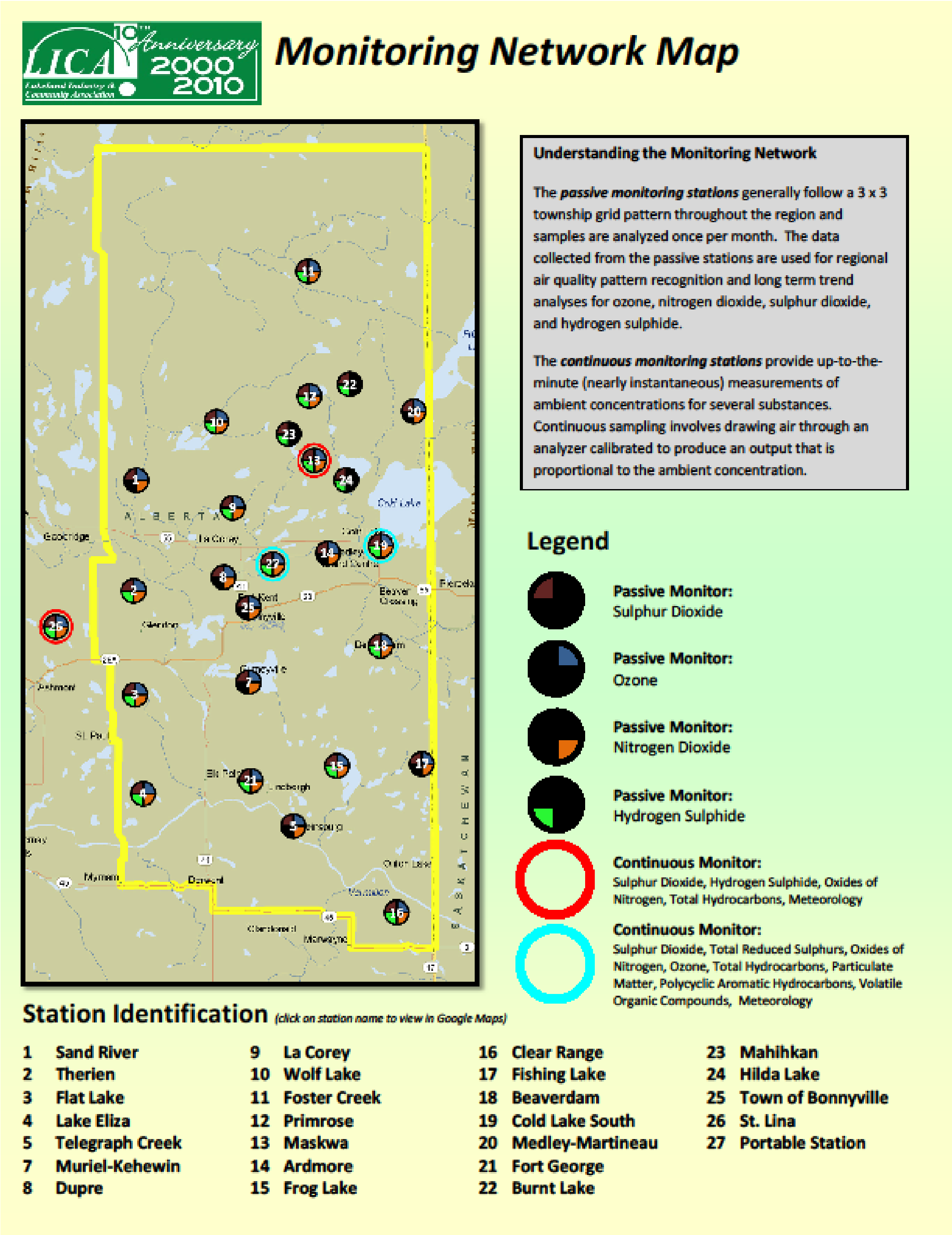
The exact role and purpose of this objective has also been hotly debated. Alberta Environments' (2010b) statement in their *Comments and Responses to Proposed* SO_2 *Ambient Air Quality Objectives* document states, "the 30-day objective is required as it provides a point of reference for assessment of passive monitoring that is being conducted across the province. Alberta Environment endorses the use of passives as a low cost monitoring alternative to continuous monitoring in areas of overall low ambient concentration". They further state that, "this addresses Alberta's need for an objective for passive monitoring which is a low cost technology and is in wide use across the province." The purpose of this objective is not clearly defined and it is unclear if Alberta Environment is attempting to address chronic or acute exposures, establish baseline data, or determine sources of non-compliance. It is therefore difficult to gauge how successful passive samplers are for meeting the intent of this objective. Furthermore, it makes it difficult to judge if passive samplers are indeed an appropriate analytical tool for the purpose of the objective.

BACKGROUND

Air Quality Monitoring in the LICA Airshed

Currently there are two continuous compliance monitoring stations measuring ambient air quality; Cold Lake South and one mobile monitoring station, where meteorological data, sulphur dioxide (SO_2), total reduced sulphur (TRS), hydrogen sulphide (H_2S), ozone, nitrogen dioxide (NO_2), total hydrocarbons (THC), particulate matter (PM), polycyclic aromatic hydrocarbons (PAH), and volatile organic compounds (VOC) are measured in the airshed. Two additional continuous monitoring stations, Maskwa and St. Lina, are more limited and monitor meteorological data, SO_2, H_2S, $NO_{2,}$ and THC. The data these four continuous monitoring stations generate are continually updated and provide real time results regarding the air quality of the area. The locations of these four continuous monitoring stations are shown in Figure 5.

LICA has also deployed 27 passive monitoring sites in addition to the four continuous air monitoring stations in the airshed since 2003 and are shown in Figure 3 (Jacques Whitford, 2006). Where permitted by geography and logistics, the stations mostly follow a 29-kilometer grid (3 townships) within the airshed. The chemical constituents monitored at the 27 passive sampling sites are SO_2, H_2S, NO_2, and O_3. The passive samples are commonly collected on a monthly basis and sent to a laboratory for analysis. The passive samplers are used to determine monthly average ambient air concentrations of each chemical to determine average monthly long-term trends and assess potential exposure risks to both ecological and human receptors.



Monitoring Network Map

Understanding the Monitoring Network

The ***passive monitoring stations*** generally follow a 3 x 3 township grid pattern throughout the region and samples are analyzed once per month. The data collected from the passive stations are used for regional air quality pattern recognition and long term trend analyses for ozone, nitrogen dioxide, sulphur dioxide, and hydrogen sulphide.

The ***continuous monitoring stations*** provide up-to-the-minute (nearly instantaneous) measurements of ambient concentrations for several substances. Continuous sampling involves drawing air through an analyzer calibrated to produce an output that is proportional to the ambient concentration.

Legend

● **Passive Monitor:** Sulphur Dioxide

● **Passive Monitor:** Ozone

● **Passive Monitor:** Nitrogen Dioxide

● **Passive Monitor:** Hydrogen Sulphide

○ **Continuous Monitor:** Sulphur Dioxide, Hydrogen Sulphide, Oxides of Nitrogen, Total Hydrocarbons, Meteorology

○ **Continuous Monitor:** Sulphur Dioxide, Total Reduced Sulphurs, Oxides of Nitrogen, Ozone, Total Hydrocarbons, Particulate Matter, Polycyclic Aromatic Hydrocarbons, Volatile Organic Compounds, Meteorology

Station Identification *(click on station name to view in Google Maps)*

1	Sand River	9	La Corey	16	Clear Range	23	Mahihkan
2	Therien	10	Wolf Lake	17	Fishing Lake	24	Hilda Lake
3	Flat Lake	11	Foster Creek	18	Beaverdam	25	Town of Bonnyville
4	Lake Eliza	12	Primrose	19	Cold Lake South	26	St. Lina
5	Telegraph Creek	13	Maskwa	20	Medley-Martineau	27	Portable Station
7	Muriel-Kehewin	14	Ardmore	21	Fort George		
8	Dupre	15	Frog Lake	22	Burnt Lake		

Figure 3. Lakeland Industry and Community Association Airshed Monitoring Network Map. Location names are found at the bottom of the figure and the legend on the right hand side indicates what air monitoring takes place at each location. From Lakeland Industry and Community Association (2010). Reprinted with permission.

As part of the LICA Airshed's Quality Assurance Plan (QAP), duplicate passive samples were required to be taken at 10% of sites on a monthly basis (RWDI, 2008). This was done to evaluate sampling procedures and analytical precision (Lakeland Industry and Community Association, 2009). However, even with the duplicate sampling taking place discrepancies have been found between the passive sampling data when compared with continuous monitors in the airshed (RWDI, 2008).

The Evolution of Passive Sampling

Passive sampling is not a new concept and historical examples of the use of passive sampling date back to 1853 when "test papers" impregnated with potassium iodide were utilized to measure ground level ozone (Namiesnik, et al., 2005). The first uses of passive samplers in Alberta dates back to the early 20th century (Bertram, 1988). Passive samplers in their current iteration however are a relatively recent development. Passive sampling has taken numerous different forms and been applied to several monitoring applications including ambient air, worker exposure, indoor air quality, water analysis, soil analysis (Zabiegala, et al., 2010).

The predecessor to today's passive sampling technology were methods such as Palmes tubes, sulphation candles, diffusion denuders, Huey plates and even dustfall buckets (cylinders) for particulate matter which were used in Alberta for the monitoring of ambient air quality for more than 75 years (Tang, et al., 1997; Bertram, 1998). Each of these samplers operated on much the same principal as modern passive samplers where ambient exposure of environmental pollutants would react with an absorbent media, which could be taken back to the laboratory and analyzed either by optical method or by extraction (Bertram, 1988). Earlier samplers also shared many of the same advantages of today's passive samplers and were used successfully to track changes over time in ambient air quality (Fenn et al., 2009). A major focus of many of today's manufactures of passive samplers is striving to reduce detection limits and increase precision and accuracy while maintaining the inexpensive nature of these samplers (Seethapathy, 2011).

A major improvement in passive sampling came with the utilization of diffusion or permeation techniques which made for a much more accurate determination of sampling rate (Bertram, 1988). The use of diffusion barriers also helps to abate some of the effects of wind velocity which is known to have a significant impact on sampling rate and therefore accuracy of passive results (Tang, et al., 1997; Tang, et al., 1999; Tang & Lau, 2000; Tang, et al, 2002a; Tang, et al., 2002b).

Passive samplers have many advantages over continuous monitors, the biggest of which is simplicity of deployment. Passives do not require power to facilitate sampling and are ideally suited for remote applications where power is not available. Yamada et al., (1999) used passive samplers to evaluate air pollutants in mountain forests where the samplers could be left in place for long enough periods to guarantee detection (based on low concentration exposure) with relatively low impact to the surrounding environment, low cost, and a high enough sample size to provide sufficient information about the study area. LICA's consultant AMEC's (2009) report regarding Potential Acid Input (PAI) in the region also indicated that passive samplers had the potential to help determine cumulative impacts within the region based on PAI because of their simplicity and portability.

Passive samplers cost significantly less than most other sampling systems and a network of several passive samplers can be deployed for the cost of a single continuous instrument. Passive samplers have been found to be useful for evaluating the air quality of large areas (Gerboles, et al., 2006). Another advantage passive samplers have is that the data they produce are essentially a time weighted average (TWA). This approach to monitoring is especially useful in the evaluation and management of cumulative impacts (Salem, et al; 2009) for the exploration of general changes is air quality of a large areas made up of typically low variability and low concentrations of pollutants. This is a direct contrast to regulatory compliance sampling which requires high resolution to monitor short-term exceedances in highly variable concentrations of pollutants in the ambient air (Legge, 2011; Nash & Leith, 2010).

METHODOLOGY

LICA leadership designed the sampling program that produced the data for this work. Passive samplers were collocated with continuous monitors at four sites in the sampling program. Even though there were fewer collocated sampling sites than duplicate passive sampling sites the conclusions drawn from the four collocated sites can still be applied to the passive sampling in general because the duplicate passive sampling data was very consistent.

Alberta Environment directed LICA to undertake a 50% duplicate sampling program for a period of two years (Alberta Environment, 2009). LICA leadership made the decision that the sampling program would be comprised of sampling half of the 27 passive sampling stations in duplicate in alternating months creating a 50% duplicate sampling regime involving 100% of the sample sites (Bisaga, 2010). Following this design, 50% of the sites would have duplicate sampling carried out one month while the remaining 50% of sites would be subsequently sampled in duplicate the following month (Bisaga, 2010). Although this program does not draw data from a random pool, it does eliminate potential spatial bias by sampling taking place at all of the available monitoring stations. This allowed the sampling program to utilize all monitoring stations within the LICA geographic area.

The parameters evaluated in the passive sampling program were SO_2, H_2S, NO_2, and O_3. Maxxam Analytics (Maxxam) provides LICA with the service of deployment and collection of the passive samplers throughout the LICA airshed on approximately monthly basis and final analysis was completed at Maxxam's facility in Edmonton, Alberta, Canada.

Statistical Evaluation

Passive samplers were exposed between 27 and 35 days so continuous data were tabulated so that hourly averages were compiled for a monthly mean which could be directly compared to the monthly TWA of the passive samplers during the same exposure period. Any continuous data sets that were missing greater than 24 hours were excluded from further statistical analysis.

The data provided in the LICA sampling program can be organized into two data sets, data from the passive samplers and data from the continuous monitors. Sites that had only duplicate passive sampler data were looked at separately from sites that had collocated passive samplers and continuous monitors. The results were evaluated to establish what distributions these data follow, what level of variation was displayed in the data, and what accuracy and precision levels are demonstrated by the passive samplers when compared to continuous monitors. Graphs of these data were also looked at for evidence of trends such as seasonality and how linear the relationship was between reported values of passive samplers when compared to continuous monitors.

In terms of precision comparisons, passive samplers were considered precise if there were no statistically significant differences between two passive samplers at the same site and accurate if there were no statistically significant differences between collocated passive samplers and continuous monitors.

Skewness and kurtosis tests were used to determine if both passive and continuous data were normal distributed. Normally distributed data was then evaluated using the Paired t Test and non-normally distributed data was examined using the Wilcoxon Ranked Sum Test. Finally, both duplicate passive sampler data and collocated passive and continuous data were graphed to compare the variability in results on a month by month basis and also to look for evidence of seasonality.

DISCUSSION AND RESULTS

Discussion

Air quality in the LICA Airshed is generally reported to be good (Lakeland Industry and Community Association, 2010). A number of anthropogenic sources within the airshed have the potential to influence the region's air quality. These include stationary sources such as numerous oil and gas production and storage facilities, mobile sources in the area's transportation corridors, and several communities (Bisaga, 2010).

With relatively few sites containing collocated samples and inconsistencies shown in statistical tests it is unclear if these statistical differences were representative of the performance of passive samplers overall. Based on this relatively small sample size and with five of fourteen sites displaying significant statistical differences this is concerning and warrants further investigation on a larger scale.

Sources of Uncertainty

Many sources of uncertainty influence passive sampler performance and results. Several of these uncertainties can be causal to the imprecision and inaccuracy of passive sampler results. The uncertainties listed below merit consideration by anyone who uses passive sampler data to ensure that the decisions based on results from passive sampling are based on validated data.

Absolute vs. Extrapolated Values

When evaluating passive sampler data, it is important to recognize that the passive sampler reported values are extrapolated values and not absolute values (Legge, 2011; Zabiegala, et al., 2010; Pippus; 2011). This is to say that passives do not directly measure pollutant concentrating it is determined inferentially (Legge, 2011; Zabiegala, et al., 2010; Huckins, et al., 2006). Meteorological data, absorptive characteristics of the absorption media, and diffusion constants across membranes all have a direct influence on passive sampler performance.

This is further complicated by many of these factors being averaged over the entire sample period to yield a single value from which data are drawn (Mukerjee, et al., 2004) and does not reflect potentially dramatic swings in these variables which in turn affect the sampling rate of the passive sampler. In the event that there are periods that vary considerably from the average these peaks or valleys are “averaged out” across the entire period of the sampling period. If the sampling rate is inaccurate, the TWA reported by the passive sampler will also be inaccurate.

Meteorological Conditions

Meteorological data such as relative humidity, wind speed and direction, and temperature are all used in the calculation of passive sampler results and affect the passive samplers sampling rate. Local meteorological information that is as site specific as possible would help insure the accuracy of the passives reported values. When meteorological data is used from sources away from the passive sampling location this does not account for what can be significant differences in regional microclimate (Mills, et al, 2009; Fraczek et al., 2009; Salem et al., 2009).

Several sources (Tang, et al, 2002a; Seethapathy, 2011, Gerboles, et al., 2006) also stated that condensed water also had an impact on passive sampler performance. Alberta's changing weather often provides opportunity for water in the form of condensation to occur at and within the passive sampler causing a large potential for uncertainty. In the case of the Maxxam H_2S passive sampler, Maxxam indicated this area requires further study (Tang, et al, 2002b).

Sampler Sampling Rate

The sampling rate of passive samplers is a function of diffusion rates across a membrane or static air layer, meteorological variables, and absorption characteristics of the absorbing media. These variables greatly complicate accurately determining the sampling rate of the passive sampler. It can also further be complicated by particulate deposits, which impede the movement of pollutants across the diffusion barrier and/or starvation effect, which can be caused by insufficient air exchange at the sampling site (Mukerjee, et al., 2004; Tang, & Lau, 2000). The sampling rate is an integral part of the equation to calculate the passive samplers reported time weighted average. Because of this, sampling rate is a major factor that influences the accuracy of these reported values.

Interferences

Ambient air monitoring typically deals with mixtures of gases, which contain multiple pollutants. Many of the pollutants in these mixtures have similar characteristics such as SO_2, NO_2, and O_3, which are all oxidants. To date it has not been quantified what relationship exists between various gas mixtures and passive sampler performance (Krupa & Legge, 2000). Some of these mixtures may have a biasing effect on reported values and until this is understood there will remain uncertainty surrounding passive performance. Harper and Purnell (1987) indicated that "the physical and chemical nature of the sorbent determines the efficiency of sampling and desorption and the magnitude of the effects of sample retention and interferences".

Non-anthropogenic sources of pollutants may also act as inferences (Fraczek et al., 2009). Natural sources of interference such as forest fires and volcanic activity can have a significant impact on ambient concentrations of pollutants such as SO_2 and H_2S and from large distances away from monitoring sites. If passive samplers are used for regulatory compliance, their data must be carefully scrutinized for these interferences to determine if non-anthropogenic interferences are influencing passive results prior to assessing the liability of parties obligated to undertake regulatory compliance sampling.

Correlation to Continuous Monitors

It is important to note that continuous monitors are not infallible devices and are not designed to be a primary standard for comparing alternative technologies. Continuous monitors require continual maintenance and calibration with certified standards to ensure quality outputs. These outputs are typically the determination of the concentration of specific chemicals in a given media, be it soil, water, or air. If passive samplers are to be correlated to a continuous instrument, great care must be taken to evaluate how the continuous instrument is operating for a validation to be quantifiable (Krupa & Legge, 2000; Legge, 2011). If the continuous monitor is out of calibration even marginally, or if the detection limit is not appropriate for comparison with the passive sampler this increases the opportunity for erroneous results and invalid conclusions regarding the performance of the passive sampler. This was the case in a validation case of NO_2 and VOC passive samplers in El Paso, Texas where validation of NO_2 passive samplers was made impossible when continuous monitor calibration gas was changed during the sampling program and the end result was that no firm conclusions could be drawn based on continuous monitor operational issues (Mukerjee, et al., 2004).

When validating passive samplers against continuous monitors, it must be recognized that the sample duration also has a significant effect on the comparison of results. There is an inverse relationship between disparity of results and sample duration. As the sampling period is extended, the disparity between continuous and passive results becomes lessened (Krupa & Legge; 2000). Over short periods, and in particular short periods where episodic events take place, the correlation between passive and continuous data can become quite disparate (Mukerjee, et al., 2004). As the sampling period is lengthened, there are significant averaging effects in the continuous data. This makes the numbers correlate more closely when the larger peaks and valleys are “averaged out”.

Several studies have compared the performance of passive samplers to continuous monitors and there is consensus that agreement of +/- 15-30% between the passive samplers and continuous monitors is realistic (Salem, et al, 2009; Seethapathy, 2011; Hsu, et al., 2010). As a comparison, continuous instruments are typically thought to be within specifications if they can produce an accuracy of +/- 2% (Haswell, 1992). This suggests that if precision and accuracy greater than +/- 15% is required for the objective of the sampling plan passive samplers are likely inappropriate for this work.

Another common thought among papers reviewed was that passive samplers could not replace continuous monitors because the two different technologies serves distinctly separate functions (Zabiegala, et al., 2010). Continuous monitors can measure short duration exposures with highly variable concentrations and maintain good accuracy while passive samplers are better suited to chronic exposures where there is less variability in ambient concentrations especially at low concentrations (Legge, 2011). Nash and Leith (2010) described passive samplers as, "… useful in indoor and outdoor air quality studies where the intent is to identify locations or circumstances where average concentrations are particularly low or high, and where high accuracy and precision are not required."

Sampling and Lab Error

Currently, no certification is required for technicians to conduct passive sampling in Alberta. This may lead to inconsistencies in how samples are deployed, handled, and transported for analysis and introduces an opportunity for systemic error. Because certification is not required, the parties responsible for conducting passive sampling may not have a fundamental understanding of how the passive samplers operate or fail to comprehend the effect sample handling and transport may have on reported values.

The Maxxam passive samplers used in this study in have relatively few procedural documents (Maxxam Analytics, 2011a; Maxxam Analytics, 2011b) and this may provide a source of potential inconsistency in sampling programs and data quality control. This is inconsistent between manufacturers as some passive manufactures include detailed descriptions of both sampling protocols as well as analytical methods (Ogawa & Co., 2006). When technicians are field sampling, it is common to vary and adapt protocols slightly, depending on the sampling conditions especially if the direction from the manufacture is limited and this can lead to uncertainty and unacceptable levels of reliability (Zabiegala, et al., 2010).

Passive samplers may also have systemic interferences such as adsorbents naturally converting to their analyte over time. An example of this is would be nitrite coated filters which naturally convert to nitrate (the analyte) over time (Havard School of Public Health, 2001). In this, and any similar scenario, it is important to have adequate field and travel blanks to correct reported values. Maxxam recommends triplicate sampling to help address many of the issues regarding passive precision and accuracy (Maxxam Analytics, 2011a). With three times as many blanks, however, the cost associated with carrying out a sampling regime of this nature becomes quite burdensome. Nowhere in the information reviewed for this project was there found any legislation that requires triplicate sampling as per the manufacturers recommendations.

Another sampling and analysis challenge that has been described with passive samplers are problems including laboratory calibration, transfer of laboratory data to the field, and the development of validation procedures based on either reference materials and/or reference sites (Mills et al., 2009). As opposed to continuous monitors that are calibrated to reference standards, passive samplers are extremely difficult to calibrate in the field making collection of duplicates samples and analytical blank correction essential as a means to help verify data quality (Havard School of Public Health, 2001).

Time Weighted Averages (TWA)

The TWA reported by passive samplers is a single number representation of the average pollutant concentration to which the sampler was exposed to during the sampling event. There are a number of drawbacks to the use of TWA’s particularly in the context of regulatory compliance including the TWA's significant potential to fail to report short-term exceedances (Krupa & Legge, 2000). Many pollutants do not require long-term high concentration exposures to have negative impacts on receptors. A short-term exposure to high concentrations of SO_2, for example, can lead to negative impacts to people by way of respiratory problems, or receptors from the environment such as foliar damage to exposed plants (Krupa & Legge, 2000; Alberta Environment, 2011; Vallero, 2010). These are typically the type of exposures that are the focus of regulatory compliance monitoring which requires more specific data and the ability to isolate when and for how long exceedances of regulatory limits has occurred. Passive samplers are not practical for this application because they display a TWA, which does not allow for the identification of the origin of these exceedances.

In contrast to regulatory compliance, TWA's can be useful in the context of assessing cumulative impacts. Under circumstances where accumulating a large quantity of data is important in developing management plans based on the trends from a baseline or changes over time, passive samplers can be quite useful. While it is important that this information be as accurate as possible, the variability of concentration from moment to moment is not as important as identifying the change in the TWA temporally (Legge, 2011). This information is useful in determining if a cumulative impact management strategy is creating the desired result.

Sampling Site Selection

Passive sampler results display the concentration of a pollutant at a specific location during a defined period and for this reason great care must be taken to ensure that the location of the passive sampler is as representative of the larger environment as possible. "While deployment of passive samplers is fairly simple, the sampling strategy involved in choosing the number and type of passive samplers for deployment, their exact locations, time, and duration of exposure, and quantification in the laboratory, require careful consideration" (Zabiegala, et al., 2010).

If the sampling location is not as representative as possible, biases either positive or negative are possible which affect how accurately the passive data characterizes the area's ambient air quality. Wind turbulence at the passive sampler deployment site is a specific concern. Where airflow is limited, and typical site conditions have low ambient pollutant concentrations a "starvation effect" can occur (Seethapathy, 2011) where analytical results will be biased low due to the lack of pollutant for the absorption media to react with. The opposite can also hold true where if the site is extremely turbulent where the passives sampling rate may also be affected (Seethapathy, 2011).

Passive samplers do not actively pump sample across the diffusion membrane and therefore their deployment location is crucial concerning guaranteeing representative exposure of the sampler to available pollutants. Continuous monitors avoid this problem by actively pumping air across the detection mechanism thereby making sure that representative air exchange takes place regardless of deployment location.

Sampling site selection can be made more robust by utilizing dispersion modeling software to help evaluate site selection. The use of air dispersion models can help with identify areas of increased ambient pollutant concentration, which may bias the overall assessment. It is important to recognize that passive samplers may not be the ideal analytical method in all ambient air sampling scenarios.

Misrepresentation of Non-Detects

Non-detects or sampling that displays results below the detection limit of the passive analytical methods are frequently reported as zero. This may not be the case of the actual ambient air concentrations of those pollutants or the actual exposure to receptors. This only indicates that the passive sampler's exposure was below the analytical methods detection limit (Krupa & Legge, 2000). This may give rise to concerns regarding the use of passive samplers for the assessment of cumulative effects such as whether the data adequately represent potential for impacts. If the detection limit of the analytical method is 7 ppb, but the ambient concentrations are continually 3-5 ppb, the exposures of 3-5 ppb may be recorded as a concentration of 0 ppb.

The detection limit of the passive sampler also plays a role in how many non-detects a sampling program observes. The detection limit of a passive sampler is an amalgamation of factors including sampler collection efficiency, duration of exposure and accuracy of the analytical method in use (Krupa & Legge, 2000; Namiesnik, et al., 2005). The passive sampler's inability to be field calibrated also hinders the ability to establish finite detection limits (Mills et al., 2009). For example, in a location where ambient concentrations of a pollutant are expected to be 5 - 10 ppb, the environmental manager designing a passive sampling program for the area may establish an exposure time that will produce non-detects if the actual ambient pollutant concentration is actually in the 2-4 ppb range.

One way to deal with non-detects in low concentration environments is to extend the duration of the sampling event (Salem, et al, 2009). Extending the sampling period to ensure an exposure adequate to reach the analytical detection limit would eliminate this uncertainty. This may not be practical for all applications and is not practicable in a prescriptive regulatory application as the Alberta Environment 30 day passive SO_2 objective where the sampling period is clearly defined (Alberta Environment, 2006).

Results

The results of distribution testing are displayed in Tables 5 through 8. It was determined that 29% of the total data sets were non-normally distributed. When the data were separated by duplicate and collocated sampling regimes only 22% of duplicate passive samples were non-normally distributed. Collocated passive sampling and continuous monitoring sites displayed non-normal distributions 71% of the time. This suggests that when comparing passive samplers to continuous monitors the assumption that the data is normally distributed cannot be made and parametric statistical tests are not appropriate for determination of statistical differences in these instances.

On a per pollutant basis, NO_2 demonstrated the lowest amount of non-normally distributed values with 24% (Table 4). This was followed by SO_2 and O_3 both with 29% (Table 3 and 6), and finally, H_2S, which had the least normally distributed values with 39% (Table 5). This information suggests that the choice of statistical test must be chosen on a case-by-case basis if the appropriate test is to be applied based on the data’s parametric or non-parametric tendencies.

Table 1 displays the average pollutant concentrations over the two-year sampling period with the seasonal variability removed by averaging the entire sampling period to a single value. The expectation is that as the sampling period is increased or the more numerous the data points which are included in the average the more closely the averages will align. Spatially there was variability shown in the results even though the overall concentrations of the measured pollutants were quite low. Duplicate passive samples infrequently matched and showed statistically significant differences at six of twenty-four sites. This indicates that 25% of duplicate sampling sites were statistically different.

At collocated passive sampling and continuous monitoring sites three of four sites displayed statistically significant differences of reported values (Table 3). What this displays is that while duplicate passive samples compare relatively well with only 25% of sites showing statistical differences, collocated sampling sites compared far less accurately with 75% sites indicating statistical differences in reported values.

Passive Sampler Trends vs. Continuous Monitoring Trends

When line graphs were plotted for each constituent by location, some very obvious trends became apparent. Passive and continuous exhibited the same trends, even when the actual values were statistically significantly different (Fig. 6, boxes A-D), and disparities between passive and continuous results were not consistent for all pollutants. For H_2S and SO_2 results, passive samplers were consistently higher than the reported values from continuous monitors with the discrepancy getting larger as concentrations increased (Fig. 6 Boxes A and D). Conversely, NO_2 results from passive samplers demonstrated consistently lower reported values than collocated continuous monitors (Fig. 6 Box C). O_3 passive results compared most closely with continuous monitors and demonstrated the best accuracy based on information from this sampling program (Fig. 6 Box B).

Seasonality

Seasonality was demonstrated in O_3, NO_2, and SO_2 and samples during the sampling program (Fig. 6 Boxes B, C, and D). NO_2 and SO_2 results both exhibited a trend with the typically higher values displayed between October and February and lower values during the period of May through September (Fig. 6 Boxes C and D). H_2S did not display a clearly definable trend, and appeared to be more random and episodic in nature.

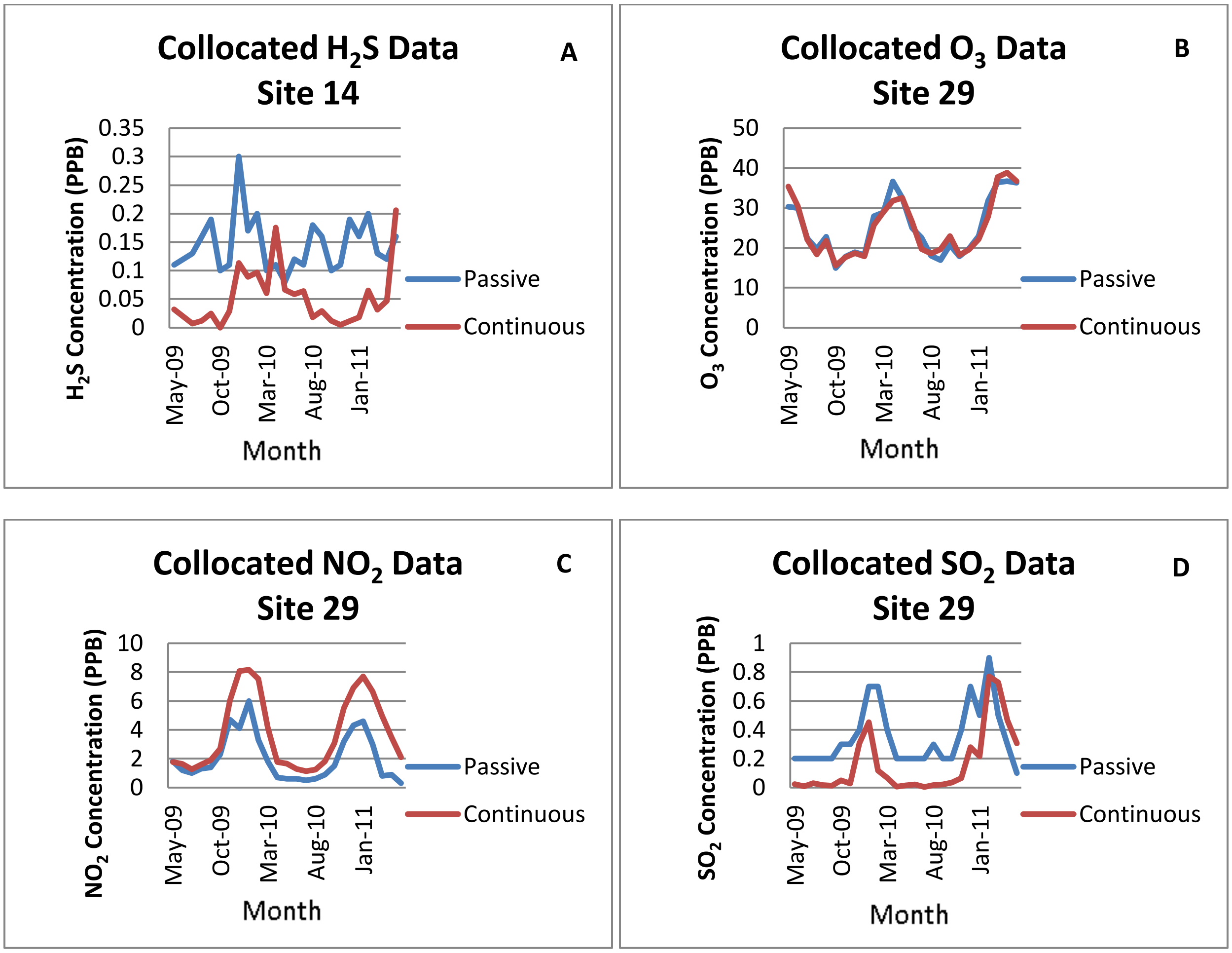


Figure 4. Typical examples of collocated passive sampler and continuous monitoring graphs. Sampling occurred from May 2009 until May 2011 for H_2S (Box A), O_3 (Box B), NO_2 (Box C), and SO_2 (Box D) at locations within the LICA airshed.

Precision and Accuracy

Duplicate passive sample trends matched very well and reported similar increases in pollutant concentration as the pollutant concentration increased in ambient air. Results from duplicate passive samples were inconsistent among pollutants with SO_2 and NO_2 displaying statistical differences at multiple locations while no statistical differences were experienced in duplicate passive samples for O_3 or H_2S (Table 2). Collocated data demonstrated that while the reported values could be statistically different, the overall trends in pollutant concentration were comparable with continuous data (Fig. 6 Boxes A-D). This suggests that the precision of the passive samplers is good, based on their consistent nature and reproducibility.

SO_2 passive sampler duplicates reported significant differences at four of twenty-four sites (Table 4) while NO_2 duplicates reported significant differences at three of twenty-one sites (Table 5). H_2S and O_3 duplicates (Table 6 and 7) reported no significant differences between samples.

Collocated passive and continuous samples were also inconsistent. SO_2 had significant statistical differences between collocated samples at one of four locations (Table 4), while two of four locations for NO_2 (Table 5), and two of three locations for H_2S (Table 6) were significantly different. O_3 had no statistical differences reported in co-located samples (Table 7).

Table 1. Summary of reported values for duplicate passive data for all pollutant parameters at all sites. Values are the mean values ± 1 standard deviation. Sampling events marked with * indicate instances where statistical differences were indicated in testing.

Site	**SO_2 (ppb) Passive 1**	**SO_2 (ppb) Passive 2**	**NO_2 (ppb) Passive 1**	**NO_2 (ppb) Passive 2**	**O_3 (ppb) Passive 1**	**O_3 (ppb) Passive 2**	**H_2S (ppb) Passive 1**	**H_2S (ppb) Passive 2**
2	0.25 ± 0.22*	0.22 ± 0.15*	0.93 ± 0.69	0.90 ± 0.20	21.73 ± 8.48	21.6 ± 7.03		
3	0.33 ± 0.25	0.35 ± 0.24	1.36 ± 0.91	1.35 ± 0.84	25.45 ± 7.96	25.57 ± 7.76	0.14 ± 0.05	0.14 ± 0.05
4	0.58 + 0.41	0.57 ± 0.42	1.46 ± 1.04	1.43 ± 0.98	28.08 ± 8.73	28.34 ± 8.61		
5	0.47 ± 0.24	0.52 ± 0.30	1.34 ± 1.19	1.23 ± 0.97	25.78 ± 8.02	25.93 ± 8.54	0.26 ± 0.21	0.25 ± 0.21
6	0.48 ± 0.32	0.51 ± 0.36	1.86 ± 1.01	1.88 ± 1.00*	26.28 ± 8.74	25.68 ± 8.25		
8	0.44 ± 0.28	0.43 ± 0.28	1.11 ± 0.95*	0.97 ± 0.70	28.28 ± 8.05	28.07 ± 7.63		
9	0.41 ± 0.26*	0.43 ± 0.25*	1.58 + 0.89	1.64 ± 1.02	26.03 ± 9.16	27.03 ± 8.96		
10	0.29 ± 0.22	0.34 ± 0.20	2.29 ± 1.66	2.19 ± 1.50	23.72 ± 6.87	23.15 ± 6.78	0.14 ± 0.06	0.12 ± 0.07
11	0.31 ± 0.24	0.34 ± 0.26	0.60 ± 0.52	0.66 ± 0.49	21.15 ± 7.87	21.77 ± 7.33	0.09 ± 0.04	0.08 ± 0.06
12	0.39 ± 0.24	0.39 ± 0.32	1.01 ± 0.76	1.09 ± .094	23.88 ± 7.38	23.80 ± 7.74	0.08 ± 0.03	0.08 ± 0.02
13	0.53 ± 0.34	0.53 ± 0.38	0.89 ± 0.55	0.86 ± 0.56	26.66 ± 8.22	27.26 ± 8.60	0.10 ± 0.05	0.10 ± 0.04
14	0.95 ± 0.39	1.02 ± 0.42	1.72 ± 1.27	1.69 ± 1.28	26.10 ± 6.61	26.41 ± 6.49	0.13 ± 0.03	0.14 ± 0.04
15	0.43 ± 0.25*	0.44 ± 0.24*	1.54 ± 1.06*	1.31 ± 0.82*	24.55 ± 8.99	25.52 ± 8.91		
16	0.44 ± 0.32	0.38 ± 0.31	1.56 ± 1.09	1.62 ± 1.15	24.65 + 6.71	24.88 ± 7.11	0.16 ± 0.06	0.16 ± 0.05
17	0.56 ± 0.36	0.49 ± 0.37	2.24 ± 1.08	2.19 ± 1.13	26.31 ± 8.11	26.62 ± 8.17	0.21 ± 0.16	0.22 ± 0.15
18	0.33 ± 0.21	0.32 ± 0.26	0.99 ± 0.70	1.00 ± 0.79	23.39 ± 7.09	22.98 ± 7.87	0.12 ± 0.05	0.12 ± 0.06
19	0.45 ± 0.34	0.48 ± 0.37	1.00 ± 0.66	1.03 ± 0.62	27.28 ± 7.72	27.02 ± 7.63		
23	0.22 ± 0.23	0.23 ± 0.20	0.42 ± 0.44	0.38 ± 0.40	21.37 ± 7.11	21.33 ± 7.32		
24	0.47 ± 0.33	0.52 ± 0.28	2.21 ± 0.99	2.23 ± 0.96	25.75 ± 8.17	25.35 ± 8.13	0.14 ± 0.06	0.15 ± 0.06
25	0.52 ± 0.29	0.50 ± 0.29					0.10 ± 0.05	0.098 ± 0.05
26	0.59 ± 0.30	0.59 ± 0.30					0.13 ± 0.05	0.14 ± 0.04
27	0.83 + 0.39	0.88 ± 0.39					0.23 ± 0.12	0.23 ± 0.12
28	0.51 ± 0.19*	0.54 ± 0.23*	4.48 ± 2.77	4.82 ± 3.36	22.30 ± 6.91	21.70 ± 6.27		
29	0.33 ± 0.18	0.30 ± 0.20	1.98 ± 1.37	2.14 ± 1.66	25.00 ± 7.47	24.68 ± 7.11	0.13 ± 0.06	0.14 ± 0.06

Table 2. Summary of reported values for collocated continuous monitors and passive sampler data for all pollutant parameters at all sites. Values are the mean values ± 1 standard deviation.

Site	**SO_2 (ppb) Passive**	**SO_2 (ppb) Continuous**	**NO_2 (ppb) Passive**	**NO_2 (ppb) Continuous**	**O_3 (ppb) Passive**	**O_3 (ppb) Continuous**	**H_2S (ppb) Passive**	**H_2S (ppb) Continuous**
14	1.0 ± 0.51	0.53 ± 0.27	1.62 ± 1.10	2.65 ± 1.68			0.15 ± 0.05[a]	0.05 ± 0.05[a]
29	0.35 ± 0.21[a]	0.16 ± 0.23[a]	2.06 ± 1.62[a]	3.76 ± 2.54[a]	25.03 ± 7.09	24.99 ± 7.19		
32	0.60 ± 0.40	0.32 ± 0.73	1.21 ± 0.97	1.79 ± 1.32	30.32 ± 7.95	30.28 ± 8.38	0.15 ± 0.05	0.04 ± 0.05
34	0.49 ± 0.25	0.16 ± 0.14	2.36 ± 2.15[a]	3.48 ± 1.95[a]	26.87 ± 7.89	26.31 ± 7.26	0.15 ± 0.04[a]	0.06 ± 0.06[a]

Sampling event marked with [a] indicate cases where statistical differences were indicated in testing.

Table 3. Summary of statistical analysis measures for SO_2 duplicate and collocated samples including description of distribution, and either of paired t test or Wilcoxon ranked sum test results.

Duplicate Site	Distribution	Paired t value	Wilcoxon value
Station 2	Not-Normal		-7.33*
Station 3	Normal	0.7333	
Station 4	Normal	0.67	
Station 5	Normal	0.11	
Station 6	Normal	0.28	
Station 8	Normal	0.84	
Station 9	Not-Normal		7.00*
Station 10	Normal	0.11	
Station 11	Normal	0.04	
Station 12	Normal	1.00	
Station 13	Normal	0.78	
Station 14	Normal	0.02	
Station 15	Not-Normal		7.00*
Station 16	Normal	0.09	
Station 17	Not-Normal		15.00
Station 18	Normal	0.76	
Station 19	Normal	0.42	
Station 23	Normal	0.50	
Station 24	Normal	0.28	
Station 25	Normal	0.34	
Station 26	Normal	1.00	
Station 27	Normal	0.65	
Station 28	Not-Normal		3.50*
Station 29	Normal	0.27	

Collocated Site			
Station 14	Not-Normal		325.00
Station 29	Not-Normal		-34.00*
Station 32	Not-Normal		-23.00
Station 34	Normal	>0.001	

*Sampling event marked with * indicate cases where statistical differences were indicated in testing.*

Table 4. Summary of statistical analysis measures for NO_2 duplicate and collocated samples including description of distribution, and either of paired t test or Wilcoxon ranked sum test results.

Duplicate Site	Distribution	Paired t value	Wilcoxon value
Station 2	Normal	0.63	
Station 3	Normal	0.73	
Station 4	Normal	0.77	
Station 5	Normal	0.30	
Station 6	Normal	0.83	
Station 8	Not-Normal		-7.00*
Station 9	Normal	0.09	
Station 10	Normal	0.31	
Station 11	Not-Normal		6.00
Station 12	Normal	0.33	
Station 13	Normal	0.42	
Station 14	Normal	0.83	
Station 15	Not-Normal		9.00*
Station 16	Normal	0.67	
Station 17	Normal	0.36	
Station 18	Normal	0.78	
Station 19	Normal	0.55	
Station 23	Normal	0.17	
Station 24	Normal	0.88	
Station 28	Not-Normal		21.00
Station 29	Normal	0.29	

Collocated Site			
Station 14	Normal	>0.001	
Station 29	Not-Normal		1.00*
Station 32	Normal	0.004	
Station 34	Not-Normal		-23.00*

*Sampling event marked with * indicate cases where statistical differences were indicated in testing.*

Table 5. Summary of statistical analysis measures for H_2S duplicate and collocated samples including description of distribution, and either of paired t test or Wilcoxon ranked sum test results.

Duplicate Site	**Distribution**	**Paired t value**	**Wilcoxon value**
Station 3	Normal	0.337	
Station 5	Not-Normal		-5.5
Station 10	Normal	0.128	
Station 11	Normal	0.077	
Station 12	Normal	0.318	
Station 13	Normal	0.429	
Station 14	Normal	0.108	
Station 16	Not-Normal		-20.5
Station 17	Not-Normal		27
Station 18	Normal	1.000	
Station 24	Normal	0.281	
Station 25	Normal	0.266	
Station 26	Normal	0.347	
Station 27	Not-Normal		14
Station 29	Normal	0.447	

Collocated Site			
Station 14	Not-Normal		-9.5^*
Station 32	Not-Normal		105
Station 34	Not-Normal		-4.5^*

Sampling event marked with * *indicate cases where statistical differences were indicated in testing.*

Table 6. Summary of statistical analysis measures for O_3 duplicate and collocated samples including description of distribution, and either of paired t test or Wilcoxon ranked sum test results.

Duplicate Site	Distribution	Paired t value	Wilcoxon value
Station 2	Normal	0.84	
Station 3	Normal	0.85	
Station 4	Normal	0.51	
Station 5	Normal	0.76	
Station 6	Not-Normal		-22.00
Station 8	Normal	0.63	
Station 9	Normal	0.09	
Station 10	Not-Normal		-41.50
Station 11	Normal	0.14	
Station 12	Normal	0.90	
Station 13	Not-Normal		26.00
Station 14	Not-Normal		32.50
Station 15	Normal	0.11	
Station 16	Normal	0.55	
Station 17	Normal	0.24	
Station 18	Normal	0.51	
Station 19	Normal	0.64	
Station 23	Normal	0.93	
Station 24	Normal	0.25	
Station 28	Not-Normal		26.50
Station 29	Normal	0.45	
Collocated Site			
Station 29	Not-Normal		160.00
Station 32	Not-Normal		11.00
Station 34	Normal	0.98	

CONCLUSIONS

Precision and Accuracy

The precision of the passive samplers was good when comparing duplicate passive samples (Table 3). Passive sampler precision was also good when comparing how passive sampler results followed continuous monitoring results. Similar changes in ambient concentrations were displayed by both data sets over the same periods (Fig. 6 Boxes A-D). There were, however, several instances where there were statistical differences in reported values of both duplicate passive samples as well as collocated samples.

Based on the fact that SO_2 and H_2S passive results typically over reported values and NO_2 passive results typically underreported values when compared to continuous monitoring, there needs to be a quantification process in place to validate passive data as passive data by itself may not accurately represent ambient pollutant concentrations. These relationships are important to recognize when evaluating passive sampler data based on the fact that SO_2 and H_2S passive results typically overestimate actual ambient concentrations and NO_2 passive results typically underestimate actual ambient concentrations based on the evidence from this study. These discrepancies make it is fair to say that passive samplers do not display the accuracy of continuous monitors and because these discrepancies do exist, data must be carefully scrutinized for validity prior to making management or regulatory decisions based on passive sampler data alone.

Level of Uncertainty

Harper and Purnell (1987) put it simply, “It should be borne in mind that accuracy is not the sole criterion for assessing the usefulness or acceptability of a monitoring method”. There is justifiable concern regarding the level of uncertainty which has been identified with passive samplers. While the overall performance of these is fair, results from passive samplers require a great deal of scrutiny to validate based on the many factors that impact their performance.

The level of accuracy and certainty achieved by continuous monitors is not a realistic goal for passive samplers. With an understanding of their limitations passive samplers can be a valuable tool but users must not try and make more of this technology than what it is capable of. It is a low cost tool which can help to supplement ambient air quality monitoring data especially in remote locations, but it cannot replace continuous monitors because of the lack of certainty they display and the types of data passives generate.

Steps can be taken to help control the level of uncertainty passive sampler's display including careful site selection, use of meteorological data that is as accurate of as possible, and predetermining if the passive samplers data are appropriate for the application of the study. This will make the data they provide more quantifiable and align more closely with the objectives of the sampling program.

Based on the volume of sources of uncertainty the environmental manager who wants to use passive samplers should first establish a set of criteria that the data must meet at the end of the day. This may exclude passives from some sampling programs. A great deal of useful information with the explicit purpose of defining data objectives can be found in the USEPA's (2006) Guidance on Systematic Planning Using the Data Quality Objectives Process where a process is outlined regarding how to plan sampling events so that they align with program objectives. Environmental managers who are tasked with designing passive sampling programs would be well served to read this document as well as the USEPA's (2000) Guidance for Data

Quality Assessment to ensure that passive samplers are appropriate for the given task. This will help ensure that the uncertainty and accuracy displayed by passives is consistent with the goals of the monitoring program.

Use of Passives in the Regulatory Context

There is significant liability for stakeholders who conduct passive sampling as a legal requirement for ambient air quality regulatory compliance sampling and it is unclear based upon the information from this work whether the use of passive samplers in the regulatory context is valid. While the passive samplers displayed good trending, the accuracy they display is questionable. Passive sampler's results are also influenced by a litany of factors including meteorological conditions, sampling duration and sampling locations which have enough effect on results to imply compliance exceedances if not correlated to continuous monitoring.

The Alberta Environment monthly passive sampler objective does not clearly define the purpose of this objective and this creates difficulty in determining if passive samplers are an appropriate tool to meet this need.

The enforceability of this regulatory objective is also cause for concern. As an example, if a set of passive results came back with a 30 day TWA of 15 ppb SO_2 (the current Alberta ambient air quality objective for SO_2 is 11 ppb) (Alberta Environment, 2010c) the question arises as to how Alberta Environment would determine liability and enforcement given that it would be extremely difficult to determine at what point in the 30 day period that the exceedances had occurred, and without site specific meteorological data there is not a realistic way to determine what direction that the exposure came from. The same example using a continuous analyzer and on site meteorological data may have a much different conclusion. The ability of the continuous analyzer to log data over the entire period will show when the exceedances occurred, and allow appropriate correlation with meteorological data to make a much more accurate case for whom or what the cause of the exceedances was.

The data from this program supports the conclusion that passive samplers are uncertain and inaccurate to a level that may preclude them from some ambient air quality monitoring programs including regulatory compliance monitoring. Several instances demonstrated statistical inaccuracy, inconsistency, and uncertainty that indicate passive sampler use as a standalone monitoring approach may not be effective concerning regulatory compliance monitoring programs.

Use of Passives as a Tool to Gauge Cumulative Impacts

Passive samplers are well suited to identifying background levels of ambient air quality for cumulative impact assessment because they are easily deployable at low cost to remote locations. Many passive samplers can be deployed at reasonable cost over a long period for the same cost as a single continuous monitor. The net result is a substantial increase in the amount of data that can be logged and with a greater geographic representation in these data. Fraczek et al (2009) indicated that a greater number of sampling points is extremely helpful with identifying sources of pollution. This also helps show how air pollution sources are influencing the overall air pollutant concentrations in a study area.

Because passive sampler data demonstrates similar trends when compared to continuous monitors, it is reasonable to use passive results to examine trends in air quality especially over longer periods. If the goal of the sampling is to examine general changes in air quality, passive samplers work well for this. That being said, passive sampler results must be critically evaluated to ensure the data are of high quality.

This research was essentially carried out on a small and geographically localized scale. It is important to develop a better understanding of this issue as it pertains to all of the Alberta airsheds and complete further research on a much more comprehensive basis. A research project carried out with the support of all the Alberta airsheds including the support of Alberta Environment and Water would have significantly more impact to the understanding of passive technology and increase the statistical significance of the study. While it is unlikely that results from such a project would be greatly disparate from the work generated here, a study of that type would eliminate many variables and provide a definitive answer to many looming questions regarding passive uncertainty, accuracy, and precision.

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