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Seasonal Pattern and Sources of Particulate Carbon in Kananaskis and Calgary, Alberta

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Seasonal Pattern and Sources of Particulate Carbon in Kananaskis and Calgary, Alberta

by

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Abstract

Sources, seasonal pattern of elemental carbon(EC), organic carbon(OC), and total carbon from dry deposition and precipitation in Kananaskis and Calgary were assessed using thermo-optical methods. Vehicle exhaust was inferred to be dominant source of carbon throughout the year with an identical OC/EC of 22±14 in Calgary and 22±5 in Kananaskis in dry deposition. Biogenic OC signal was absent in Kananaskis in precipitation or dry deposition. Biomass burning, with a lower OC/EC both in winter and summer, was potentially associated with recreation and tourism in Kananaskis. Sources from long-range transport impact both locations simultaneously. A lower boundary layer at night concentrates TC and a higher boundary layer in the day lower the concentration in both locations. OC is much more easily removed by precipitation than EC due to is larger surface area and size and OC/EC ratios in precipitation reaching 130 were observed in Calgary while those in Kananaskis reached 46.

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List of Abbreviations

AADT	Average Annual Daily Traffic
AAWT	Average Annual Weekday Traffic
ASDT	Average Summer Daily Traffic
BC	Black Carbon
CCN	cloud condensation nuclei
CRAZ	Calgary Region Airshed Zone
DRI	the Desert Research Institute
EC	Elemental carbon
FID	flame-ionization detector
IMPROVE	Interagency Monitoring of Protected Visual Environments
ISL	the Isotope Science Laboratory
NH4H2PO4	Ammonium dihydrogen phosphate
NO_x	Oxides of Nitrogen
OC	Organic Carbon
PCA	principal component analysis
PCM	Particulate Carbonaceous Matter
PCS	principal component scores
PL	probability level of significance
PM	particulate matter

PM 10	particulate matter 10 micrometers or less in diameter
PM 2.5	particulate matter 2.5 micrometers or less in diameter, also known as fine particles
POC	Primary Organic Carbon
r	correlation on coefficient
RH	relative humidity
SO2	Sulphur Dioxide
SO4	Sulfate
SOC	Secondary Organic Carbon
TC	total carbon
TOR	thermal/optical reflectance

Chapter One: Introduction

1.1 Atmospheric Particulate Matter and its Impacts

Atmospheric particulate matter (PM) is defined as a complex mixture of all solid particles and liquid droplets suspended in the atmosphere, including particulate carbonaceous matter, ammonium, nitrates, sulfates, mineral dust, trace elements, and water (Harrison and Jin, 2000). Atmospheric PM pollution (also called aerosol pollution), which affects Earth's energy balance and the hydrologic cycle, has been viewed as integral to achieving a deeper understanding of anthropogenic effects on regional and global climate change (Penner, et al., 2001). Aerosols and their associated feedbacks introduce some of the largest uncertainties of climate prediction today (Ramaswamy et al., 2001). The first order effect of PM on global climate is the enhancement of the planetary albedo by scattering solar radiation back. This decreases the energy absorbed by ground and causes cooling. Cooling results in slower evaporation from the ocean, slowing down the hydrological cycle. Also, PM forms more cloud droplets (Twomey, 1977) and therefore, influences precipitation. PM can be transported locally by boundary layer turbulence and globally by winds (Gupta et al., 2006), influencing climate over large spatial scales.

Besides climate effects, PM 10 (particulate matter 10 micrometers or less in diameter) and PM 2.5 (particulate matter 2.5 micrometers or less in diameter, also known as fine particles) are commonly present in the atmosphere and can cause health problems when people are continuously exposed. Recent epidemiologic studies have presented that long-term exposure to increasing

amounts of PM 2.5 may potentially induce carcinogenic and mutagenic effects (Ostro et al., 2007; Ito et al., 2011).

1.2 Particulate Carbonaceous Matter in Atmosphere

Of all the PM types present in the atmosphere, Particulate Carbon (PC, sometimes called 'Carbonaceous Aerosol') is one of the largest sources of uncertainty in quantifying the effect of PM on climate change (Ramaswamy, et al., 2001). PC was estimated to contribute to an average of 50% of PM mass based on 28 samples collected from Eastern Canada (Fan et al., 2004) and often dominates PM especially in urban areas. In recent years, PC (same as total carbon, TC) has drawn attention due to its role on visibility reduction and the radiative budget of the atmosphere (Malm and Day, 2000; Jacobson, 2001). Also, some toxic carbonaceous products react between atmospheric aerosols and trace gases and could pose potential risks to the environment (Lary et al., 1999). Emissions of TC depend on the time of year and the characteristics of pollution sources such as local industry and heating systems near the measurement sites, while meteorological and geographic features could affect ambient concentrations of TC (Querol et al., 2009). Based on the calculation with the global model GATOR-GCMM, Jacobson (2002) concluded that controlling the amount of fossil-fuel PCM could be the most effective approach to slowing down global warming. Atmospheric TC is generally classified into two fractions depending on its chemical presence: Organic Carbon (OC) and Elemental Carbon (EC).

Organic carbon is an aggregate of hundreds of organic compounds with a wide range of chemical and physical properties. Organic carbon can be divided into Primary Organic Carbon

(POC) and Secondary Organic Carbon (SOC) according to its different formation processes. Previous research has clearly indicated that the hygroscopic growth of secondary aerosols, which includes SOC, changes the scattering property of the atmosphere and decreases the visibility of the ambient environment (Malm et al., 1996). Field observations showed that SOC was considerably underestimated in current global models both in the boundary layer and in the free troposphere (De Gouw et al., 2005; Volkamer et al., 2006).

Elemental carbon, determined by chemical methods, is similar to Black Carbon (BC), which is determined by optical methods, and is optically absorptive and highly polyaromatic. Elemental carbon has direct effect on solar radiation absorption and scattering and employs a positive forcing of +0.09 W/ m^2 to +1.26 W/ m^2 for the industrial-era (1750-2005) on the atmospheric circulation (Haywood et al., 1998; Bond et al., 2013). This forcing redistributes energy within the atmosphere, stabilizing the vertical atmosphere and potentially reducing convection and precipitation events (Chung and Zhang, 2004).

The residence time of EC in the atmosphere largely depends on the speed that EC is processed by atmospheric oxidants (Johnson et al., 2005). Processed EC develop a hydrophilic coating, so that it acts as cloud condensation nuclei (CCN) and can be washed out by precipitation (Zuberi et al., 2005). EC tends to have a longer residence time in the air than OC because of differences in OC and EC volatility and scavenging rate. EC is non-volatile and thermally very stable, while OC contains many semi-volatile species that are partitioned between gas and particle phases. When air containing OC and EC is transported and diluted with clean air, some OC likely evaporates to reestablish gas-particle equilibrium. Additionally, fog water and rainwater will be

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more efficient in scavenging some water-soluble OC than hydrophobic EC in the atmosphere (Lim et al., 2003). EC in clouds may also enhance the absorption of solar radiation and cause in-cloud heating and evaporation, shortening the cloud lifetime (Ackerman, et al., 2000; Kaufman et al., 2005). Finally, EC deposited on snow and ice at high altitude and in high-latitudes decreases the surface albedo and causes increased melting of glaciers and mountain snow packs (Chylek et al., 1983; Twohy et al., 1989). All the above indicate the important role of EC in the global energy balance, hydrologic cycles, high-latitude ecology, and changing risks for natural disasters.

1.3 Global Particulate Carbon

Changes in particulate carbon (PC) cycles between atmospheric, terrestrial, and aquatic environments are significant in the climate system. Regionally, anthropogenic disruptions to carbon biogeochemical cycling occur because of the roles PC plays in aquatic systems (e.g., Smith and Hollibaugh, 1993; Cole and Caraco, 2001). Large deposition of carbon from human activities in rivers and oceans tend to turn aquatic systems from a carbon sink to a carbon source. Globally, PC transport from oceans to continents was tracked based on air mass trajectory examination (Moorthy and Babu, 2006). Previously, the global atmospheric circulation was assumed to be the main transport mechanism for PC. Thus, knowledge of carbon sources, transport, and removal processes is fundamental to understanding regional and global biogeochemical changes to OC and EC.

1.3.2 Particulate Carbon Transport

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Most monitoring programs worldwide do not provide data on PC concentrations in the atmosphere, and data on emissions inventories are sparse. Thus, information is insufficient to support engineering and scientific studies of methods for controlling carbonaceous particle concentrations. Understanding the transport of PC will help trace the sources of pollution and inform policy makers to create regulations to prevent wide spread emission.

After release into the atmosphere, PC experiences a series of transformations, including changes in size, physical structure, and chemical composition. Particulate EC and a large fraction of OC particles that are far less than 0.1 micrometers in diameter, are too small to be removed immediately after production. The size of PCs grows as PC collides with each other or undergoes chemical processes. Dry deposition or precipitation will remove PC from the atmosphere when the size is larger than 0.1 micrometers (Suman, 1989). Wolff et al., (1982) observed that high concentrations of EC in the fall in Warren, MI, USA coincided with elevated sulfate, which was transported into southeastern Michigan by the atmospheric circulation. Rahn et al., (1967) presented evidence that EC could be transported over much longer distances from Eurasia to the Arctic. These analyses strongly suggest that PC and associated sulfate haze, might be transported overseas and the mean transport time could reach on the order of twenty days.

Global model simulations, assisted by measurements, proved that PC existed throughout the year over Europe, North America, and Asia, especially in dry seasons.

1.3.3 Formation of Secondary Organic Carbon

Even though organic carbon (OC) accounts for a great fraction of urban PM (Stader et al., 1999), the relation between primary and secondary OC sources has long been disputed. The formation of secondary organic carbon (SOC) is characterized by converting volatile compounds into oxidized products with a low enough volatility to condense into liquid or semisolid particles based on gas-to-particle partitioning theory (Saylor et al., 2006). This chemical process is complicated, and multiple oxidation reactions are expected. SOC may be produced in any step of the reaction and is therefore, hard to measure and model.

Because EC and POC are both from combustion processes, EC was used as a tracer for POC by several investigators (Wolff et al., 1983; Novakov, 1982). An important concept that these researchers utilized is the ratio of OC/EC versus POC/EC. If there is no SOC, OC/EC should equal to POC/EC. When OC/EC is higher than POC/EC, SOC is formed in the atmosphere. These investigators indirectly inferred the amount of SOC by comparing observed ratios of OC/EC with expected ratios. Consequently, the presence of SOC was not directly measured. A method introduced by Castro in 1997, which assumed a minimum value of OC/EC that remained constant, has commonly been used in recent studies. The details of this method are described in Chapter 3.

1.3.4 Removal of Particulate Carbon in the atmosphere

Particulate carbon can be removed from the atmosphere by direct deposition. It may be scavenged in fog, rainwater, or snowflakes, which is called precipitation or wet deposition. When PC settles directly out of the atmosphere, the process is named dry deposition (Wesely et al., 2000). The magnitudes of these two methods vary depending on local climate (Baumgardner et al., 2002), physical and chemical properties of OC and EC, terrain and surface characteristics.

1.3.4.1 Precipitation

In areas with sufficient precipitation, removal of PC from the atmosphere is mostly dominated by wet deposition (Cerqueira et al., 2010). Wet removal rate of PC is strongly affected by the affinity of chemical composition of OC and EC with water. Particulate OC is highly (44–74%) water-soluble (Weber et al. 2008), but newly emitted EC is hydrophobic (Zuberi et al., 2005) even though BC acquire hydrophilic properties by chemical aging (Tritscher et al., 2011). Measuring wet deposition of OC and EC is crucial for the understanding of the global circulation, lifetime, and climatic forcing from organic compounds. Currently, a standard analytical method has not been developed for measuring OC and EC concentrations in precipitation. Various analytical methods have been considered for this purpose, but the feasibility of these methods on a global scale has not been assessed, yet.

1.3.4.2 Dry deposition

Until recently, the direct measurements available for OC were those related to precipitation (Raymond, 2005). Indirect estimates of dry deposition of OC have been reported elsewhere in Europe (Raymond, 2005), but few data exist for North America (Likens et al., 1983). Therefore, a reliable assessment of global and regional dry deposition of OC can contribute to our understanding of OC and its variation at regional scales.

The removal rate of dry deposition of EC strongly depends on its size. Extensive size distribution measurements operated in Denver showed that the geometric median diameter of the EC particles was 0.28 μm, which is around the center of the stable accumulation mode (Figure 1-1 shows the idealized particle distribution, and EC is in the center of all particles) (Huntziker et al., 1982). Thus, EC removal by dry deposition is expected to be small in amount, and the atmospheric lifetime of EC should be several days to several weeks depending on the meteorological conditions.
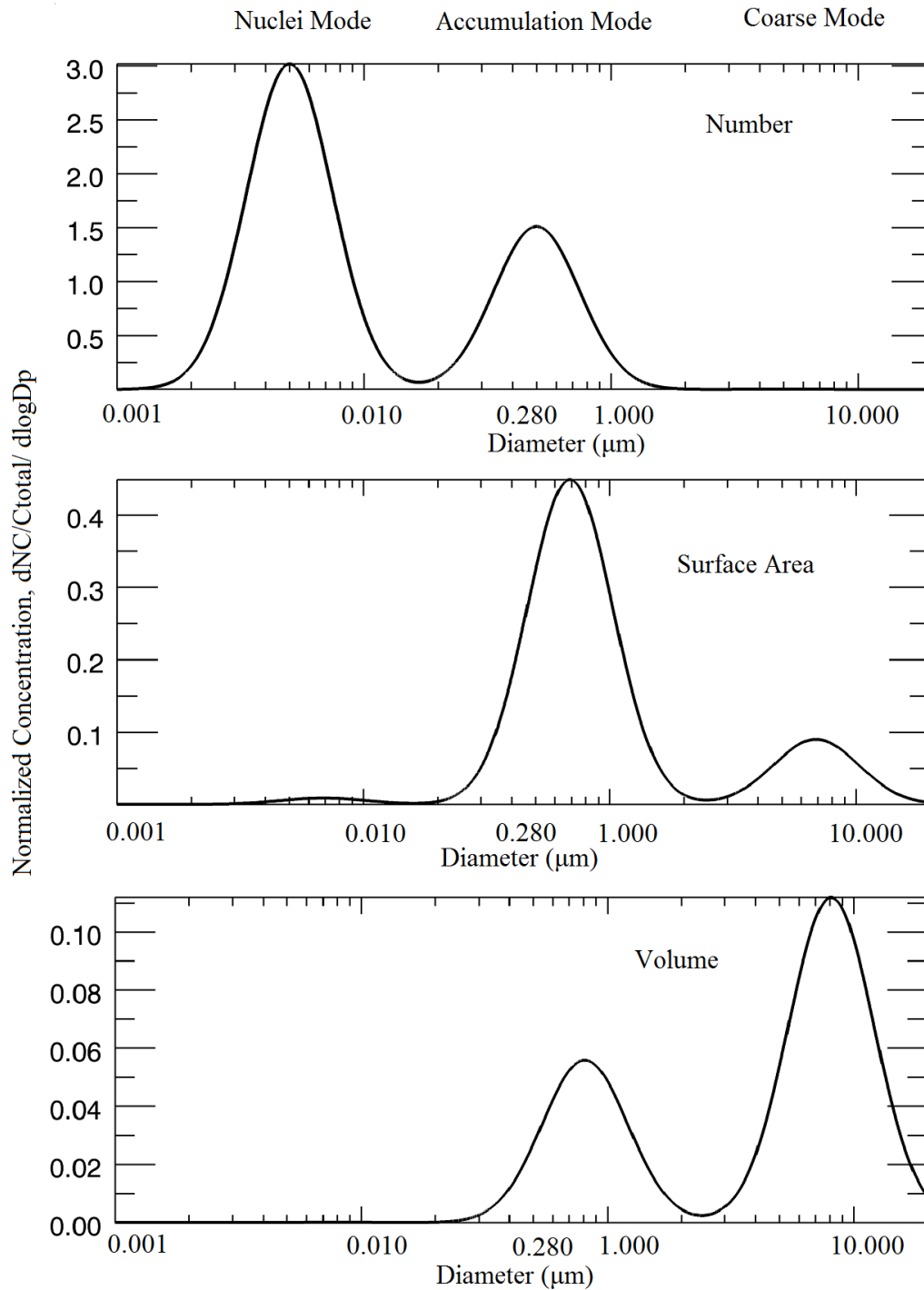
Figure 1-1 Idealized particle number, surface area and volume weighted size distributions.

Note that a logarithmic scale is used for particle aerodynamic diameter. (Kittelson, 1998)

1.4 Measurement of Particulate Carbon in the atmosphere

Total carbon (TC) can be easily determined from the final amount of carbon dioxide via thermal or chemical oxidation methods. Discriminating OC and EC is usually based on thermo-optical or thermo-chemical gas analysis. At present, several approaches have been developed to distinguish OC and EC. Commonly, EC is operationally measured as the component that does not volatilize in the first non-oxidation step of the analysis. OC is calculated as the difference between TC and EC (TC= OC+ EC).

Factors such as sampling artefacts can influence the quantification of OC (Salma et al., 2007). On one hand, quartz filter papers are used to capture particulate matter, as well as the gaseous OC present in the air. The measured OC concentrations will be enhanced because of the gaseous OC, which is known as a positive artefact. On the other hand, some semi-volatile components of OC possibly evaporate from the filter papers, resulting in a negative artefact which underestimates the OC concentration (Novakov et al, 2005). Processing filtered samples in an OC-free environment and quick filtration can reduce the uncertainty from sampling artefacts. Such influences are not negligible when a new experiment is designed for measurements.

Starting from the 1980s, scientists set up many experiments to characterize OC and EC in various areas around the world (Table 1-1). There are few measurements conducted in Canada so far. Most experiments focused on quantification of aerosol OC, EC and TC in different locations. Table 1-2 summarizes a selection of experiments done in North America and Europe. Aerosol samples from urban and rural areas were analyzed and found to have seasonal differences.

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Meteorological conditions also had an influence on the concentrations of EC and OC (not shown in table).

Quantifying concentrations of PC is comparatively harder in deposition samples than in aerosols due to factors related to sampling and analysis. These factors affect the comparability and reliability of datasets. Figure 1-2 lists the possible differences of methods to quantify OC and EC in sample collection, handling and analysis.

Table 1-1 Examples of experiments to characterize OC and EC around the world.

Location	Purpose	References
European Arctic	Size-segregated measurement of particulate elemental carbon	Heintzenberg, 1981
Los Angeles	Characteristics of particulate OC and EC concentration in atmosphere	Gray et al., 1986
Central Amazonia	Particulate carbon concentration in precipitation	Andreae el al., 1990
New England	Budget of Organic carbon	De Gouw et al., 2005
Nepal	Seasonal and elevational variation of EC in snow and ice	Kaspari et al., 2014
Northeastern USA	Wet deposition of OC sources	Ivarivska et al., 2017

Table 1-2 Examples of concentrations of Organic Carbon, Elemental Carbon and Total carbon in North America and Europe.

Location	Rural/Urban	Season	Year	Concentration (ug C m^{-3})			References
				OC	EC	TC	
Lennox, USA	urban	Summer	1984	6.3	1.7	8	Turpin et al., 1991
Pasadena, USA	urban	Summer	1984	12.1	2.5	14.6	
Azusa, USA	urban	Summer	1984	13.5	4.1	17.6	
Upland, USA	urban	Summer	1984	10.8	2.8	13.6	
San Bernardino, USA	urban	Summer	1984	8.0	1.4	9.4	
Birmingham, England	urban	Winter	1994	4.8	3.4	8.2	Castro et al., 1999
	urban	Spring	1994	4.8	1.4	6.2	
Areao, Portugal	rural	Winter	1993	6.8	1.7	8.5	
	rural	Spring	1994	1.9	0.8	2.7	
	rural	Summer	1994	1.0	0.3	1.3	
Birmingham, USA	urban	Summer	2002	3.15±0.35	2.48±1.14	5.63±1.49	Zheng et al., 2002
Cattle Creek, USA	rural	Summer	2002	0.67±0.08	0.50±0.20	1.17±0.28	
Gulfport, USA	urban	Summer	2002	1.17±0.13	0.75±0.49	1.92±0.62	
Oak Grove, USA	rural	Summer	2002	2.22±0.36	0.48±0.28	2.70±0.64	
Jefferson St., USA	urban	Summer	2002	1.87±0.23	1.75±0.70	3.62±0.93	
Yorkville, USA	rural	Summer	2002	1.03±0.11	0.74±0.27	1.77±0.38	
Thessaloniki, Greece	urban-traffic	Summer	2011	19.74±5.08	11.85±3.68	31.59±8.76	Samara et al., 2014
Thessaloniki, Greece	urban	Summer	2011	12.34±8.85	1.62±1.00	13.96±9.85	
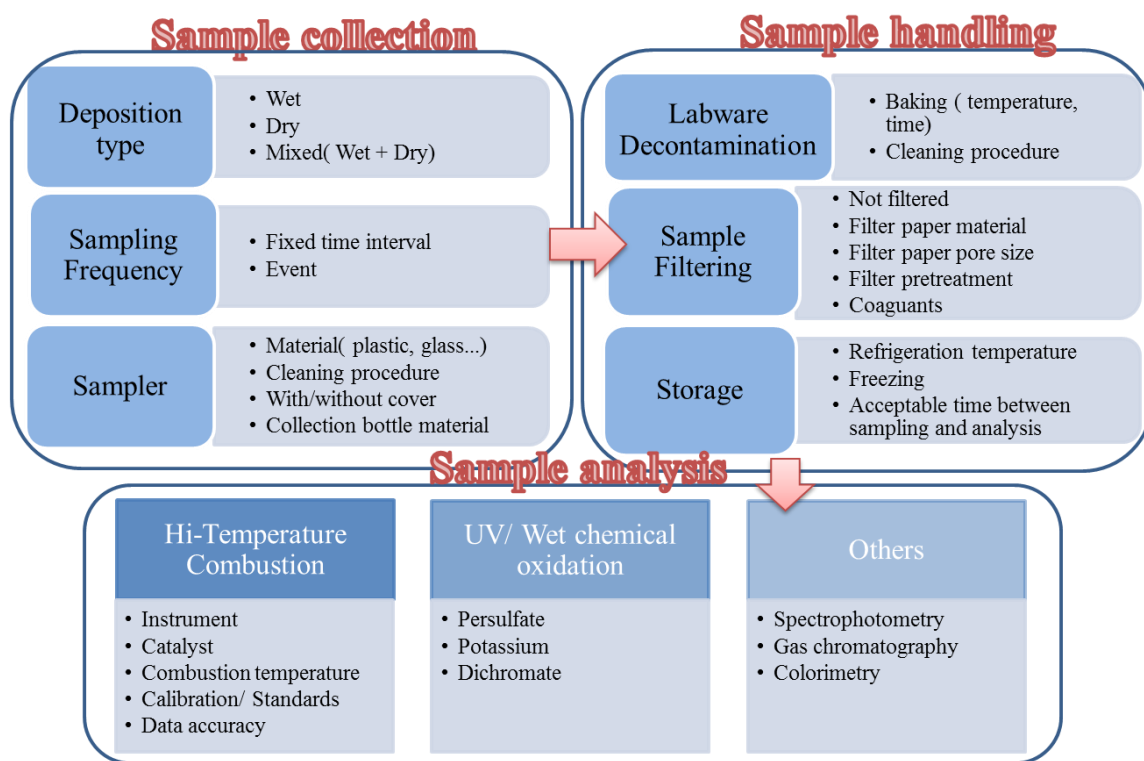
Figure 1-2 Factors affecting quantification of particulate carbon in deposition samples.

1.3.1 Particulate Carbon Sources

Particulate carbon matter is highly heterogeneous in time, space, and chemical and physical composition. Studies on the sources of anthropogenically-derived and naturally-derived particulate carbon are key to discerning how human activities impact the climate systems between atmospheric, terrestrial, and aquatic environment. Particle-phase carbon compounds have a variety of sources and may be emitted directly from combustion sources like biomass burning and fossil fuel emissions or formed from volatile precursors through secondary chemistry. In this chapter, due to the large amount of studies worldwide, the focus will be on studies in North America and at mid to high latitudes.

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1.3.1.1 Organic Carbon Sources

Major OC sources include 1) contemporary biogenic (e.g., vegetative emissions, biomass burning) and 2) anthropogenically-derived fossil fuel (e.g., burning of gas and diesel) sources (Lewis et al., 2004). Fossil fuels were formed tens of millions of years ago and therefore, lack active radio Carbon-14, which has a half-life of 5730 years (Currie et al., 1997). The signatures of Carbon-14 can therefore be used to estimate fossil fuel-derived contributions to OC. Contributions of biogenic and anthropogenic sources are highly seasonal to OC. At a southeastern US location, biomass burning accounted for over half of the OC concentrations in winter (NDJ), while SOC formation remained low. However, during the summer and fall periods, SOC contributed more than 40% of the OC concentration (Kleindienst et al, 2007).

1.3.1.2 Elemental Carbon Sources

Elemental carbon is directly generated from anthropogenic sources like incomplete combustion of biofuels or fossil fuels and partly from natural sources such as wildfires (Plaza et al., 2006). In the urban environment, combustion of gasoline and diesel from vehicles contribute most to EC, while in rural areas, the major contributions are from burning for land clearing, recreation, and residential heating. Although most global EC is from land, water and air transport contribute a significant amount to the atmospheric EC over oceans (Ramanathan et al., 2008). Based on the latest Canadian Elemental Carbon Inventory in 2015 (Figure 1-3) (ECCC, 2015), non-industrial sources (e.g., power generation and residential home heating) and off-road transport account for over 60% of total EC emissions.
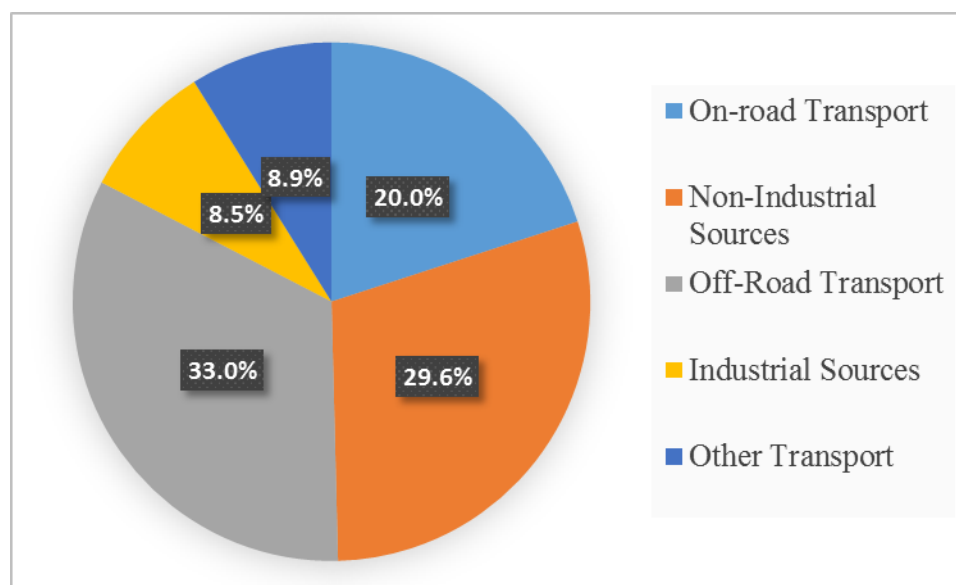
Figure 1-3 Elemental carbon emissions by source type in 2014 (ECCC, 2015).

1. 5 Models of Particulate Carbon in the atmosphere

Simulating aerosols is the focus of a significant body of atmospheric research. Projects such as AEROCOM assemble a large number of observations and global models to document and compare results of the global aerosol modelling (Koffi et al., 2016). However, current models have difficulties capturing the variability of PC because of the complicated aerosol processes involved, the lack of in-situ data, and unknown background sources.

To date, models like the Community Atmosphere Model version 5.1 (CAM5), which can tag EC sources by region and type, have been employed to estimate the relationship of atmospheric EC and its deposition over western North America with low bias (Ma et al, 2013). However, OC, especially SOC, is still difficult to simulate and not able to be imported as a boundary source in

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models. This is not due to the negligible magnitude of these atmospheric compounds, but, rather, due to a lack of measurements and quantitative knowledge of emissions.

1.6 Relationship between Elemental Carbon and Sulfate

Both PC and sulfate (SO_4) aerosols play an important role in balancing the solar radiation absorbed by the atmosphere. EC and SO_4 are two major fractions of anthropogenic aerosol production in the fine particle size range (Finlayson-Pitts and Pitts, 1986). These two components also share the same production mechanisms in some areas (Orgen and Charlson, 1984), with a significant correlation of a typical mass ratio for a particular region. The role of EC is thought to be a potential catalyst in atmospheric sulfur and possibly nitrogen aerosol formation. The resulting aerosols have a significant impact on acidic precipitation (Wolff et al., 1981). Experimental data in Hungary showed that in summertime, sulfate and EC are mixed with no correlation (not shown), while in winter (Figure1-4) an important fraction of sulfate particles was internally mixed with EC (Meszaros and Meszaros, 1989). Internal mixing in Figure 1-4 is evident in sulfate less than 8 $\mu g/m^3$ for both daytime and nighttime. Figure 1-4(a) shows that sulfate in daytime in winter correlates with the concentration of EC, and Figure 1-4(b) shows that formation of sulfate during nighttime has a close relation with the presence of EC both for foggy and non-foggy conditions. The relationship between EC and sulfate has not been examined in Canada and is the focus of this study.
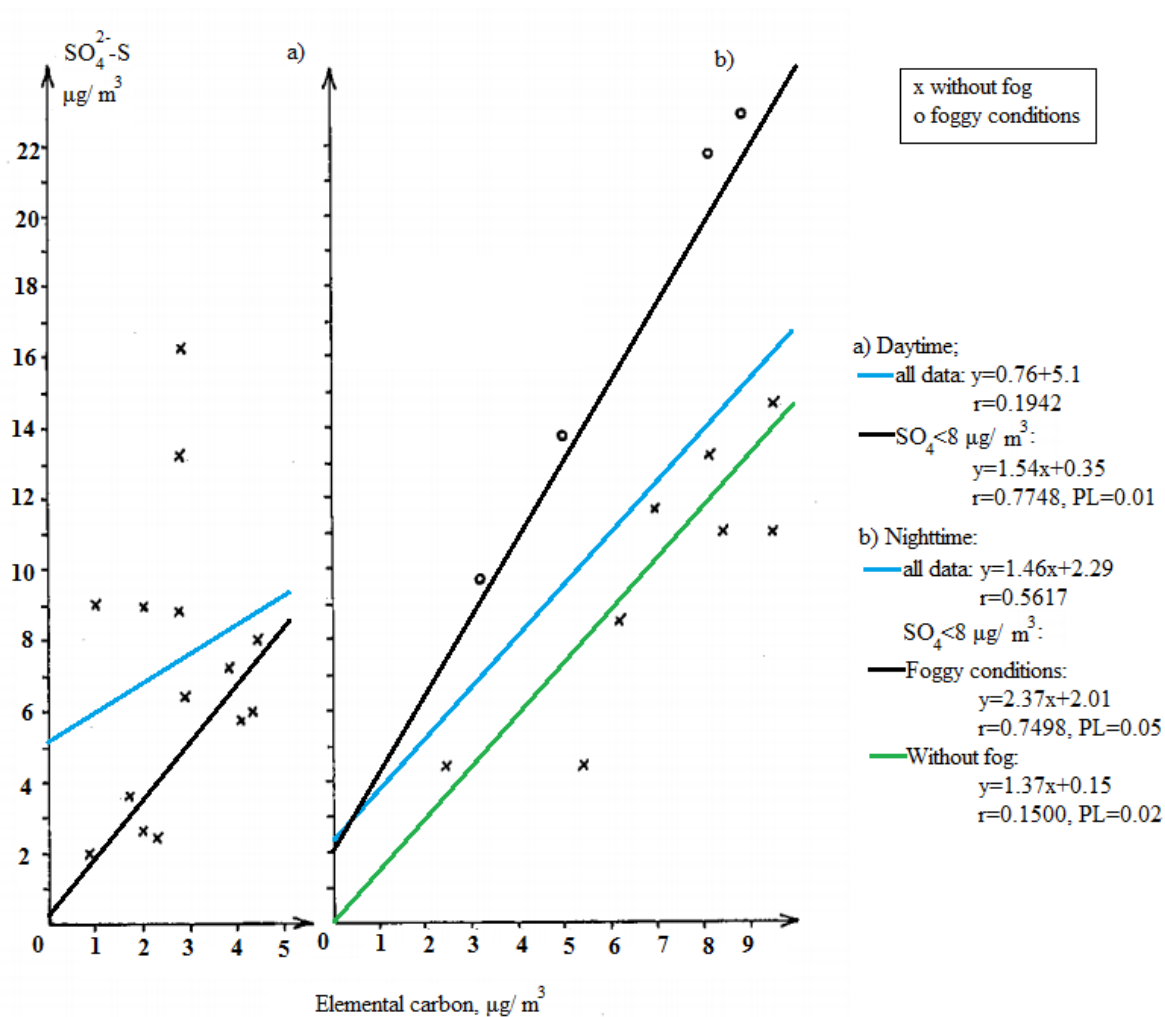
Figure 1-4 Relationship of the mass concentration of elemental carbon and sulfate particles in a suburban environment in Hungary in winter. (a) Daytime; (b) Nighttime (without fog and foggy conditions) (Meszaros and Meszaros, 1989). Abbreviation: y, SO₄; x, Elemental carbon; r, correlation on coefficient; PL, probability level of significance.

1.7 TC, EC and OC in Rural and Urban Alberta

The previous sections 1.1-1.4 showed that rural and urban particulate carbon, EC and OC have been informative to understand the sources for aerosol carbonaceous matter in the atmosphere. Only a few studies have been done around the world related to the particulate carbon in dry deposition and precipitation (e.g. Cerqueira et al., 2010; Zhang et al., 2015; Kuchiki et al., 2015), but no study has been conducted in Canada.

There are several expectations for sources of OC and EC in our study for Kananaskis and Calgary, which encompass the continental rural and relatively unpolluted urban environment:

Both Locations:

1. Particulate carbon from vehicle exhaust exists thorough the year in both rural and urban locations.

2. The organic component of biological emissions occur only in summer. This is expected to cause high OC/EC ratios since no EC is emitted from vegetation.

3. Biomass burning happens both in winter and summer, predominantly in Kananaskis associated with recreation and tourism, especially in the evenings. This is expected to result in low OC/EC ratios.

4. Sources from long-range transport are expected to impact both locations simultaneously.

5. A lower boundary layer at night increases PM concentration and a higher boundary layer in the day lowers the concentration at both locations.

6. In both locations, OC is much more easily removed by precipitation than EC. This occurs because freshly released EC and OC are hydrophobic (Zuberi et al., 2005) but OC is more easily oxidized to form organic acids which are soluble and hydrophilic (Petters et al., 2006).

Calgary:

1. Vehicle exhaust is the dominant source of carbon in Calgary due to the lack of significant urban industrial activities.

2. A morning and evening peak in particulate matter is expected due to higher traffic volumes.

3. More EC from biomass burning at night from firepits and/or woodstoves would lower the OC/EC ratio.

4. Pollutants from rural industrial activities from upstream oil and gas exploration and production can be transported into the city and influence the carbon concentration in conjunction with aerosol SO_4 (Norman et al., 2004).

1.8 Objective

The present study aims to increase the current knowledge about the cycle of carbonaceous matter in the atmosphere in the southern Alberta region. During the last two decades, a significant number of studies were performed on this topic, with a focus on aerosol composition and the origins of PM. However, due to the difficulty of monitoring carbonaceous particles and their sources, a full understanding of the composition and transport mechanism has not yet been

achieved. A four-year IMPROVE program (Interagency Monitoring of Protected Visual Environments) to measure chemistry components in aerosol at the same Kananaskis site as our samples has created a large dataset, which has not yet been analyzed and published and to which we are able to compare our precipitation data. In addition, current carbon inventories are far lower than the actual carbon sources, which calls attention to those unreported sources. Removal of PC from the atmosphere is another step in the carbon cycle that will add more information to global climate models relating soil, ground water, and air.

The overall objectives of this study were to characterize particulate OC and EC depositions at two locations in western Canada to investigate the differences between PC in urban areas and rural areas. Chapter Two reviews background data from the IMPROVE network for aerosol OC and EC. Chapter Three describes the methods used to measure PC, cations and anions in precipitation and dry deposition samples. It also includes the methods to estimate SOC from OC/EC values. Chapter Four presents measurements of precipitation and dry deposition events at an urban location (Calgary) and a rural location (Kananaskis). Chapter Five presents a discussion of historical compared to our measured data sets. The last chapter concludes the findings and recommendations for OC and EC in southwestern Alberta.

Chapter Two: Improve Data Review

2.1 Introduction to IMPROVE network

Under the Clean Air Act, the US Congress recognized the value to establish current visibility conditions, track changes in visibility, and determine causal mechanisms for visibility impairment in national parks and wilderness areas. The Interagency Monitoring for Protection of Visual Environments (IMPROVE) program (http://vista.cira.colostate.edu/improve/) was designated as a visibility monitoring network and conducted a long-term monitoring campaign across the United States over the past thirty years. The Biogeoscience Station of the University of Calgary in Kananaskis was chosen as the background site to compare the visibility data with the US sites. The IMPROVE program monitors current visibility and aerosol conditions in mandatory areas; identifies chemical species and emission sources; records long-term trends in visibility; and provides regional haze monitoring in sampling areas.

Barrier Lake station (51.029° N, 115.0336° W, elevation of 1391 m), which is located at the north end of Kananaskis Country in Alberta, Canada, was one of the IMPROVE network monitoring sites following standard operating protocols (http://vista.cira.colostate.edu/Improve/ sops/). It was sponsored and run by Environment Canada between January 2011 to October 2014. Figure 2-1 shows the map of the IMPORVE network and the location of Barrier Lake station (marked yellow). The dataset includes atmospheric organic and elemental carbon collected using quartz filters with a PM2.5 cut-point cyclone head. Total PM2.5 and PM10 were also collected on Teflon filters. This dataset obtained from Barrier Lake station is the only continuous interannual

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monitoring resource for carbon analysis in Alberta and Canada. Understanding the importance of carbonaceous aerosols will help figure out the background of dry deposition and precipitation for particulate carbon in our experiment.

Figure 2-1 Map of IMPROVE Network. Barrier Lake station is marked yellow on the map.

(http://views.cira.colostate.edu/fed/SiteBrowser/Default.aspx?appkey=SBCF_Default)

2.2 Experimental Approach

IMPROVE samples for PM2.5 and PM10 were collected every three days and were of 24-hour duration. Organic and elemental carbon (OC and EC) are measured on quartz–fiber filters (25 mm diameter, Pallflex® Tissuquartz, Pall Corporation, Port Washington, NY) in the IMPROVE sampler. The sampler drew air at a flow rate of 16.9 L/min at standard temperature and pressure through a PM 2.5 size-selective inlet.

The Desert Research Institute (DRI) routinely analyzed IMPROVE samples using the DRI thermal/optical reflectance (TOR) carbon analyzer as described for our dry deposition and precipitation samples in Chapter 3 section 3.3.3.1.

2.3 Results

2.3.1 PM2.5 and PM10 Concentrations and Ratios

The daily average concentration of PM2.5 varied from 0.2 to 21.7 $\mu g/m^3$ and that of PM10 varied from 0.4 to 33.2 $\mu g/m^3$, respectively (not shown). The seasonal average concentrations of PM2.5 and PM10 for the period analyzed were both highest in fall (September, October and November (SON)) with the concentrations of PM2.5 and PM10 reaching 6.0 $\mu g/m^3$ and 9.4 $\mu g/m^3$ respectively and lowest in spring (March, April and May (MAM)) reaching 1.5 $\mu g/m^3$ and 2.9 $\mu g/m^3$, respectively, for PM2.5 and PM10 (Figure 2-2). The seasonal ratio of PM2.5 and PM10 varied around 1.6 with no significant seasonal variability.
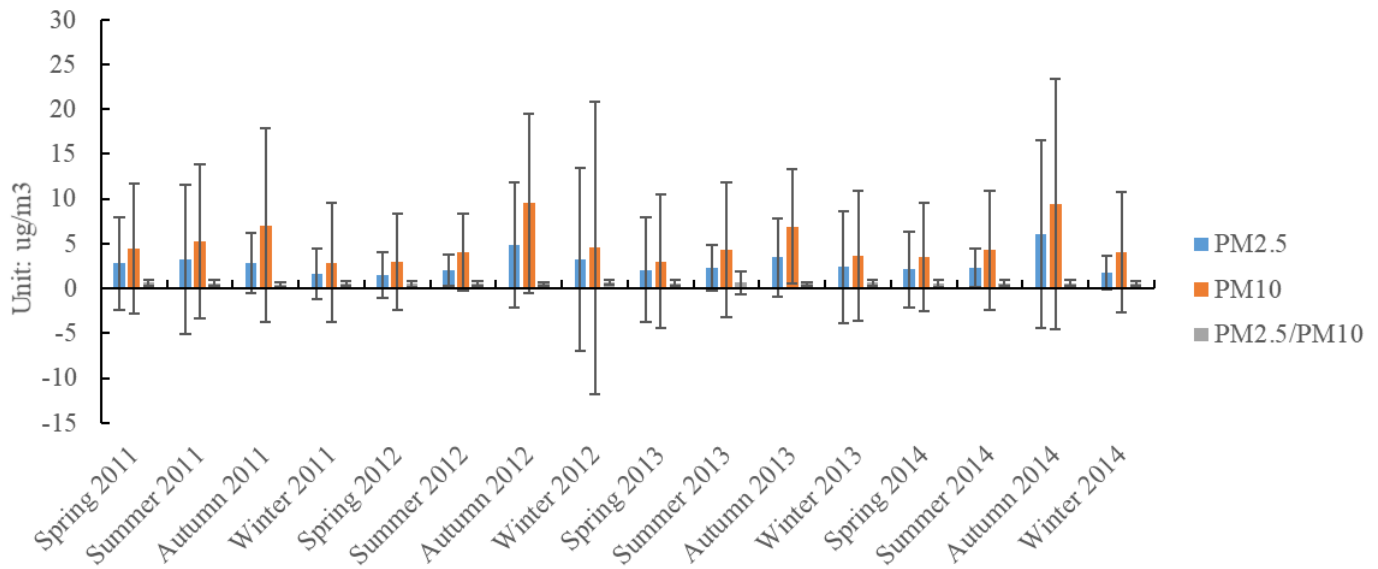
Figure 2-2 Seasonal variation of PM2.5, PM10, and PM2.5 to PM10 ratio at Barrier Lake for 2011-2014.

2.3.2 Concentrations and Seasonal Variations of TC, OC and EC

Figures 2-3, 2-4, 2-5 summarized the monthly mean values for OC, EC and TC in PM2.5 at Barrier Lake, Kananaskis. From 2011 to 2014, both OC and EC presented a high four-year average concentration (highest at 0.9 μg /m³ for OC and 0.7 μg /m³ for EC) in summer and comparatively stable in other seasons. The four-year monthly average concentrations of OC and EC were 0.4 ± 0.3 μg/ m³ and 0.3 ± 0.2 μg/ m³ respectively (Figure 2-3, 2-4). Organic carbon and Elemental carbon both had an unusual lower value of 0.04 ± 0.03 μg/ m³ and 0.03 ± 0.02 μg/ m³ in February 2013 (not shown), which will be discussed in Chapter 5. The fraction of TC in PM2.5 varied with the change of seasons as 0.2 ± 0.1 (Figure 2-5). Seasonal trends of TC in PM2.5 showed a higher fraction in the middle of winter and the beginning of summer and lower fraction in the

beginning of winter and mid spring. Although in summer, the amount of TC (OC+EC) increased sharply compared to other seasons, the contribution of TC to PM2.5 stayed at a low level of 0.2 ± 0.1 throughout the year. This means other components increased in summer as well as carbonaceous matter. Since the seasonal ratio of PM2.5 and PM10 had little variation during the sampling period (Figure 2-2), the additional contributor to PM is likely to include both PM2.5 and PM10.
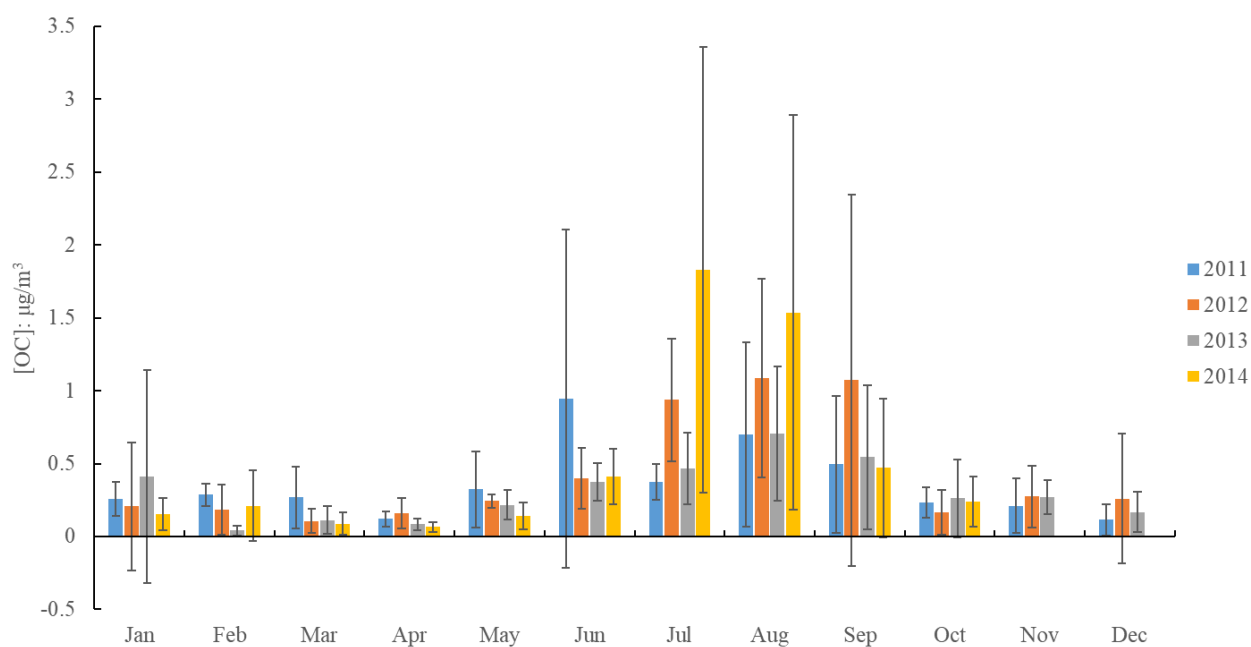
Figure 2-3 Monthly variation of Organic Carbon (OC) for of Barrier Lake 2011-2014 for PM2.5.
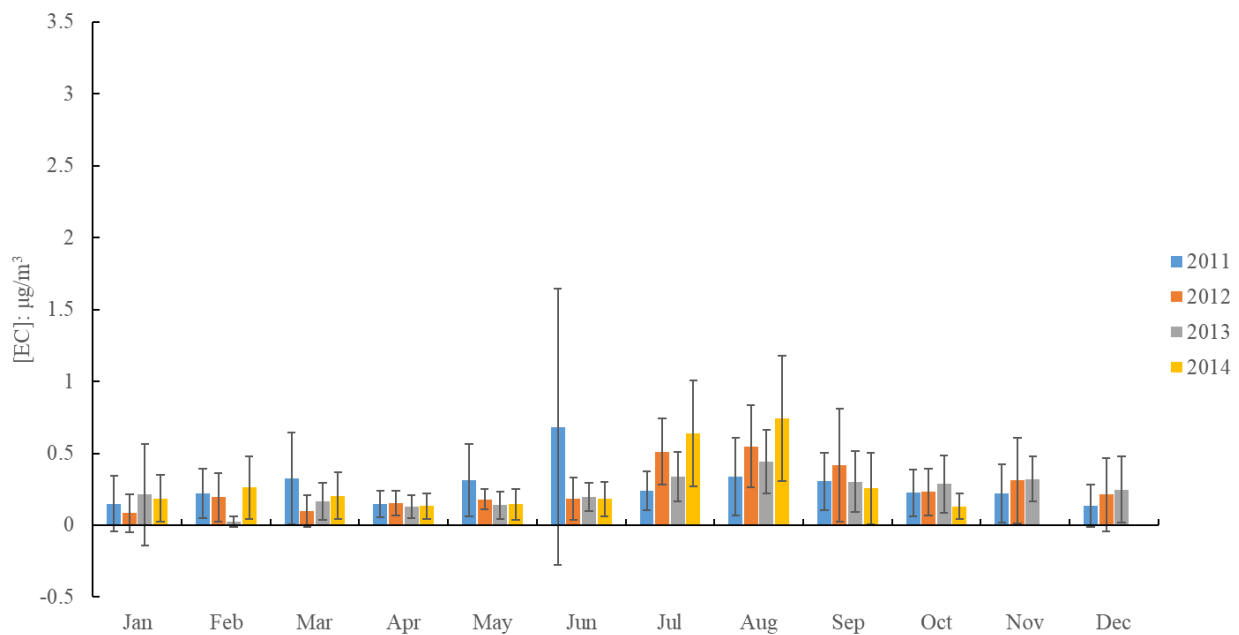
Figure 2-4 Monthly variation of Elemental Carbon (EC) of Barrier Lake for 2011-2014 for PM2.5.
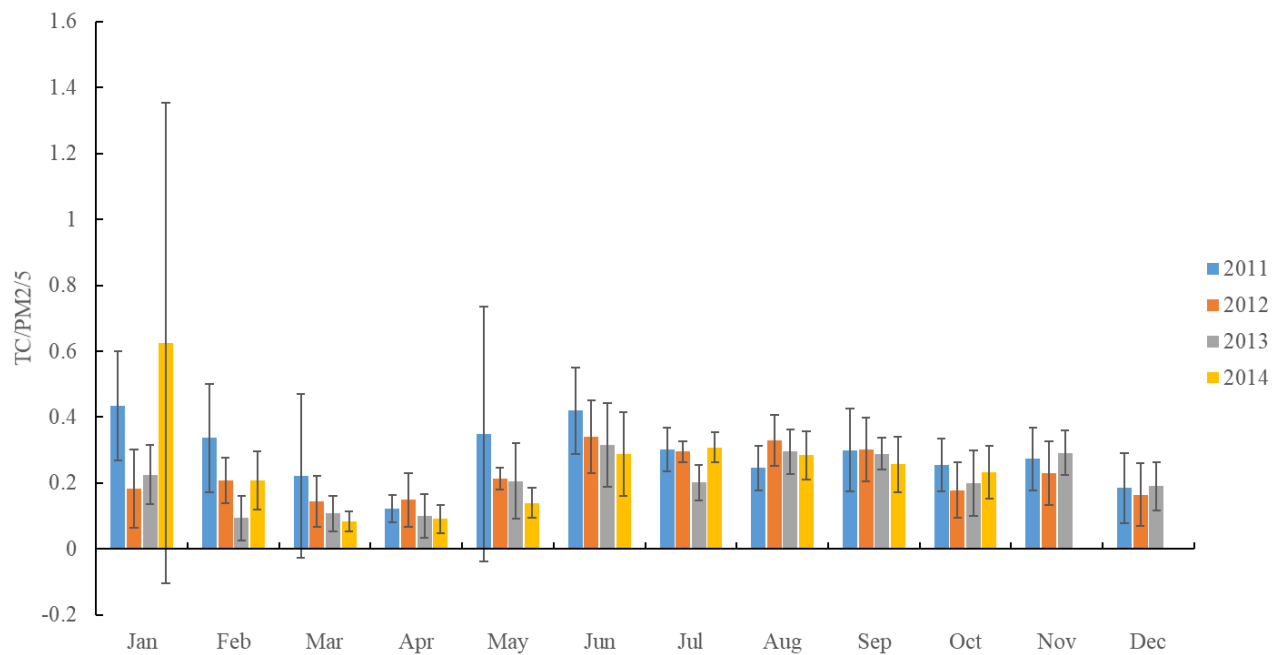
Figure 2-5 Monthly variation of Total Carbon (TC) of Barrier Lake in PM2.5 for 2011-2014.

Consistent with the percentage of TC in PM2.5 (Figure 2-5), OC/EC (Figure 2-6) is uniform throughout these four years with low variabilities. An exception is that, OC/EC have a relatively higher variability in January (3.3 ±3.6 µg/ m^3) and March (1.5 ±2.4 µg/ m^3) than other months (1.7 ±1 µg/ m^3).
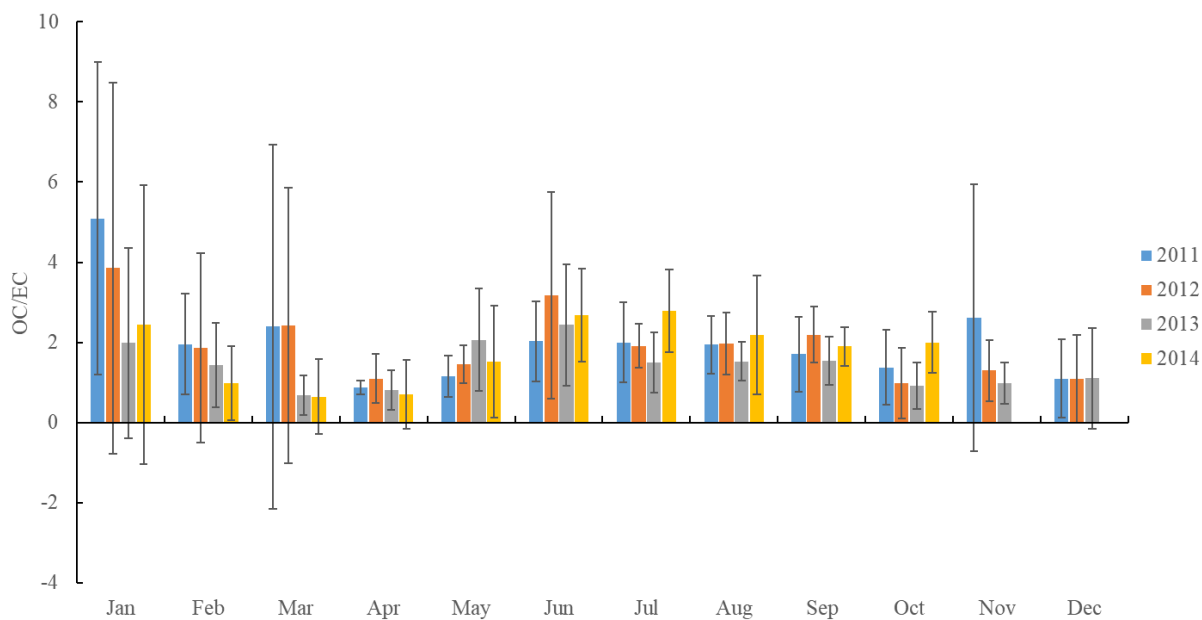
Figure 2-6 Monthly variation of OC/ EC for 2011-2014 for PM2.5.

2.3.2 Eight carbon fractions

All eight carbon fractions examined had a trend of high concentrations of 0.7 μg/ m^3 in fall and low concentrations of 0 μg/ m^3 in summer (Figure 2-7 and Figure 2-8). It is interesting to note that for elemental carbon fractions, EC1 varied with season more obviously than the other two EC fractions. The variation of EC3, which has the highest temperature of all EC components, can hardly be observed since its concentration was as low as 0 μg/ m^3 (Figure 2-7). Of the organic carbon fractions, OC3 is most sensitive to the seasonal changes while OC1 stays at a low concentration (0.02 μg/m^3) during the whole period. The average abundance of carbon fractions (Figure 2-9) shows that EC1 and OC3 are the major two components of carbon fractions.
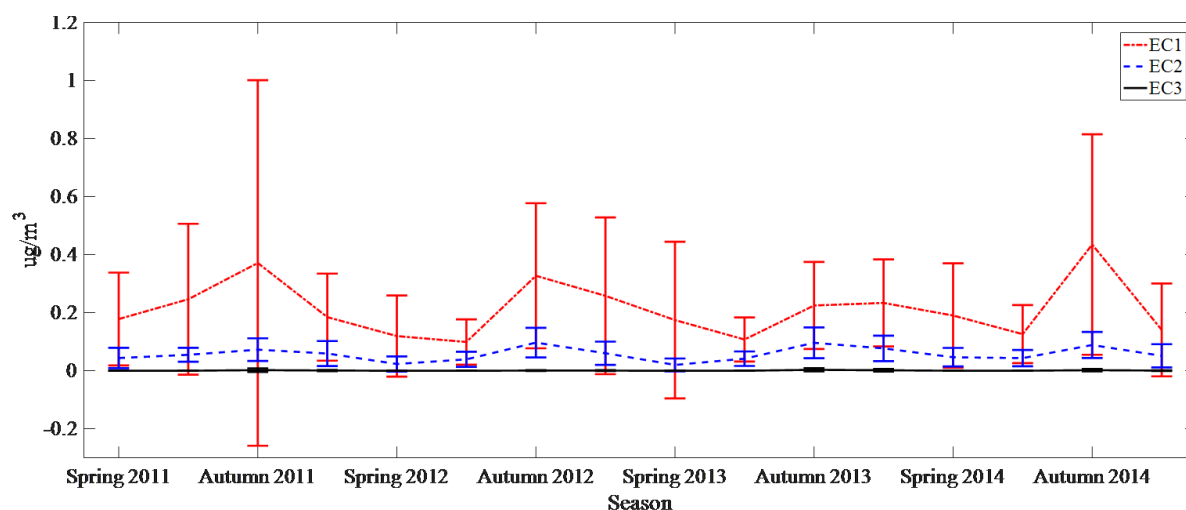
Figure 2-7 Seasonal variation of elemental carbon fractions in PM2.5 for 2011-2014.
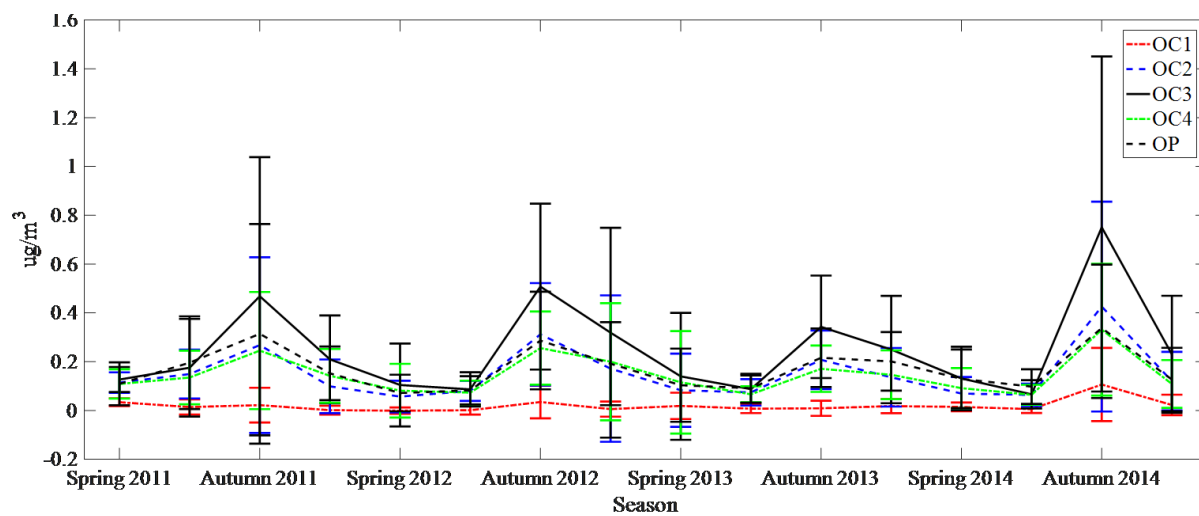
Figure 2-8 Seasonal variation of organic carbon fractions in PM2.5 for 2011-2014.
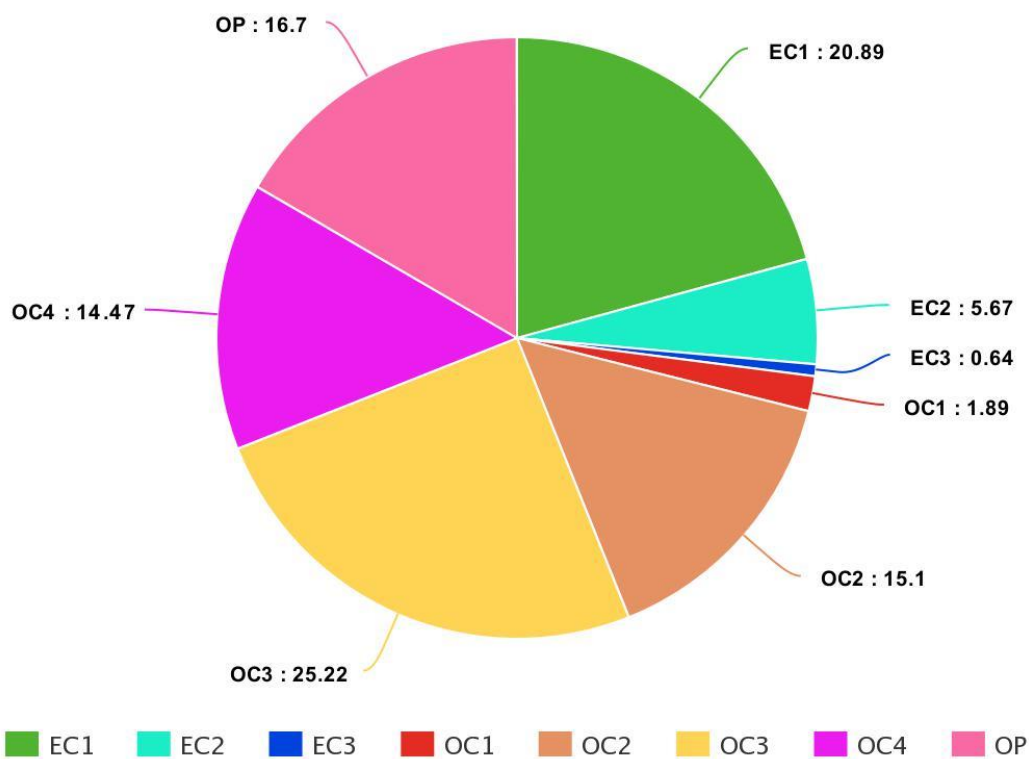
Figure 2-9 Average abundance of carbon fractions in percentage (%).

Chapter Three: Methods

3.1 Study Sites

Two study sites, Barrier Lake and Calgary in South Alberta, Canada, were chosen to analyze the carbonaceous particles in rural areas and urban areas, respectively.

3.1.1 Locations

Barrier Lake is located in the Kananaskis Valley in the front ranges of the Rocky Mountains (51° 2'N, 115° 3'W), approximately 86 km west of the largest nearby major city of 1.2 million, Calgary, Alberta (Figure 2-1). The Barrier Lake station sits about 200 meters southeast of Highway 40 (Kananaskis Trail) and about 9 km south of the Trans-Canada Highway. Highway 40 was estimated to have an Average Annual Daily Traffic (AADT) of 640 and an Average Summer Daily Traffic (ASDT) of 780 in 2016 (Government of Alberta ministry of Transportation, 2017). The Trans-Canada Highway close to the Barrier Lake station was estimated to have an AADT of 1230 and an ASDT of 1480 in 2016. At the station, propane is used for heating. Barrier Lake site is relatively remote from large transport sites like bus stations or parking lots, communities, and point source emissions.

University of Calgary (51° 4'N, 114° 7'W) is in the northwest sector of the City of Calgary, Alberta. Samples were collected on the rooftop of Science B building at the main campus of the University of Calgary (Figure 2-2), at a height of about 20 meters. The building is about 420 meters

west of Crowchild Trail, a major highway of the city with an Average Annual Weekday Traffic

(AAWT) of 79,000 (The City of Calgary, 2017). Two roads, 32 Ave (with an AAWT of 22,000)

and 24 Ave (with an AAWT of 12,000) lie on the northern and southern side of the campus.
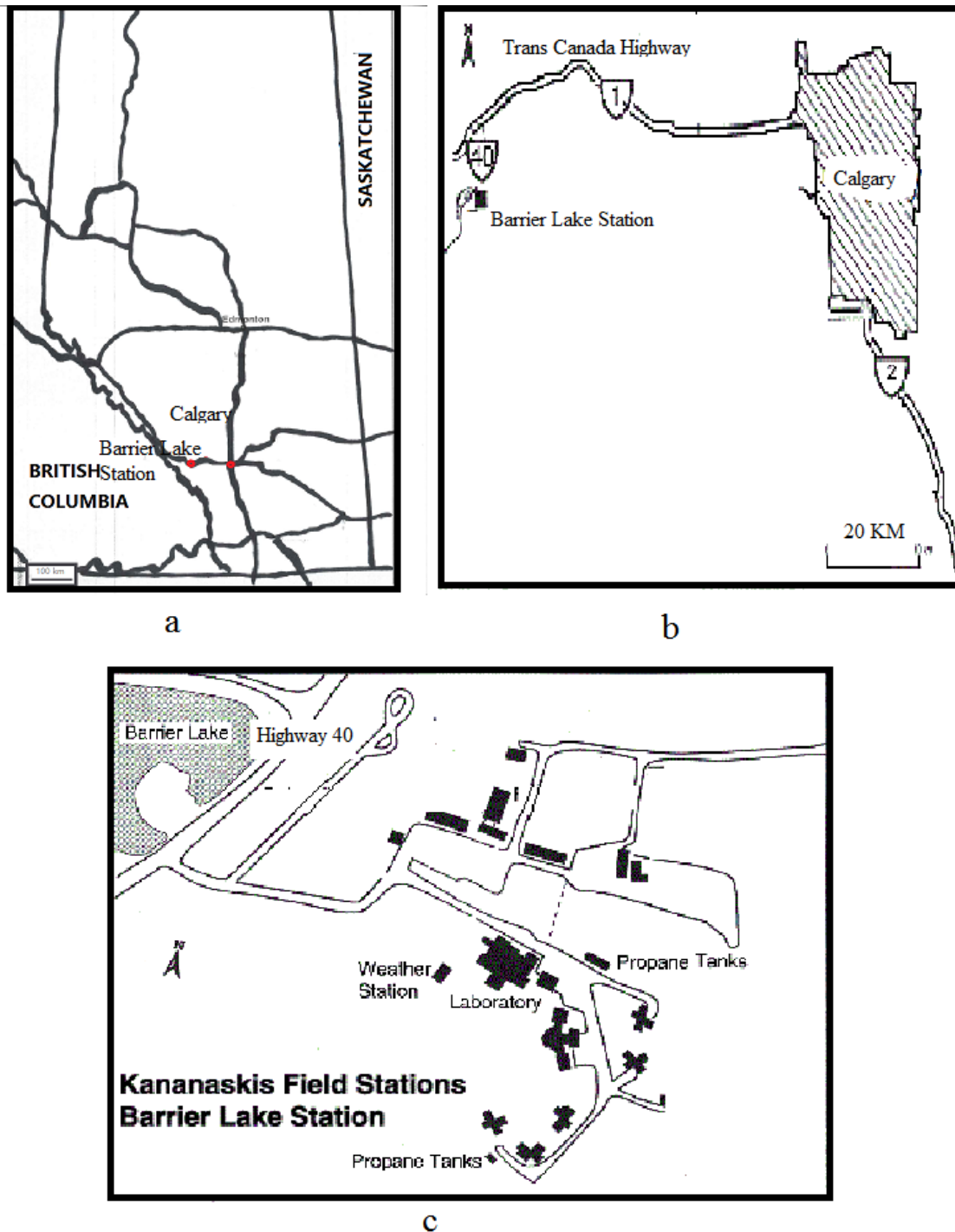
Figure 3-1 Map of Barrier Lake station. (a) A map of Alberta, where Barrier Lake station and the University of Calgary are marked red; (b) A map of locations of the Barrier Lake station and Calgary; (c) Structures at the Barrier Lake station.
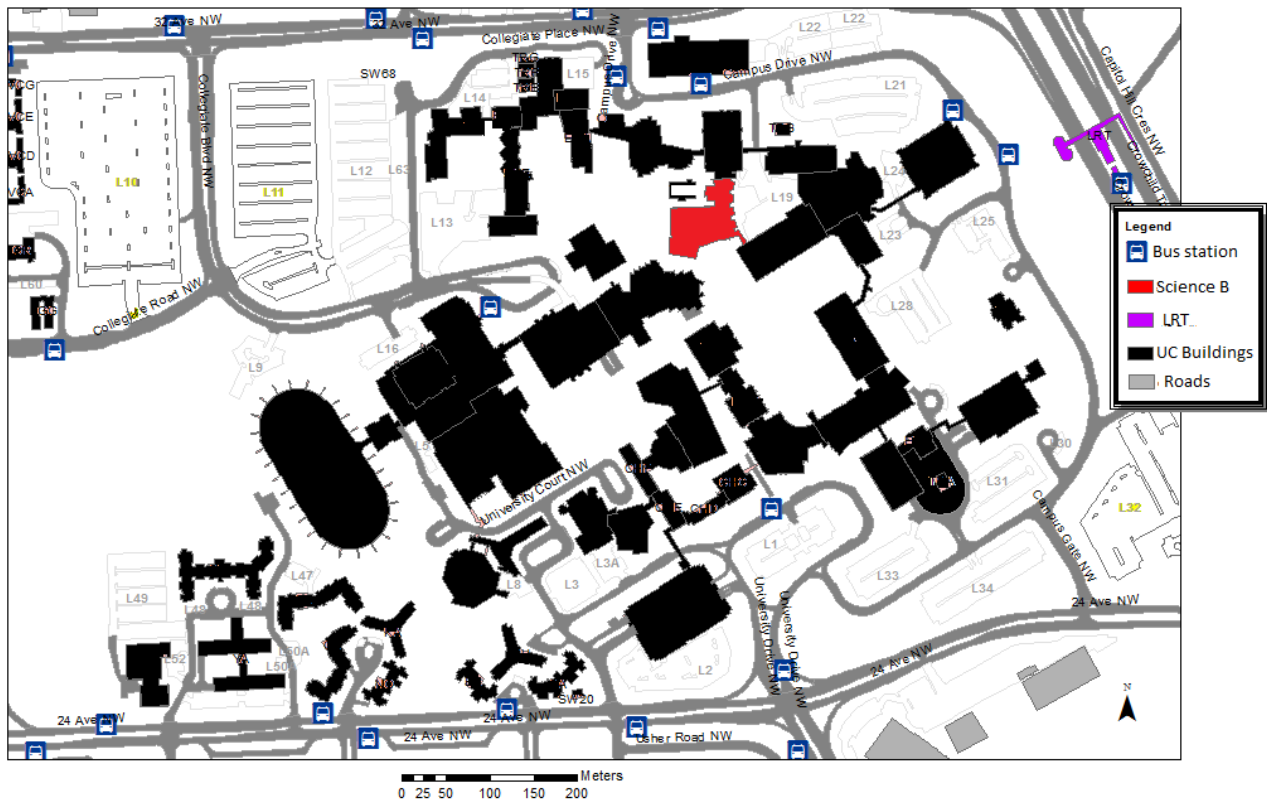
Figure 3-2 Map of University of Calgary (http://wcmdm7.ucalgary.ca/map/). Sampler sits on the roof top of Science B, about 20 meters above ground.

3.1.2 Climate

Southern Alberta has a transitional climate between cordilleran and continental. In this study, we define the four seasons as spring (MAM), summer (JJA), autumn (SON) and winter (DJF). Based on the historical weather data (Government of Canada, 2017), Barrier Lake has an average winter temperature at around -10℃ and summer temperature at around 15℃, while Calgary has an average at around -8℃ in winter and at around 17℃ in summer. Frequent Chinook events during the winter raise temperatures at these two locations above freezing causing snow to

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melt. Abnormal warm days with high precipitation amount sometimes happen in summer. Freezing temperatures can occur every month of the year. Calgary and Barrier Lake have similar climate patterns. Monthly precipitation for Calgary and Barrier Lake sites are shown in Figure 3-3 (CRAZ program and **http://vista.cira.colostate.edu/Improve/monitoring-site-browser/**). The relative humidity (RH) in Calgary is about 10% lower than that in Barrier Lake. The wind speed at a height of ten meters in Barrier Lake is around 10 km/h slower than that in Calgary. Figure 3-4 and Figure 3-5 presents the wind rose diagrams for Barrier Lake and Calgary during the studied period. South winds at a low speed of 0.5 to 2.1 m/s (1.80 to 7.56 km/h) dominated in Kananaskis. Comparatively high winds with an average of 3.52 m/s (12.67 km/ h) occurred in Calgary, of which the majority was west winds.
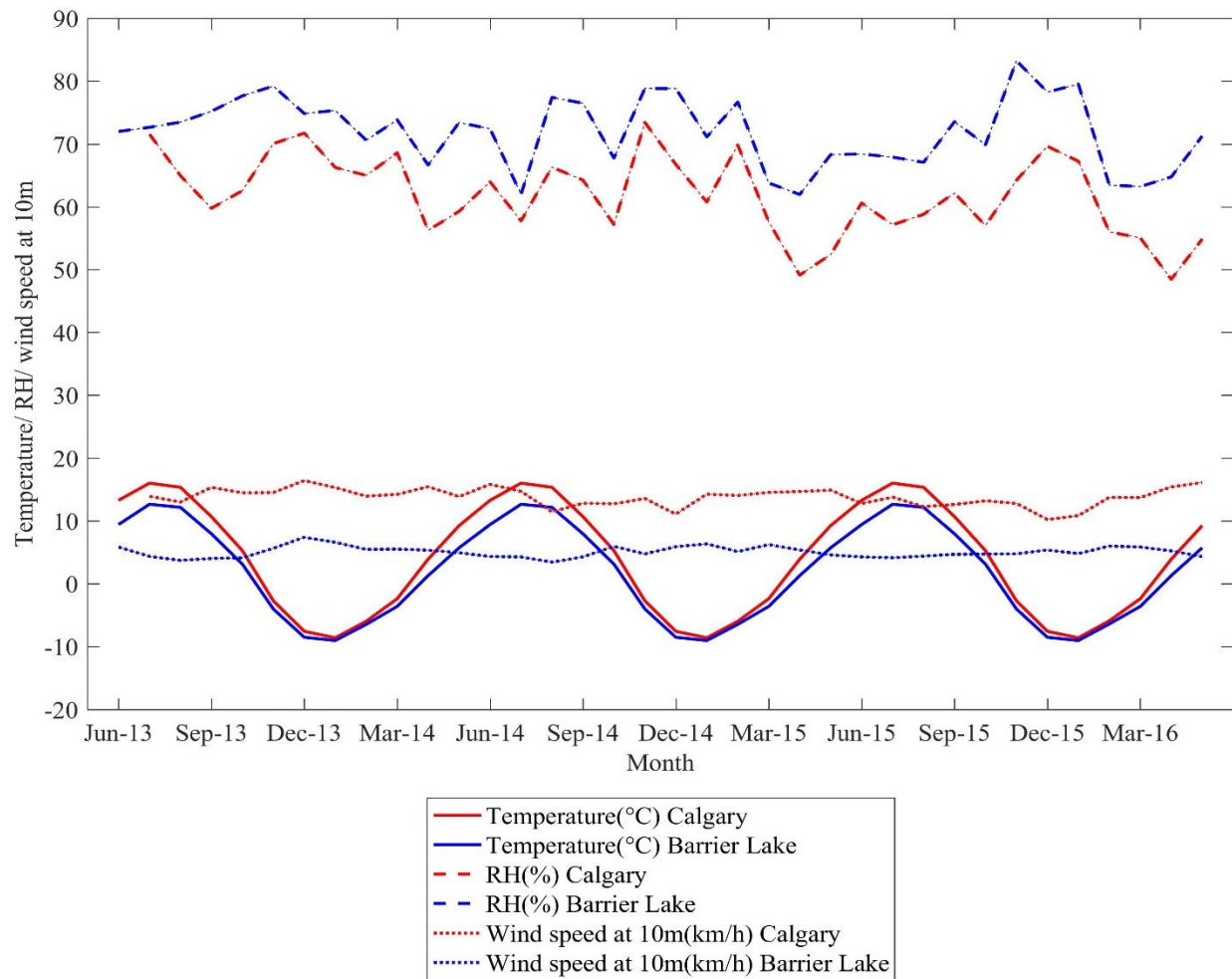
Figure 3-3 Daily average meteorological conditions of Calgary and Kananaskis, including temperature, relative humidity(RH), and wind speed at 10 meters.

(http://vista.cira.colostate.edu/Improve/monitoring-site-browser/)

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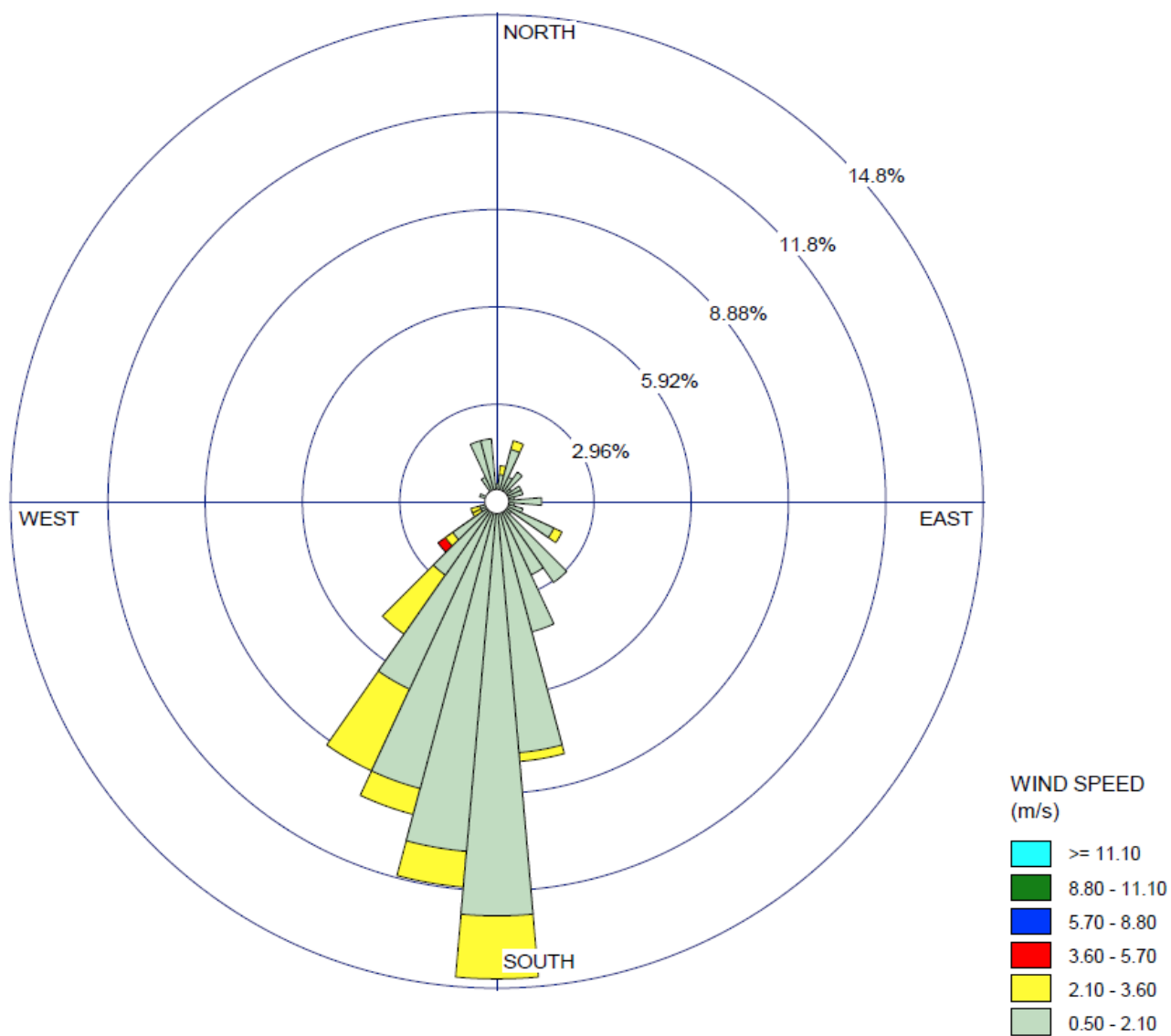
Figure 3-4 Daily wind rose diagram for Kananaskis during the studied period.

(Data source: https://agriculture.alberta.ca/acis/alberta-weather-data-viewer.jsp)
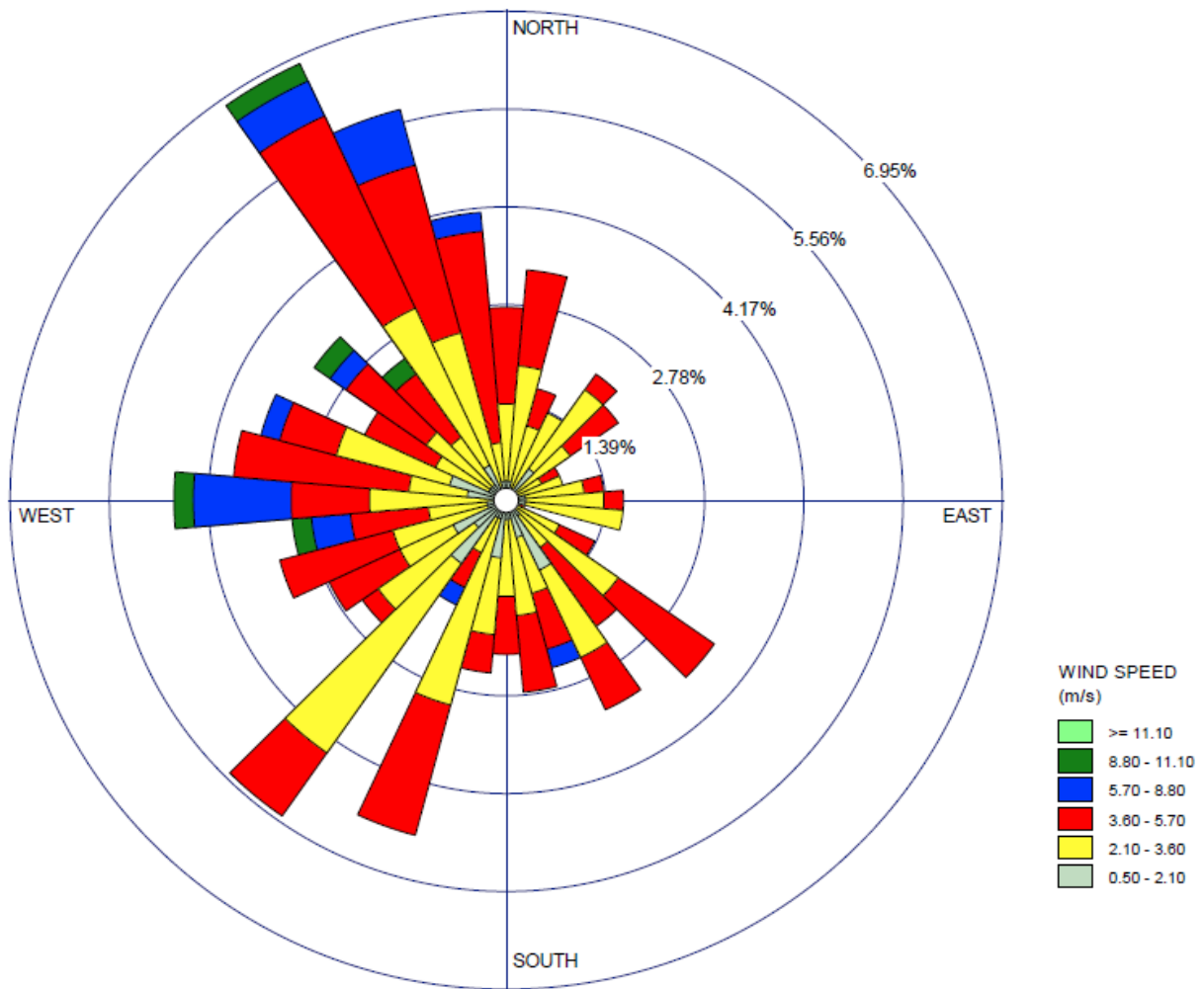
Figure 3-5 Daily wind rose diagram for Calgary during the studied period.

(Data source: https://agriculture.alberta.ca/acis/alberta-weather-data-viewer.jsp)

3.1.3 Air Quality Data

Hourly air quality data provided by Calgary Region Airshed Zone(CRAZ) from 1st July 2016 to 31st July 2017 is used in this thesis. Air quality data is analyzed to identify ambient air

quality issues in Calgary and assist in understand in major factors affecting particulate carbon deposition. Data of Oxides of Nitrogen (NO_x), Particulate Matter (PM), and Sulphur Dioxide (SO_2) from Calgary Southeast and Calgary Northwest stations are used to distinguish oil and gas emission events that may affect our sampling results.

Thermo Environmental Instruments model 42i, Sharp 5030, 43i, and 48i were used at these two monitoring stations for NO_x, PM, SO_2, and CO at a sampling height of 4 meters.

3.2 Sample Collection

From July 2016 to June 2017, dry deposition, and wet deposition (rain and snow) samples were collected on the rooftop of Science B of the University of Calgary and the Barrier Lake station, Alberta, Canada.

A sampler was constructed with an open-mouth plastic funnel mounted on a one-liter plastic collection bottle, shown in Figure 3-6. During each collection, a squirt bottle with 50 mL Deionized-distilled (DD) water was used to wash off particles on the funnel. The flow was shown in Figure 3-6 to ensure that all the particles on the inner surface of the funnel were washed off. Immediately after the collection, samples were sealed to prevent evaporation and then transferred to a refrigerator set at 4 °C at the Isotope Science Laboratory (ISL) at the University of Calgary for further processing.
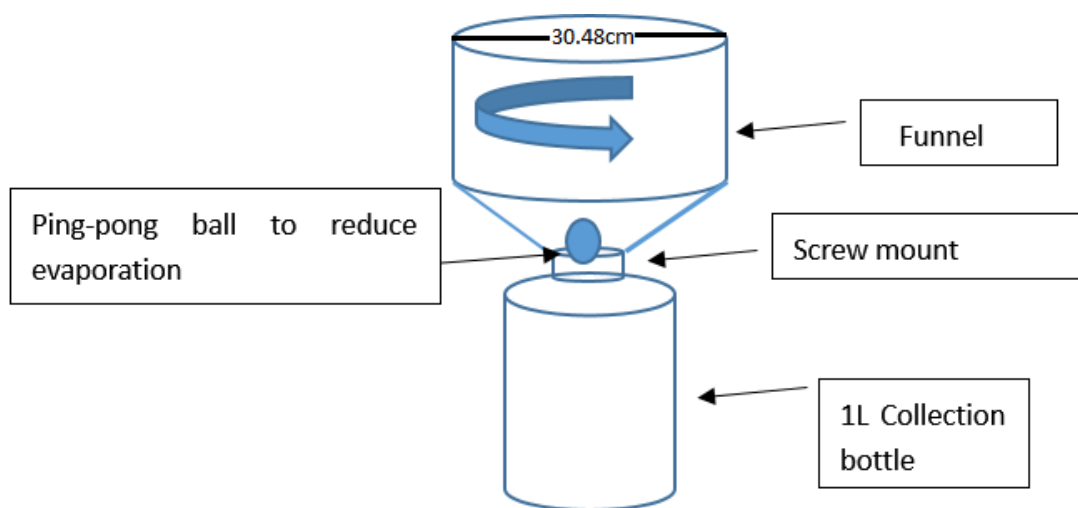
Figure 3-6 Diagram of a sampler for dry deposition and precipitation sampling.

Samples were collected twice a day on weekdays: nighttime samples were collected from 4:30pm (-1 day) to 8:30am (16 hours in total) and daytime samples were collected from 8:30am to 4:30pm (8 hours in total). During weekends, samples were collected from 4:30pm on Friday to 8:30am on Monday of the following week (64 hours in total). Since samples with little precipitation amount (<1 mm) could not be collected, they were considered dry deposition samples.

Dry deposition and precipitation were collected with sampler continuously exposed to the atmosphere. Winter precipitation (mainly snow) samples were captured in the sampler and melted at room temperature at ISL after collection. Another same-design sampler was used to collect samples when melting snowpack in winter.

3.3 Sample Preparation

3.3.1 Sample Separation

Precipitation samples were prepared for each precipitation event. When precipitation continued during the collection interval, the precipitation that occurred before and after the collection were considered as the same precipitation event. Samples for the same event were poured into same container to create a single sample.

Precipitation may be affected by particles suspended in the atmosphere prior to a precipitation event. Therefore, dry deposition samples were collected whenever precipitation events did not occur so that the dry deposition contribution could be examined separately. Further dry deposition was examined as a day-versus-nighttime interval during weekdays and pooled over the weekend.

Dry deposition samples for daytime (nighttime) were poured together every week to create a weekly daytime (nighttime) deposition, to ensure the concentration of carbonaceous materials in one dry deposition sample was sufficient for analysis.

3.3.2 Sample Processing

Samples, referred to here as both dry deposition and precipitation, were initially filtered through Whatman No.1 filter papers (11 μm in pore size) to remove large particles like sticks and

bird droppings. The volume of each sample was then measured using a measuring cylinder to 1 mL accuracy. Half of the sample was used for organic carbon and elemental carbon (OCEC) analysis and the remainder was prepared for isotope, anions and cations concentration analysis. The minimum volume of samples is 50 mL for OCEC analysis.

3.3.2.1 OCEC pre-treatment

Numerous studies have performed OC analysis in the past (e.g. Quideau and Bockheim, 1997; Tobon et al., 2004; Rosenqvist et al., 2010). Aerosol TC, EC, and OC have been quantified using thermal/optical methods since 1994 (Sempere and Kawamura, 1994). The procedure below uses the thermal/optical technique described in Torres et al.'s research in 2014.

Quartz filter papers (Whatman ® QM-A quartz membrane filters, 47 mm in diameter, 2.2 μm in pore size) were preheated at 550 °C for six hours on aluminum foil in a clean oven and cooled overnight to remove carbonaceous components. 2-mL 0.2M Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was added to every 100-mL sample as a coagulant (Torres et al., 2014) to improve collection efficiencies of OC without any apparent interferences. Torres's work presented the efficiency of coagulants, showing that $NH_4H_2PO_4$ was among the most suitable for this study (Figure 3-7). Particulate carbon was collected by filtering the samples through quartz filter papers not under vacuum. After filtration, the wet quartz filter papers were placed in aluminum foil cases in a desiccator to dry thoroughly at room temperature for three days. The dried quartz filter papers were wrapped with aluminum foil and stored in a dust-free plastic bag in a freezer at -26 °C at the Stable Isotope Laboratory, University of Calgary prior to analysis.
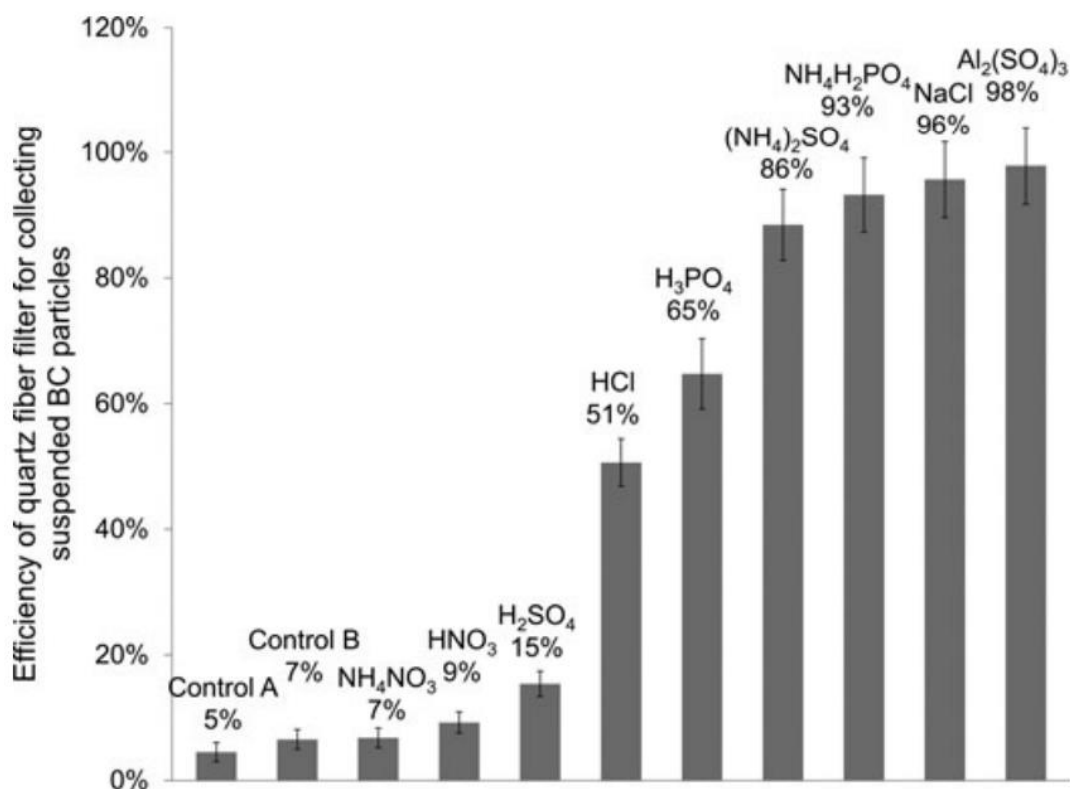
Figure 3-7 Quartz fiber filter efficiency from Torres et al. (2014) for collecting elemental carbon in solution (300 μm/L). Controls A and B were samples without coagulant aid. The concentration of acids and salts in solution can be found in Appendix 1. Vertical error bars represent the uncertainty of the OC/EC analyzer measurements.

3.3.2.2 Isotope, Cation and Anion Analysis

A second independent study by a student in our group, Alex Matheson, has looked at the anion and cation concentrations and $\delta^{34}S$ values for co-collected precipitation samples in Calgary from May 2016 to February 2017.

Samples for isotope, cation, and anion analysis were filtered through glass filters (Whatman® glass microfiber filters, 47 mm in diameter, and 0.4 µm in pore size). Then two 10.00 ± 0.02 mL samples were pipetted into sealed plastic bottles for ion chromatography analysis.

3.3.3 Sample analysis

3.3.3.1 OCEC measurement

A Sunset Laboratory OCEC Carbon Aerosol Analyzer (see Figure 3-8) was used to determine the concentrations of four organic carbon components and six elemental carbon components captured on the quartz filter papers. It was fully compliant with the IMPROVE protocol, which was mentioned in Chapter Two.
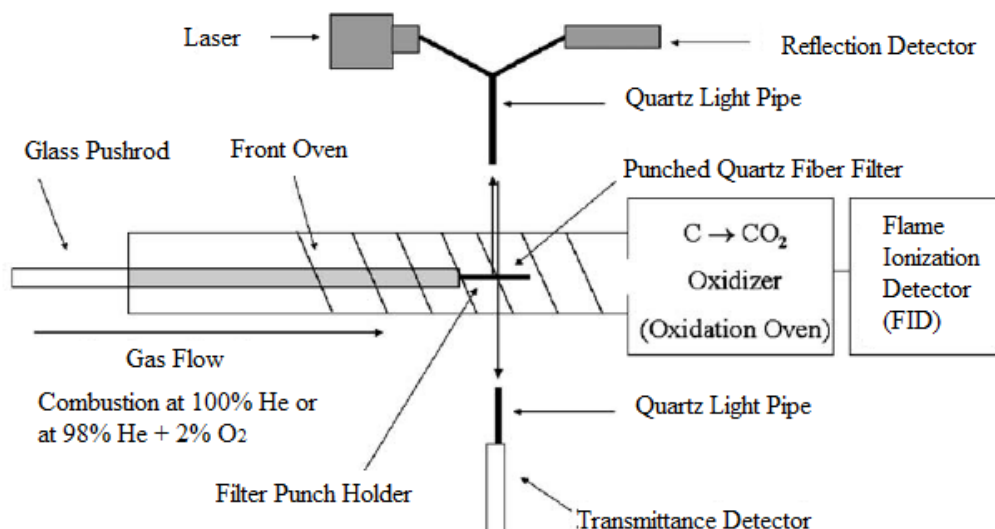
Figure 3-8 Diagram of OC/ EC Carbon Aerosol Analyzer used in the analysis of samples for this thesis.

At first, a piece of filter paper of 1x1 cm^2 in area was punched and sent into the analyzer using the pushrod (Figure 3-8). The operation of the analyzer was based on the preferential oxidation of OC and EC at different temperatures. Figure 3-9 shows the temperature stages and time of the operation. The measurement principle relied on the fact that OC can be volatilized in a non-oxidizing helium atmosphere, while EC must be combusted with an oxidizer, which was oxygen. The analyzer liberated carbon compounds from the piece of filter paper under a sequence of temperatures and with 2% oxygen through 98% helium streams. Those compounds were converted to carbon dioxide by passing the volatilized compounds through an oxidizer (not shown in figure). The carbon dioxide from organic and elemental compounds was reduced to methane. Finally, the methane equivalents were quantified using a flame ionization detector (FID) and later converted to signals representing carbonaceous components.
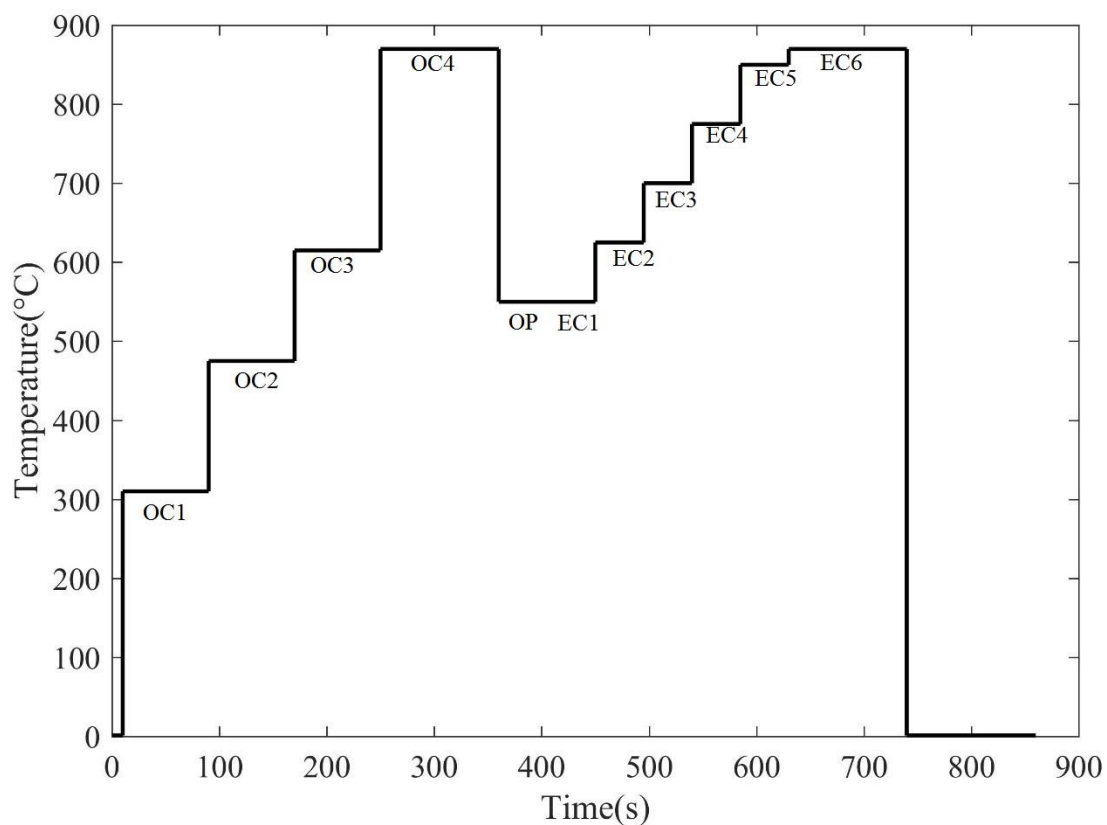
Figure 3-9 Temperature and Time of the operation using the OCEC analyzer.

Concentrations of two of the elemental carbon fractions, EC5 and EC6, were two to three magnitudes lower than the lowest of the other four fractions and below the reliable detection ranges. Therefore, EC5 and EC6 were excluded from this study, and:

$$OC = OC1 + OC2 + OC3 + OC4 + OP \quad (1)$$

$$EC = EC1 + EC2 + EC3 + EC4 - OP \quad (2)$$

$$TC = OC + EC \quad (3)$$

where OP represented pyrolyzed carbon, which is man-made and is not thought to be found in nature. Generally, it is produced by heating a hydrocarbon to its decomposition temperature. The principle function of the optical component of the analyzer is to correct OP for OC compounds to EC. Without this function, the OC fraction can be underestimated while EC may include some OP. The correction for OP is made by monitoring the filter reflectance or transmittance via a constant wavelength laser (depending on the chosen operation mode) and a laser detector.

Carbon values per punch were converted to µg C/cm^2 by:

$$\mu g\ C/\ cm^2 = (\mu g\ C/\ punch)/\ (punch\ area/punch) \quad (4)$$

where punch area was 1*1 cm^2. Systematic coming from the punch instrument rather than random error could be introduced if the punch area was not precisely 1*1 cm^2 and its effect on the results can be reduced by taking the ratios of samples well above detection limits.

Then, carbon values were converted to µg C/filter by:

$$\mu g\ C/\ filter\ =\ (\mu g\ C/\ cm^2)\ (filter\ deposit\ area/filter) \quad (5)$$

where filter deposit diameter was 1.6 cm $\pm$ 0.01 cm, therefore filter deposit area was 8.0384 cm^2 $\pm$ 0.0003 cm^2.

Finally, carbon values for the samples could be calculated by:

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Wet deposition per event:

$$\mu gC\ /L = \frac{(\mu g\ C\ /filter)}{\left(\frac{measured\ volume,ml}{filter}\right)*\frac{1L}{1000mL}} \quad (6)$$

Dry deposition per hour:

$$\mu g\ C/\ m^2 \cdot h = \frac{(\mu g\ C/\ filter)\ (1\ filter)}{(sampler\ area,cm^2)*\frac{1\ m^2}{10000\ cm^2}} / (sampling\ hours) \quad (7)$$

where sampling hours are 8 hours for daytime and 16 hours for nighttime.

Before samples were analyzed, two blanks were run. The first blank was analyzed without a filter to assess the condition of the instrument and ensures consistent blanks over time. The second blank was analyzed with an unexposed filter to check that no contaminant was introduced from sample handling and analysis. If the blanks exceeded a set of acceptance, the instrument status and protocol would be reviewed. However, all blanks analyzed as part of this suite of data were below acceptance values. Acceptance runs for blank quartz filters were $<1.5\mu g/cm^2$ OC, $<0.5\mu g/cm^2$ EC, and $<2.0\ \mu g/cm^2$ TC, indicated by the manufacturer's manual. The minimum quantifiable carbon value using the instrument as configured is $0.1\ \mu g$ C.

3.3.3.2 Secondary Organic Carbon Calculation

Based on the assumption that elemental carbon (EC) can serve as a tracer for primary organic carbon (POC), measurements of EC have been used to derive POC using the empirical primary OC/EC ratio approach (Turpin and Huntzicker, 1995; Strader et al., 1999). In this method, the POC and SOC could be estimated as follows:

$$POC=(OC/EC)_{min}*EC \quad (8)$$

$$SOC=OC-POC \quad (9)$$

where OC is the measured total OC. For more robust estimation, $(OC/EC)_{min}$ was chosen as the average of the three lowest value of OC/EC.

3.3.3.2 Uncertainty

The uncertainty of carbon values (δC) was automatically calculated by the system. It was derived from the detection limit of the instrument (0.2 $\mu g/cm^2$) and a random variability of 5% based on the experiments by the manufacturer. This relative error relies on duplicate measurement itself and on slight variations due to sample deposition and handling. As mentioned in the sample processing method, a blank filter was run before sampling filter as the baseline of EC, OC, and TC of the sampling filter. Blank filters were tested to be under acceptance and had a range of variability between 0.8% to 3% due to the filter treatment and sample handling. This variation was assumed

to be included in the relative error of 5% accepted by the manufacturer. Measurement for each EC and OC component had its own uncertainty, and this was combined with the uncertainty for the blank filter. These values for uncertainties were combined to produce our final results.

The uncertainty of each carbon compound was converted to determine the uncertainty of deposition samples using partial derivation rules for error propagations:

Uncertainty of wet deposition per event:

$$\delta \left(\mu g\ C/\ L\right) = \sqrt{\left(\frac{\delta C}{\mu g\ C}\right)^2 + \left(\frac{\delta V}{\text{Measured volume}}\right)^2} * \mu g\ C/\ L \quad (10)$$

Uncertainty of dry deposition per hour:

$$\delta \left(\mu g\ C/\ m^2\right) = \sqrt{\left(\frac{\delta C}{\mu g\ C}\right)^2 + \left(\frac{\delta\ \text{area}}{\text{Measured area}}\right)^2} * \mu g\ C/m^2 \quad (11)$$

To assure the quality of measured values and focus on defect prevention, values lower than one sigma were discarded in results.

3.4 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is a statistical technique that can be applied to a set of variables to reduce their dimensionality, which will replace a set of inter-correlated variables

with a smaller number of independent factors. These new factors are of the original simple linear combinations variables.

The first step is to normalize all carbon concentrations into a dimensionless standardized form Z_{ik}.

$$Z_{ik} = \frac{(C_{ik} - \bar{C_i})}{\sigma_i} \quad (12)$$

where i=1,2,3…n, the total numbers of elements in the analysis; k= 1,2,3…m, the total number of samples. C_{ik} is the concentration of element i in sample k. $\bar{C_i}$ is the arithmetic mean concentration of element i, and σ_i is the standard deviation of element i for all samples in the analysis.

Regressing the data on the principal component scores (PCS) gives estimates of the coefficients which convert the PCS into contributions from each source for each sample. For each score identified, the weighted regression of each carbon element's concentration on the predicted contributions yields estimate of that factor in each source. Hence,

$$Z_{ik} = \sum_{j=1}^{n} W_{ij} P_{jk} \quad (13)$$

where j=1, 2, 3…p, the number of sources contributing to the element. P_{jk} is the jth component's value for sample k. W_{ij} is the coefficient matrix of the components. And for each of the pollution

sources identified in the PCA, it is possible to derive information regarding the elemental composition of carbonaceous particles from that source.

Chapter Four: Results

The source of and removal of particulate carbon from the atmosphere by dry deposition or precipitation are valuable to understand. The importance of sources as well as the form of deposition varies with carbonaceous species and location. Therefore, dry deposition and precipitation samples from Kananaskis (a rural area) and Calgary (an urban area) were analyzed and compared for carbonaceous content.

The Kananaskis site (Barrier Lake Station) is a rural site with infrastructure that may provide local emissions associated with the Biogeoscience Center and can be used to understand background conditions to help interpret data for the Calgary site.

4.1 Carbon Concentration in Dry Deposition

Dry deposition is a continuous process, while wet removal can be realized only in the presence of precipitation. Therefore, despite the slow rate of dry deposition (or deposition velocity), which ranges from 0.055 cm/s to 100 cm/s depending on particle size, wind speed, and surface roughness, the cumulative amount and proportion of particulate carbon removed from the atmosphere is important in closing the aerosol carbon budget of the atmosphere (Mohan, 2016).

Dry deposition samples were collected daily and bulked into weekly sets for analysis from July 21st, 2016 to July 21st, 2017 for both Kananaskis and Calgary. Weekly Elemental Carbon and Organic Carbon were measured and then divided by the number of sampling days to achieve a

daily average concentration for each week. Table 4-1 shows the number of weekly sets collected at the two locations. No samples were collected during holiday weeks. Weeks crossing two seasons were assigned to the second season. For example, the week from November 28th, 2016 to December 4th, 2016 covered autumn and winter; the sample of that week was categorized as a winter sample.

Table 4-1 Numbers of weekly sets collected at Kananaskis site and Calgary site during the studied period.

Location	Collection period	# of samples in total	spring	summer	autumn	winter
Kananaskis	Nighttime	39	13	8	8	10
	Daytime	38	13	7	8	10
Calgary	Nighttime	47	14	8	12	13
	Daytime	45	13	7	12	13

4.1.1 Nighttime Dry Deposition

Total carbon (TC= EC + OC) for nighttime dry deposition had a range of 4.2 to 92.5 μg/ ($m^2 \cdot$ 8hrs) in Kananaskis and a range of 70.5 to 121.9 μg/ ($m^2 \cdot$ 8hrs) in Calgary. The TC increased significantly by April in Kananaskis with an average of 25 ± 25 μg/ ($m^2 \cdot$ 8hrs) while it remained stable in Calgary with an average of 95 ± 13 μg/ ($m^2 \cdot$ 8hrs) (Figure 4-1-A). However, TC was not

as informative as EC and OC in understanding the role of carbonaceous material for dry deposition or precipitation characteristics because of differences in their hydroscopicity. Appendix 2 includes all carbon ranges in this chapter.
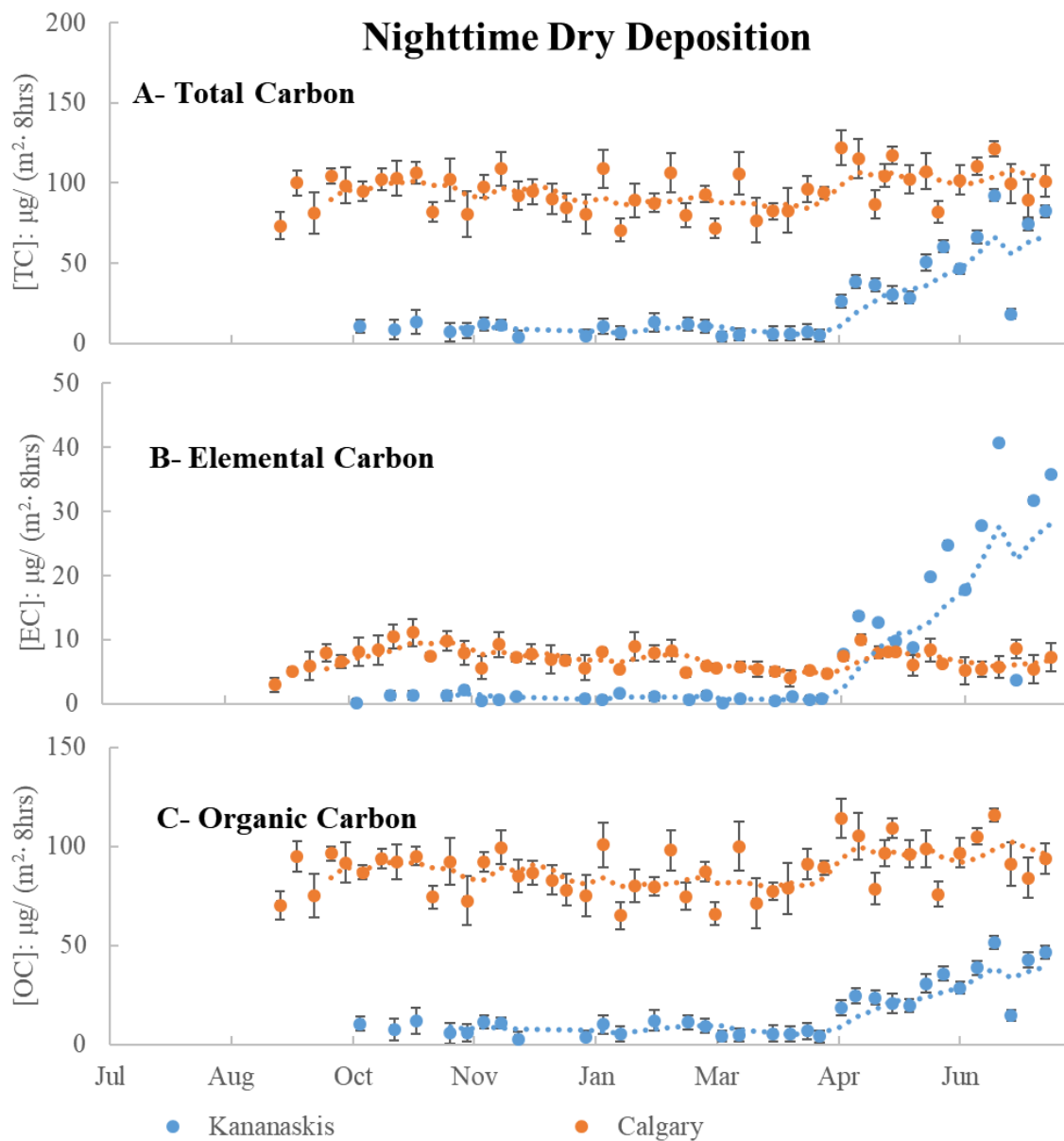
Figure 4-1 Carbon concentrations for nighttime dry deposition in Kananaskis (blue) and Calgary (red) from July 2016 to June 2017. The dotted lines show four-point moving averages.

The concentration of EC for nighttime dry deposition samples in the Kananaskis site ranged from 0.4 to 25.3 µg/ (m^2· 8hrs) with an annual average of 8 ± 12 µg/ (m^2· 8hrs). In Calgary, EC ranged from 3.0 to 11.1 µg/ (m^2· 8hrs) with an annual average of 7 ± 2 µg/ (m^2· 8hrs) for nighttime. It is worthwhile noting that the average for Calgary and Kananaskis were similar but the seasonal variability in Kananaskis was six times larger. Elemental carbon had a maximum seasonal average of 25 ± 12 µg/ (m^2· 8hrs) in summer in Kananaskis and 8 ± 2 µg/ (m^2· 8hrs) in autumn in Calgary. The concentration of EC in Kananaskis increased towards the end of April and reached a peak in summer, while the concentration of EC in Calgary remained stable throughout the year (Figure 4-1-B).

Organic carbon at night for dry deposition measured in Kananaskis ranged from 2.8 to 51.7 µg/ (m^2· 8hrs) with an average of 17 ± 14 µg/ (m^2· 8hrs), and OC in Calgary had a range from 65.0 to 115.7 µg/ (m^2· 8hrs) with an average of 89± 12 µg/ (m^2· 8hrs). This was much higher than EC for both sites. Maximum OC seasonal averages appeared in summer both in Kananaskis and Calgary reaching 36 ± 12 µg/ (m^2· 8hrs) and 95 ± 7 µg/ (m^2· 8hrs) respectively. Similar to the trend of EC for nighttime, OC concentrations increased in spring and summer in Kananaskis remained stayed stable during the entire sampling period in Calgary (Figure 4-2).

4.1.2 Daytime dry deposition

Total carbon (TC= EC+ OC) for daytime dry deposition ranged from 48.1 to 65.5 µg/ (m^2· 8hrs) in Kananaskis and 69.8 to 116.2 µg/ (m^2· 8hrs) in Calgary. The TC had an average of 56 ± 5 µg/ (m^2· 8hrs) in Kananaskis and an average of 91 ± 11 µg/ (m^2· 8hrs) in Calgary (Figure 4-2-A).

The average TC for daytime dry deposition was double that for nighttime dry deposition in Kananaskis. However, unlike for nighttime, daytime dry deposition did not show significant seasonal variability. The average and lack of seasonal variations were similar in Calgary for both nighttime and daytime.
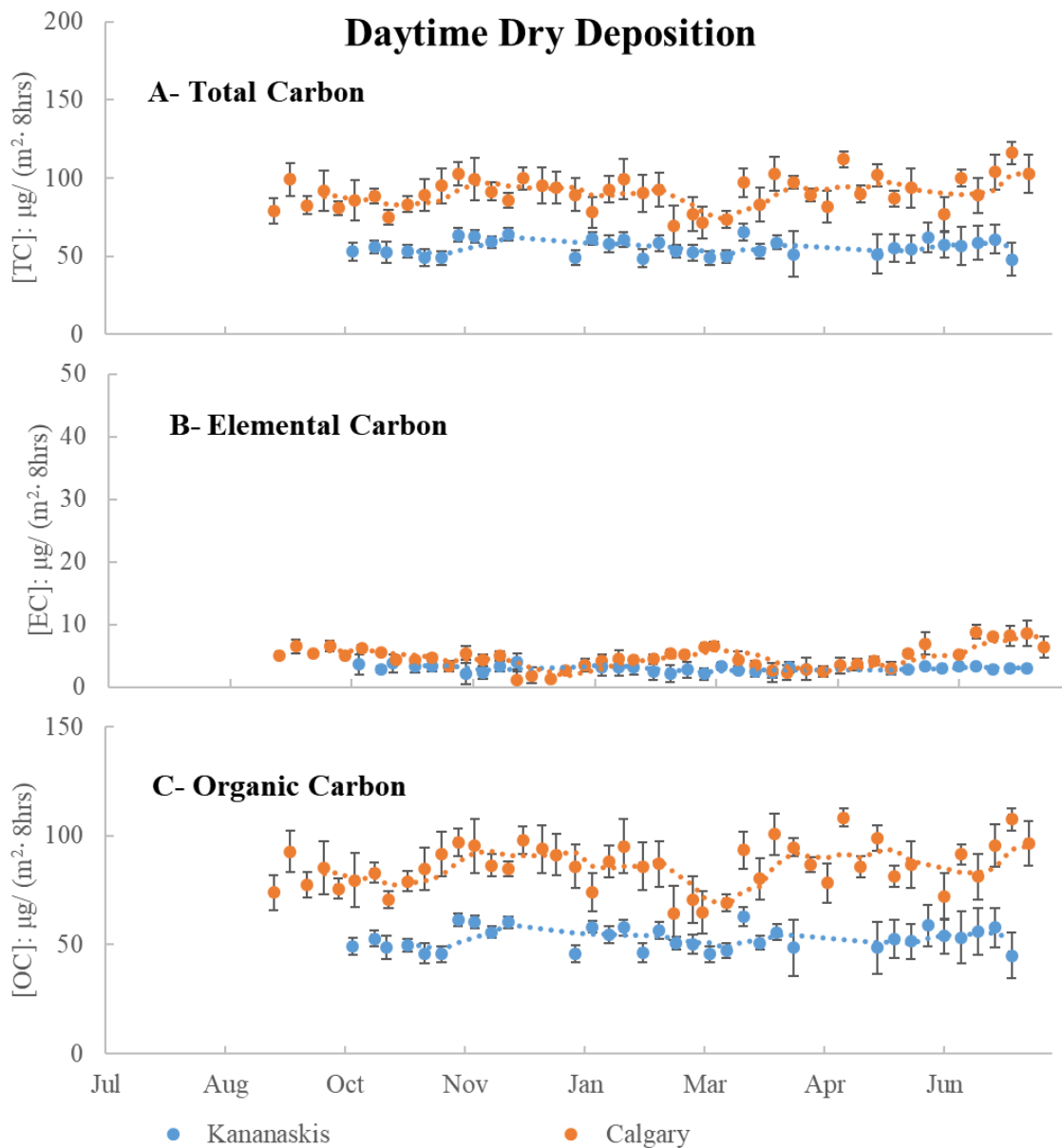
Figure 4-2 Carbon concentrations for daytime dry deposition in Kananaskis (blue) and Calgary (red) from July 2016 to June 2017. The dotted lines show four-point moving averages. No valid data were measured for EC in daytime dry deposition samples at Kananaskis during April 17th to May 15th, 2017.

The concentration of EC for daytime dry deposition samples in Kananaskis had an annual average of 3 ± 1 µg/ (m^2· 8hrs) and that in Calgary had an average of 5 ± 1 µg/ (m^2· 8hrs). Note that EC for dry deposition was slower during the day than at night at Kananaskis and Calgary. Seasonal variation in EC concentration was low both for Kananaskis and Calgary (Figure 4-2-B).

Organic carbon had an average of 53 ± 3 µg/ (m^2· 8hrs) in Kananaskis and 86 ± 8 µg/ (m^2· 8hrs) in Calgary. All four seasons had similar concentrations of OC. Kananaskis showed more intra-annual variability than Calgary but not clear seasonality. The lowest concentration of OC was observed at the end of February 2017 in Calgary, reaching 64.6 µg/ (m^2· 8hrs) (Figure 4-2-C).

Comparing EC and OC concentrations for nighttime relative to daytime dry deposition samples, a smaller amount of EC was observed at both locations in the day except for the Kananaskis samples in winter. OC in the daytime at Kananaskis increased to about three times that at night, while in Calgary, daytime and nighttime OC concentrations were similar for dry deposition samples.

The other notable feature for dry deposition is the pronounced seasonal variation for OC and EC at night for Kananaskis that is absent in the data for Calgary.

4.2 Carbon in Precipitation

Precipitation samples in Kananaskis before October 2016 were not collected, therefore carbon data for Kananaskis precipitation are only shown after October 2016 are shown in the figures below.

4.2.1 Precipitation data

In total, 47 and 76 daily precipitation samples were collected respectively in Kananaskis and Calgary throughout the study period. Most samples (28 at Kananaskis, 52 at Calgary) were collected in spring and summer (Figure 4-5). The average amount of precipitation ranged from 4.2 mm day^{-1} in autumn and winter to 8.6 mm day^{-1} in spring and summer at Kananaskis and from 3.4 mm day^{-1} in autumn and winter to 9.4 mm day^{-1} in spring and summer at Calgary (ECCC, 2017). Most precipitation at both locations were sampled and indicated by grey-shaded regions in Figure 4-5.
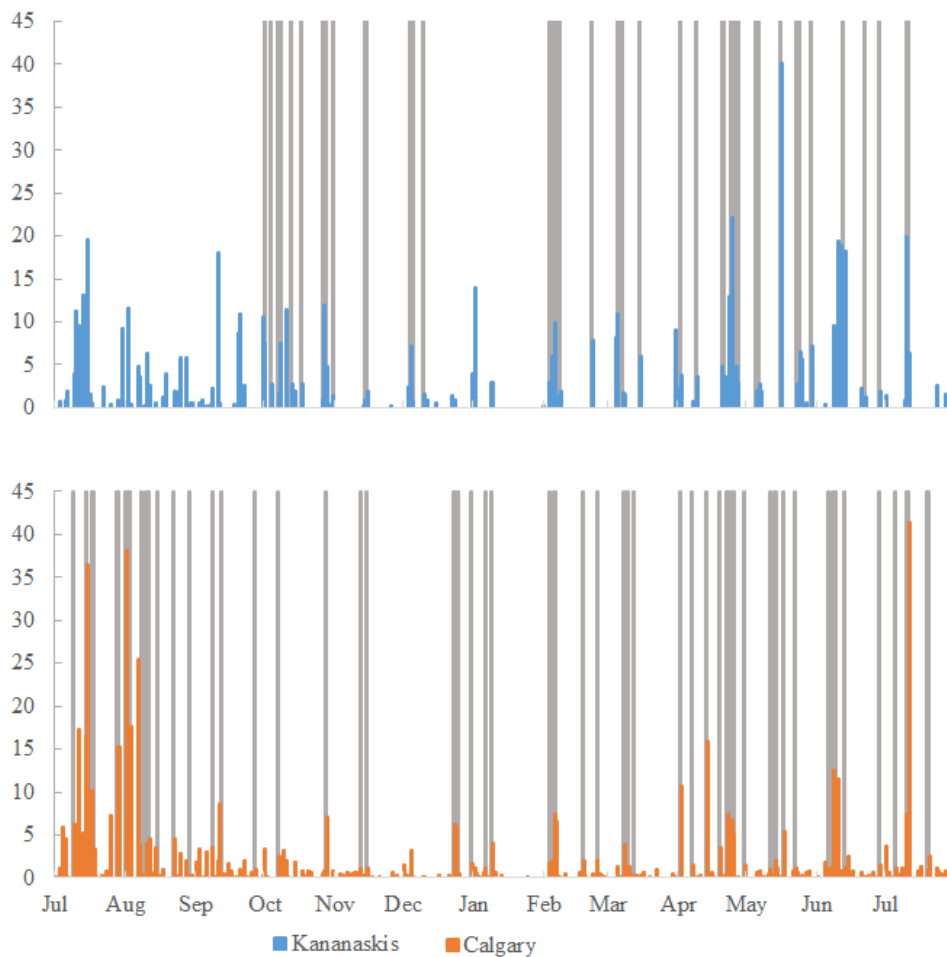
Figure 4-3 Time series of the daily precipitation in Kananaskis and Calgary during the study period. Grey boxes indicated periods when precipitation samples were collected. (Data source: http://climate.weather.gc.ca/historical_data)

4.2.2 Carbon concentration

Total carbon in precipitation had an average of 540 ± 163 μg/ L in Kananaskis and 2249 ± 2125 μg/ L in Calgary (Figure 4-4). In Kananaskis, TC had its lowest seasonal average of 447 ±

103 μg/ L in summer and highest seasonal average of 626 ± 204 μg/ L in winter. Oppositely, TC in Calgary had its lowest seasonal average of 883 ± 340 μg/ L in winter and highest seasonal average of 2982 ± 2827 μg/ L in summer.
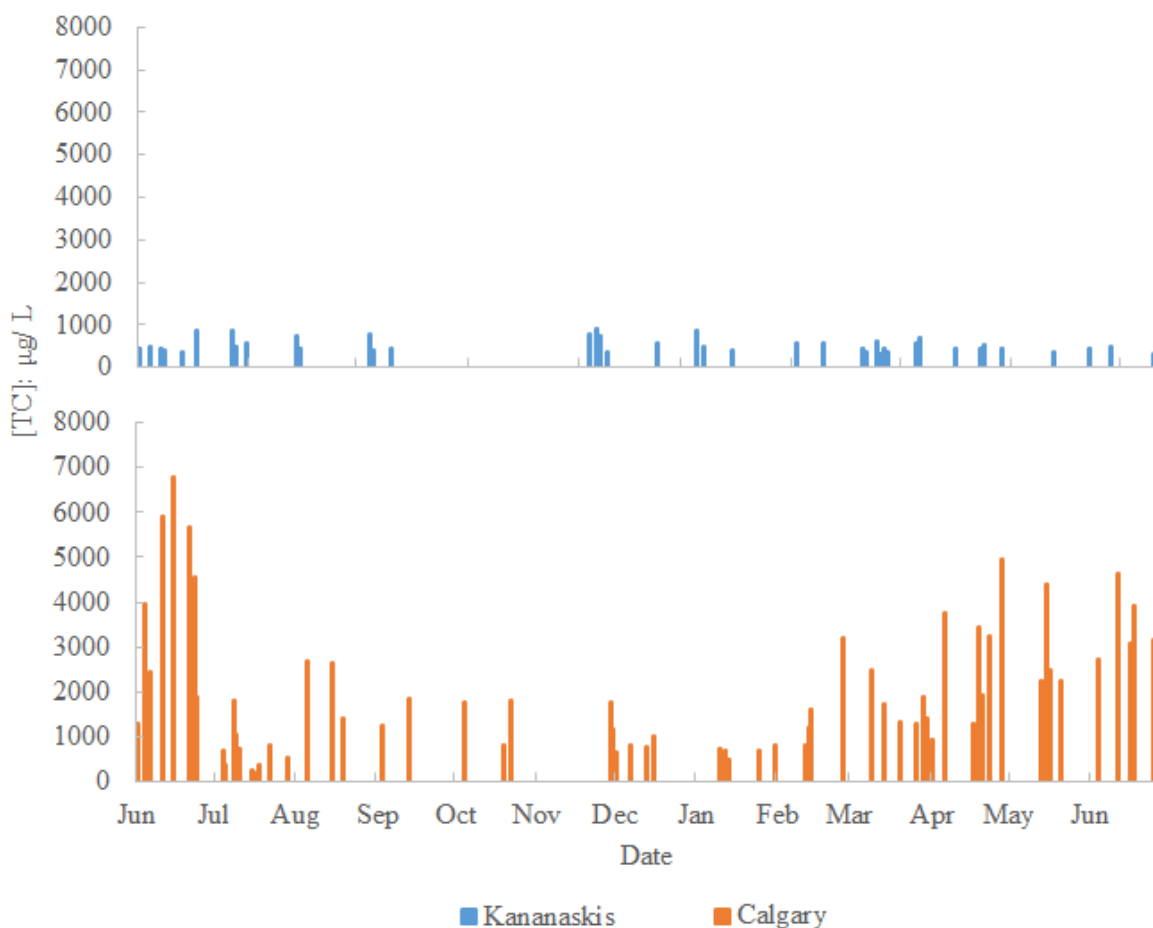
Figure 4-4 Total carbon concentration in precipitation samples.

In Kananaskis, precipitation events had an average EC concentration of 23 ± 16 μg/ L and OC concentration of 517 ± 104 μg/ L. EC and OC concentrations in Calgary had an average of 66 ± 16 μg/ L and 2493 ± 109 μg/ L respectively (Figure 4-5 and Figure 4-6). No obvious seasonality was observed in Kananaskis for both EC and OC, while both EC and OC had noticeable high

values in summer and early autumn 2016. Three extremely high OC values over 5,000 µg/ L were measured in Calgary on 4th, 12th July and 25th July 2016.

Seasonal organic carbon and elemental carbon concentrations in precipitation collected at the two locations are listed in Table 4-2. Overall, average EC and OC values in Calgary were about 2.8 and 4.8 times higher, respectively, than those measured in Kananaskis. Calgary had the highest seasonal average of EC in winter, which was about 2.8 times higher than that in Kananaskis. By contrast, OC had the smallest seasonal average in winter and the largest seasonal average in summer. Opposite to Calgary, Kananaskis had low concentrations of OC in summer and high concentrations of OC in winter.
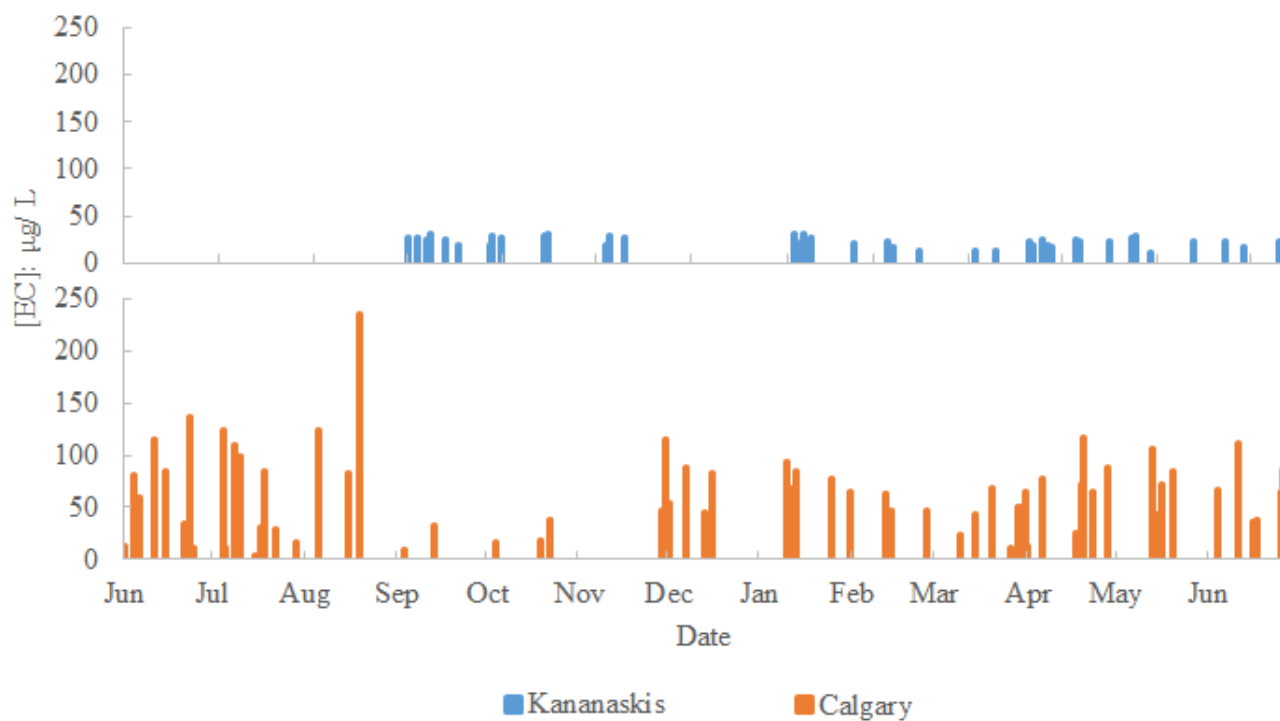
Figure 4-5 Elemental carbon concentration in precipitation samples in Kananaskis and Calgary from June 2016 to July 2017. Note the scale for EC is 32 times lower than that in Figure 4-4.
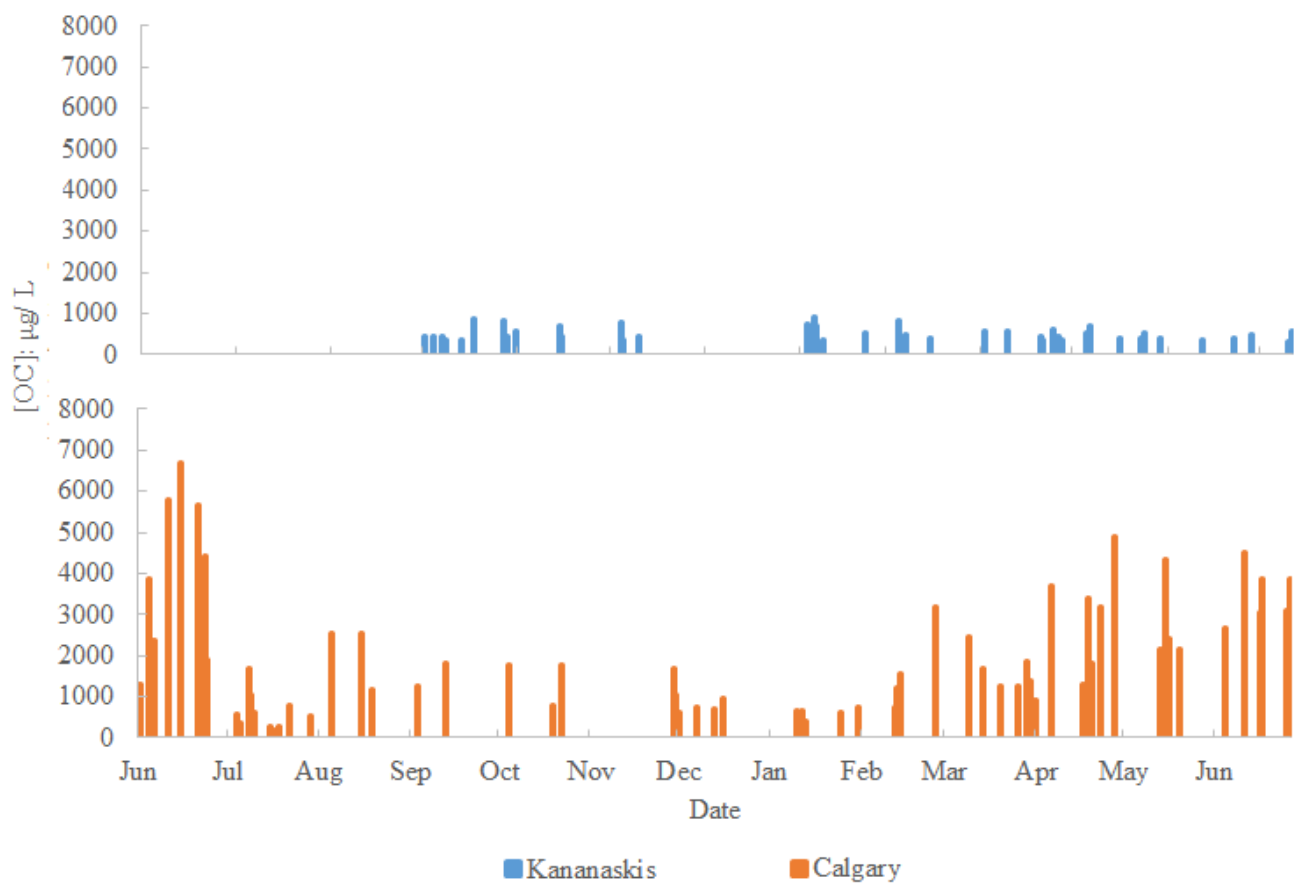
Figure 4-6 Organic carbon concentration in precipitation samples in Kananaskis and Calgary from June 2016 to July 2017. Note the scale for OC is 32 times larger than that in Figure 4-5.

Table 4-2 Seasonal volume-weighted average and volume-weighted standard deviation of OC and EC in precipitation in Kananaskis and Calgary.

Season	Kananaskis μg/ L		Calgary μg/ L	
	EC	OC	EC	OC
Spring	20 ± 6	494 ± 132	53 ± 27	2040 ± 1164
Summer	22 ± 3	425 ± 109	70 ± 43	3524 ± 3665
Autumn	28 ± 4	535 ± 181	62 ± 40	1589 ± 572
Winter	26 ± 4	599 ± 205	75 ± 22	808 ± 343
Overall	23 ± 6	540 ± 163	65 ± 42	2248 ± 2125

4.3 OC/EC ratio

OC/EC ratios give an indication of the origins of carbonaceous PM (Chow et al., 1996; Turpin and Huntzicker, 1991). The ratios are influenced by emission sources, secondary organic carbon formation and different OC/EC removal rates by deposition (Cachier et al, 1996).

As shown in Figure 4-7, in Kananaskis, dry deposition samples had an average OC/EC around 22 for nighttime and around 18 for daytime with few variations. Precipitation had an average of OC/ EC of approximately 24 which was higher than dry deposition over the year. Overall, OC/EC removed by deposition was relatively stable in Kananaskis.
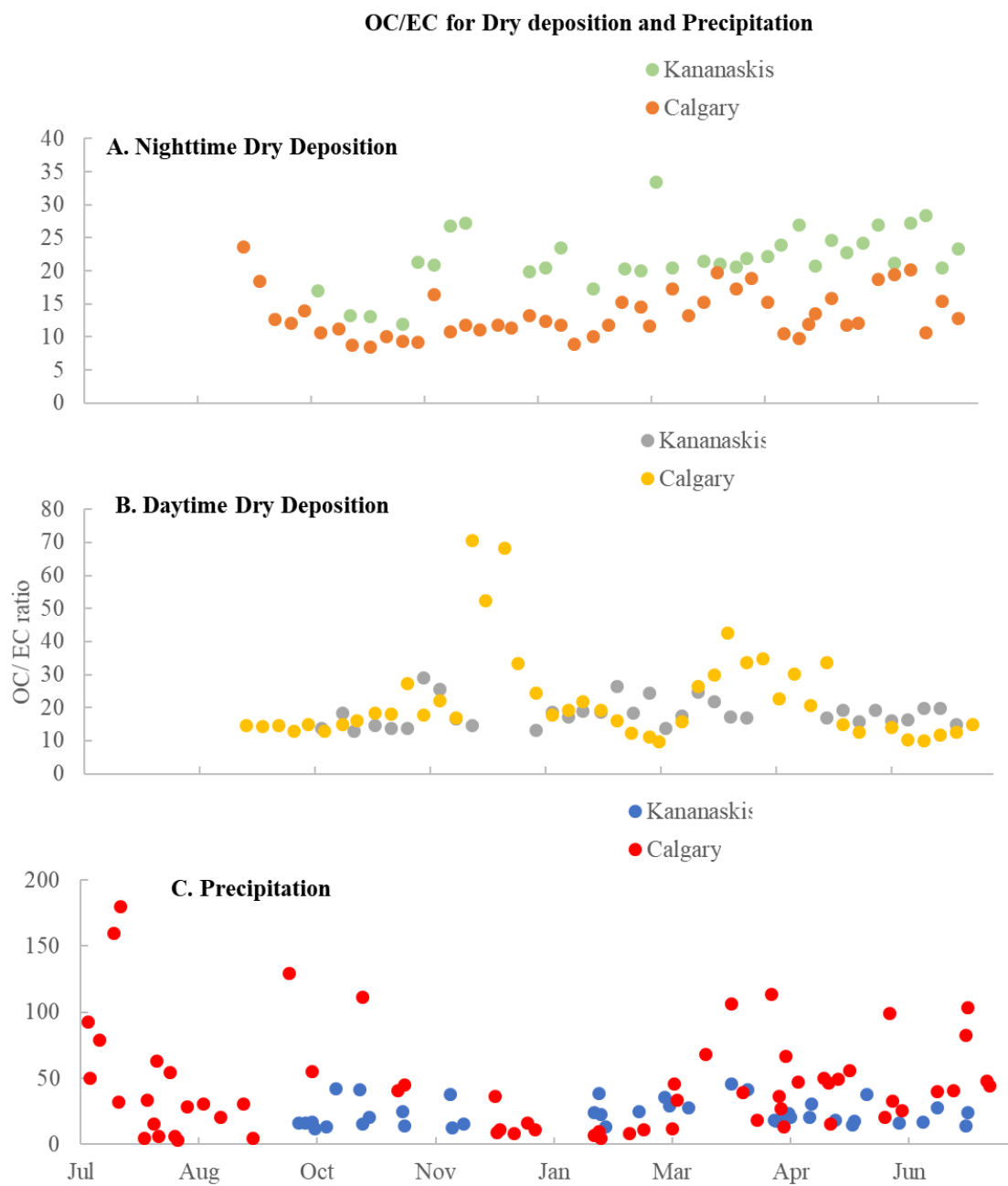
Figure 4-7 OC/EC ratios for all samples collected in Kananaskis and Calgary from July 2016 to June 2017.

In Calgary, OC/EC for dry deposition had an average of 13 ± 4 for nighttime during the year with no extremely large or small values. For daytime, the dry deposition ratios varied around 22 with three exceptions in late December, which were over 50. Both OC/EC for nighttime and daytime in Calgary were lower than those in Kananaskis. Considering the variable emission sources, OC/EC changes over the year especially in summer and autumn in Calgary. Two events in 15th July and 18th July had extremely high values of OC/EC over 150. OC/ EC in precipitation in Calgary had no obvious seasonal features. Also, OC/EC in precipitation events did not have a strong correlation with precipitation amounts (See Table 4-3).

Table 4-3 R-square and P values between OC/EC and precipitation amount in Kananaskis and Calgary

OC/EC vs precipitation amount	R square	P
Kananaskis	0.02	0.76
Calgary	0.06	<0.05

4.3 Ion concentrations versus EC, OC and TC

Variations in ion concentrations and deposition can help identify sources that affect particulate carbon. Anion and cation concentrations from an independent study by an undergraduate student who collected and analyzed simultaneous samples of precipitation (Alex Matheson) were used to compare with the concentrations of EC, OC, and TC. Since not enough samples were analyzed for ion concentrations due to the limitation of sample volumes, only ion

concentrations data for precipitation in Calgary were analyzed. Data for 22 precipitation samples were overlapped.

Since TC (which is composed of both OC and EC) and SO_4 are two major fractions of anthropogenic aerosols in the fine particle size range (Finlayson-Pitts and Pitts, 1986), it is worthwhile comparing these two components. When a particular fraction of aerosol shares the same production mechanisms (Orgen and Charlson, 1983), a significant correlation may be apparent for some regions. TC, EC, and OC were all compared to the ion concentration in precipitation, where both organic and inorganic constituents were measured. Samples from summer shared no correlation of TC, EC, or OC with ion concentration. However, 11 precipitation samples in Calgary displayed a positive relationship between EC and SO_4 from the end of October to the end of February (Figure 4-8).
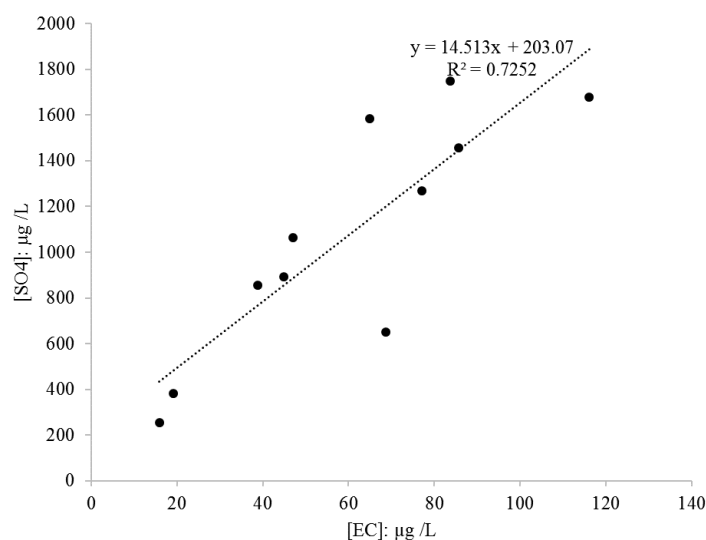
Figure 4-8 Relationship between elemental carbon and sulfate from the end of October 2016 to the end of February 2017 in Calgary.

Chapter Five: Discussion

5.1 Discussion on IMPROVE Dataset

The IMPROVE dataset is essential for understanding sources and processes that may affect the variance of carbonaceous components in a relatively remote continental location (Malm et al., 1994). The possible sources of organic and elemental carbon in the atmosphere can be determined by analyzing the amount of and trends for particulate matter. Here we aim to understand the temporal and spatial distribution of carbon components and to gain better understanding of deposition and transport of total as well as organic particulate matter. This continuous four-year IMPROVE dataset is relevant to a better understanding of background aerosol concentration for total particulate matter in PM 10 and 2.5. It also facilitates a comparison of deposition of OC and EC in PM2.5 to measurements of OC and EC for dry deposition and precipitation in the Kananaskis and in Calgary.

5.1.1 Particulate matter

The seasonal variation of Particulate Matter (PM) from the IMPROVE dataset demonstrates higher PM 2.5 and PM10 in autumn than in other seasons (Figure 2-2). Biogenic volatile organic compounds (BVOC) are expected to be higher in the growing season (summer) than in winter and contribute to the ~60% organic matter in total aerosol (Li and Barrie, 1993). However, BVOC are emitted in the gas phase and undergo oxidation to form PM2.5, not PM10. PM10 is associated with primary emissions. Figure 2-2 shows that the concentration of PM10 is

about two times higher than PM2.5 in fall. Primary plus secondary organic matter is more important in fall than in other seasons. This is not consistent with a biogenic source of PM. Also, the ratio of PM2.5/ PM10 remains relatively constant throughout the seasons. Therefore, there is likely a common source for both PM2.5 and PM10. To focus on concentrations near the surface of the ground, it can be assumed that the boundary layer heights were similar for autumn and spring in the sampling area and the concentration would not be influenced by pressure and duration of sunlight.

Between October and April, windy (Figure 5-1, Figure 5-2) and dry (Figure 5-3) weather conditions were favorable for PM dispersion while low humidity would lower the production of secondary organic carbon, which was thought to be an important carbonaceous component, resulting in the relatively low concentration of PM. During fall (Figure 2-2), the high concentration of PM could be a result of the enhanced emission from local heating systems and unfavorable meteorological conditions such as low mixing layer heights and frequent inversions above the surface of the ground. Although strong winds in fall and winter helped lower the concentration, precipitation events were limited, which could promote the accumulation of PM within the boundary layer. The sampling location experienced dominant southwest winds, therefore wind direction (Figure 5-2) would not influence seasonal variations of PM concentrations.
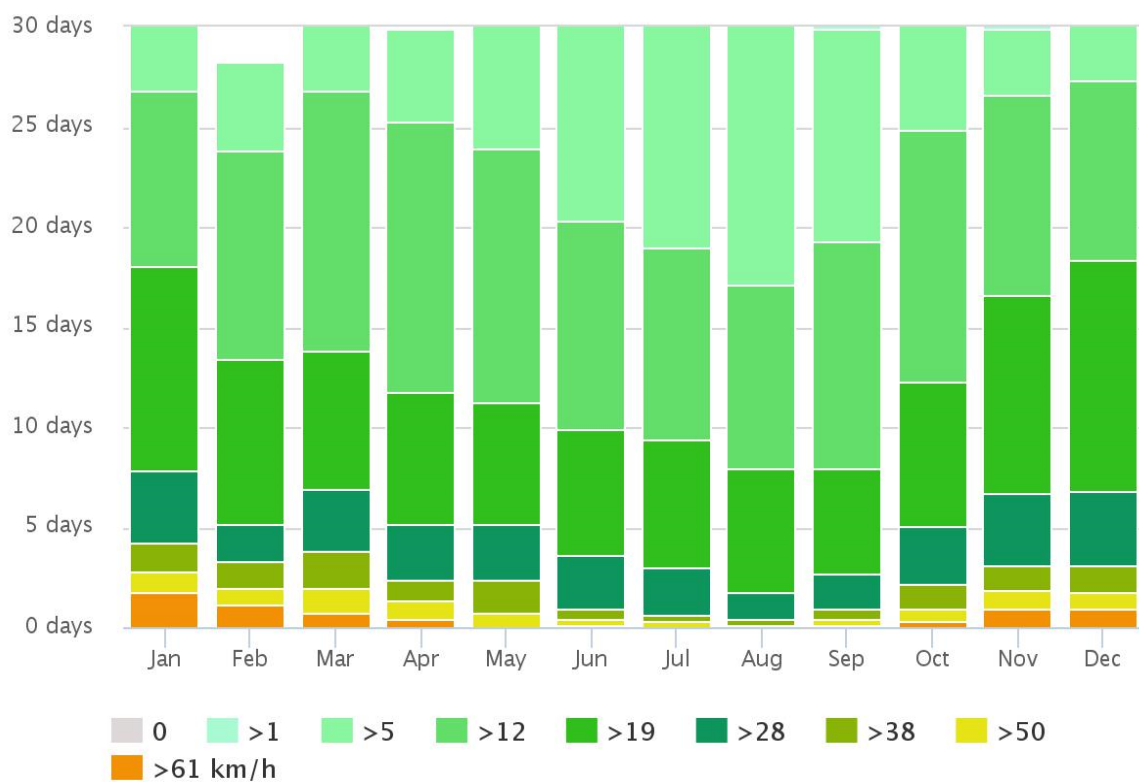
Figure 5-1 Historical 4-year wind speed for Barrier Lake for the IMPROVE dataset from
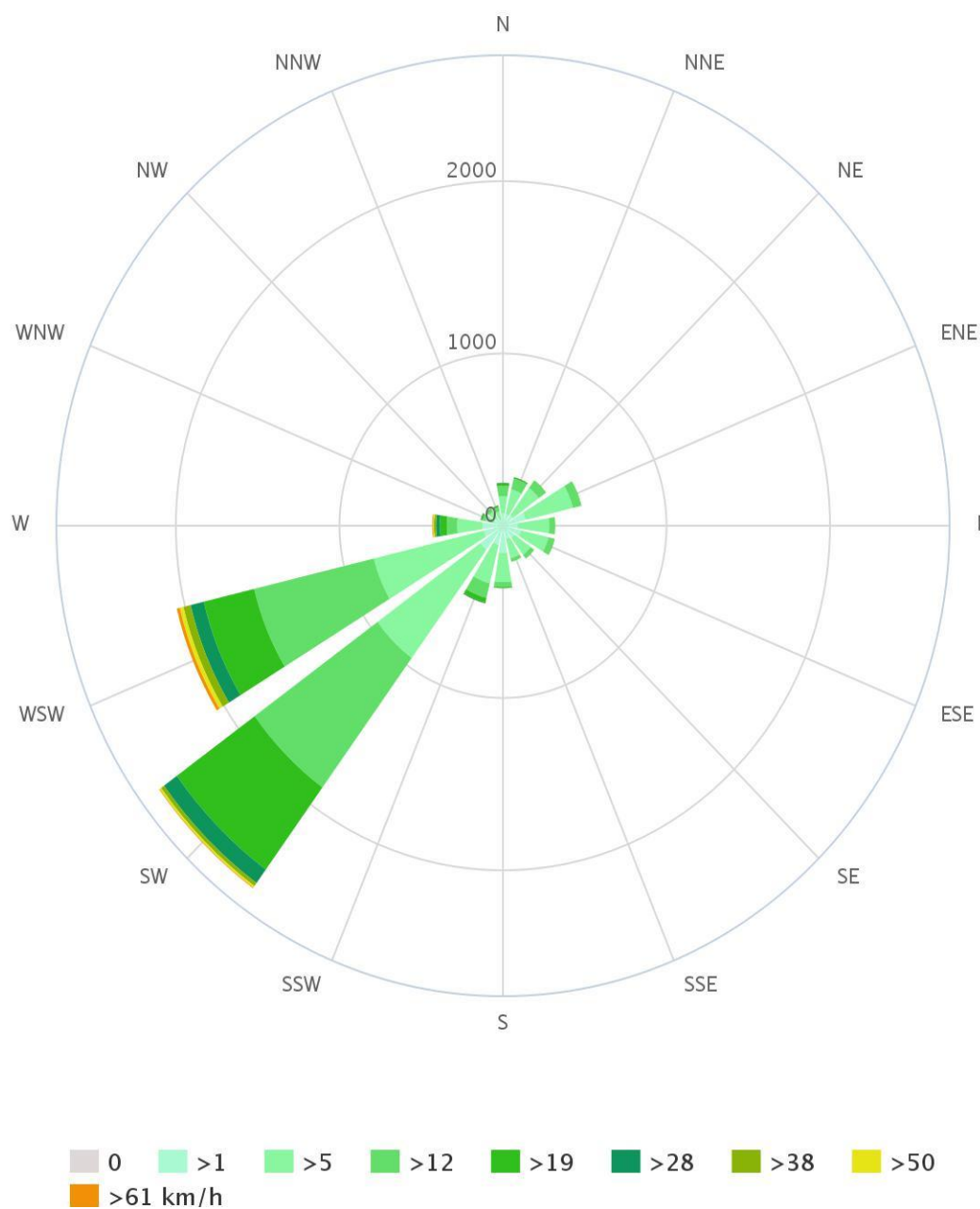
2011 to 2014.

Figure 5-2 Historical 4-year annual wind rose for Barrier Lake for the IMPROVE dataset from 2011 to 2014.
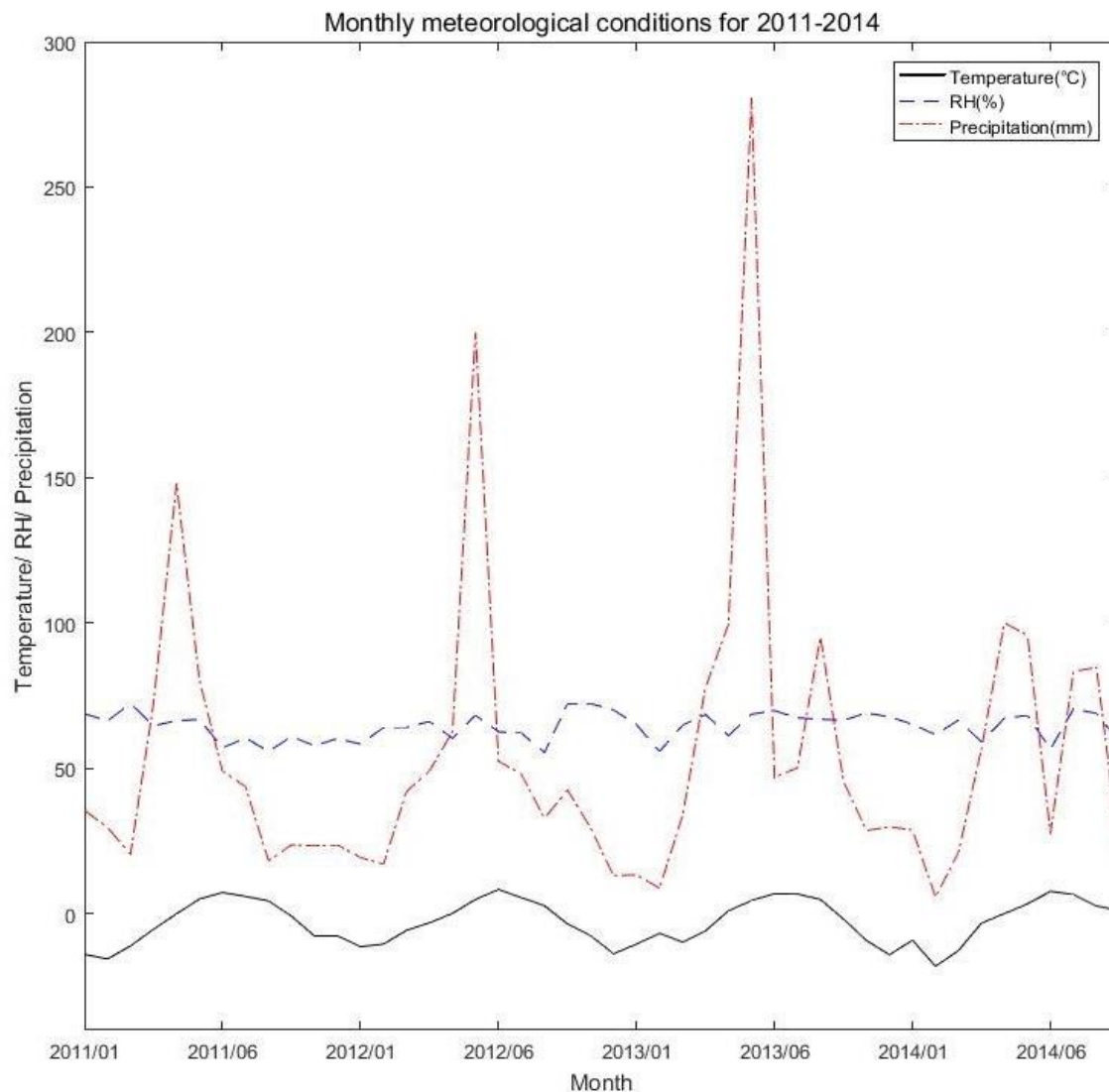
Figure 5-3 Monthly meteorological conditions for 2011-2014 at Barrier Lake field station.

Of four meteorological factors: wind, temperature, relative humidity, and precipitation (Figure 5-1, 5-2 and 5-3), relative humidity did not vary much during the four sampling years, and therefore was not among our focuses. Winds help distribute PM at the surface of the ground. The boundary layer height, which has a negative relation with PM concentration, largely depends on temperature (Tai et al., 2010). Precipitation has an obvious effect on the removal of PM.

5.1.2 Carbon Components

5.1.2.1 Total Carbon, Organic Carbon, and Elemental Carbon

High concentrations of OC and EC in PM2.5 in summer from the IMPROVE dataset in Figure 2-3 and 2-4 could be the result of increasing numbers of people participating in outdoor activities in Kananaskis. Even though intermittent rainfall may have decreased the amount of total and carbonaceous particles, low wind speed prevented particle dispersion. TC/ PM2.5 was high in winter reaching 0.4 and low in other seasons with an average of 0.2. Such seasonal variation in TC/PM2.5 (Figure 2-5) could be attributed to frequent removal processes like precipitation and wind speed seasonality. Another possible reason could be the slower production of PM2.5 due to the snow cover. A high percentage of TC in PM2.5 at the beginning of each year (January) was unexpected (Figure 2-5). It could result from increasing use of heating systems such as propane and wood burning at the coldest time of the year (Figure 5-3). Also, contribution of biomass burning like forest fires to PM2.5 in summer and early fall was significant during all four years. Wildland fire from northeastern British Columbia and northern Alberta every year could heavily influence the air quality at the sampling station (http://cwfis.cfs.nrcan.gc.ca/maps/fm3).

Considering the unexpected high wintertime and high fall OC/EC ratios (Figure 2-6), three main reasons were evaluated: First, at the beginning of fall, wood burning for camping still existed and will have increased the emission of volatile organic precursors to aerosol PM along with copious EC. This would drive OC/EC ratios down and this is opposite to what is observed in Figure 2-6. However, when it turned colder, a higher proportion of propane burning could have increased

the concentration of OC and then increased OC/EC ratios as observed in November, January and March in Figure 2-6. Second, the absorption and condensation of semi-volatile organic compounds onto the existing solid particles would be enhanced due to the low ambient temperature (Wania et al., 1998; Lei and Wania, 2004). More newly created OC would be absorbed by existing particles and then deposited onto the ground, lowering the ratio. Third, the low mixing layer height in winter would provide chances for chemical reactions and then enhance SOC formation (Andreae and Crutzen, 1997).

5.1.2.2 Particle Sources of OC and EC

Carbon abundance in eight carbon fractions (EC1, EC2, EC3, OC1, OC2, OC3, OC4, and OP) was used to distinguish different carbon sources (Waston et al., 1994; Chow et al., 2004b). Table 5-1 summarizes source identification associated with elemental and organic carbon fractions in previous studies and expected sources in the Kananaskis. The abundance in source samples shows specific characteristics of source compositions. Kim and Hopke's research (Kim et al., 2003a; Kim et al., 2004) first used carbon fractions to perform source apportionment of carbonaceous aerosols. Other studies further explained that EC1 was abundant in vehicle exhaust samples (Cao et al., 2005); EC2 and EC3 came from coal combustion and vehicle exhaust. OC1, OC2, were rich in biomass burning and coal combustion, and OC3 and OC4 were mainly from road dust profile (Chow et al., 2004). Yu's group extracted a large OP fraction in water for polar organic compounds suggesting a strong relation between OC and transport of polar organic compounds (Yu et al., 2002).

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Gasoline exhaust was found to be abundant of EC1, OC2 and OC4 in previous studies. The similarity in engines and fuels worldwide suggests this could be true for our samples as well.

Diesel exhaust was determined by Cao et al., (2005) to the dominant source of EC2. EC2 in this dataset shifted in fall and suggests an increase in the number of heavy-duty vehicles like trucks around the sampling site. This would make sense if construction or other diesel vehicles were present in the fall but not other seasons, but no construction projects took place at or near the Biogeoscience center in fall between 2011-2014 (Personal communication: Norman, 2018). A previous study has shown that EC2 is most abundant in fresh exhaust from diesel-fueled vehicles rather than from gasoline-fueled vehicles (Watson et al., 1994). The low EC2 abundance at the Barrier Lake station indicates that carbonaceous emissions from local diesel-fueled vehicles were possibly not as important as emissions from gasoline-fueled vehicles.

Coal combustion was found to emit EC2, EC3 and OC2 from previous studies (Cao et al., 2005, Watson et al., 1994, Kim et al., 2004). In this study, coal combustion matches the same temperature as EC2 (600 $^\circ$ C) or even higher temperature as EC3(700 $^\circ$ C), therefore coal combustion could be a source of EC2 and EC3. Because no coal combustion exists in the Kananaskis valley except minor contributions from recreation events like barbecues using charcoal, little high-temperature EC3 in the atmosphere was expected. OC2 from coal combustions is considered similar to what is expected from charcoal briquettes. Future work to characterize this source under controlled conditions would help clarify whether or not these attributes are observed from charcoal combustion during barbecues.

Biomass burning, like woodfire combustion and forest fire from nearby areas, is considered to emit both EC1 and OC1, which are in lowest temperatures of EC and OC fractions. However, since EC component of forest fire is in larger particle size than OC, then it will be removed from the atmosphere more quickly than OC during transport. Therefore, if forest fire emissions from long-range transport were present, only an increase in OC should be observed. Also, since forest fires are typically confined to the warmer summer and autumn seasons, emissions from forest fires are expected to display seasonal variations.

Propane exhaust is expected to have little EC and perhaps an OC component that is similar to light hydrocarbons (like gasoline), so it could be evident in forming OC1 when combusting propane. This assumption needs to be tested in the future study.

Biogenic volatile organic compounds (e.g. terpenes) are thought to form SOC at ambient temperature via oxidation (Sahan and Weijers, 2008). Therefore, biological emissions are related to OC2 which is produced during the process of SOC formation.

Road dust at our site could release OC3 and OC4, if it is as assumed that the attribution from literatures shown in Table 5-1 apply in general. Even though road dust and gasoline exhaust share similar carbon fractions, chemistry can be used to distinguish them since road dust has more ions like calcium and magnesium.

Long-range transport is related with of OP, which is a substantial water-soluble polar compound used as a marker to tracing particles in the transport of atmosphere.

Table 5-1 Comparison of source identification associated with elemental and organic carbon fractions from the literature and in this study.

Carbon Fraction	Source	Reference	Source in our study
Elemental Carbon			
EC1	Vehicle exhaust (Gasoline)	Cao et al., 2005	Gasoline exhaust & Biomass burning
EC2	Coal combustion & Vehicle exhaust(Diesel)	Cao et al., 2005	Diesel exhaust & Barbecue
EC3	Coal combustion	Watson et al., 1994	Barbecue
Organic Carbon			
OC1	Biomass burning	Chow et al., 2004	Biomass burning
OC2	Coal combustion	Kim et al., 2004	Biological emission & Barbecue
OC3	Road dust & Vehicle exhaust (Gasoline)	Chow et al., 2004; Kim et al., 2004	Road dust & Gasoline exhaust
OC4	Road dust & Vehicle exhaust (Gasoline)	Chow et al., 2004; Kim et al., 2004	Road dust & Gasoline exhaust
OP	Polar organic compounds	Yu et al., 2002	Long-range transport

5.1.2.3 Estimation of secondary organic carbon

There is no direct measurement technique to analyze the concentration of Secondary Organic Carbon (SOC), therefore, Castro's equation mentioned in Chapter 2 was applied for estimation of SOC in the IMPROVE dataset.

In contrast to many other seasonal studies reported in the literature from Asia and North America (Lee and Kang, 2001; Park et al, 2008) where a winter peak was found, SOC at Barrier Lake reached its peak during summer and remained at a low average value of 0.1 ± 0.2 μg/ m^3 the rest of the time (Figure 5-4). The SOC/OC ratio was uniform across all months except for March 2013 when the ratio was close to zero (Figure 5-5). The stable SOC/OC ratio corresponded to increasing concentrations for both SOC and OC, which also meant that the total OC and primary OC (POC= TOC-SOC) increased significantly in summer and early fall.

The presence of volatile organic compounds (VOCs), which undergo many atmospheric oxidation processes, enhances SOC formation. The majority of biologically generated VOCs are produced by plants, animals, microbes and fungi that are mostly active in summer and early fall. Anthropogenic sources, including fossil fuels and benzene exhausted from cars, could also provide VOCs. In summer and fall, the number of vehicles travelling to the Kananaskis Valley was higher than that during spring and winter for entertainment like camping and barbecues (Government of Alberta ministry of Transportation, 2017). Therefore, higher SOC in summer than the rest of the year could be a result of both anthropogenic and biological emissions.

An exception occurred for the ratio of SOC/OC in February 2013, which was lower than '0' (Figure 5-5). The concentration of SOC is a calculated number instead of a measured value, and is based on the equation

$$SOC=OC-EC*(OC/EC)_{min} \quad (1)$$

where OC was the measured organic carbon concentration. OC/EC in February 2013 is the minimum value of all OC/EC values. Therefore when $(OC/EC)_{min}$ was calculated from the lowest 3 values, the February 2013 value, as expected, fell below this average. This demonstrates the measure of error in the calculation of SOC which is taken into account in deriving the uncertainties in SOC. Once the error in SOC/OC for February 2013 is taken into consideration (± 0.9), then the value of SOC/OC (- 0.7 $\pm$ 0.9) is indistinguishable from 0 ± 0.9.

In late fall and winter (October to February), when the concentration of SOC fell in the range of 0.05 $\mu g/m^3$ to 0.14 $\mu g/m^3$ (Figure 5-5) and the ratio of SOC/OC went down, a high correlation between OC and EC occurred (Table 5-2). This high correlation in fall and winter indicates common sources for OC and EC in PM2.5 at the Biogeoscience Center in Kananaskis. This result differs from the literature reports that suggest sources of OC and EC in fall-winter are mainly from a range of carbon sources (Park et al., 2003). SOC and OC data in this study demonstrate that a small amount of SOC maintains a balance with primary organic aerosols in the atmosphere. Aerosols in PM2.5 maintained a relatively constant ratio with PM10 (Figure 2-2). Since OC is the dominant component of PM2.5, both OC and PM2.5 co-vary with PM10, which are larger particles that represent local emissions. The possible local sources responsible for SOC

in fall could be motor-vehicle exhaust. In winter SOC sources could be vehicle emissions and local propane heating systems.

Table 5-2 Positive correlations (P < 0.05) between OC and EC concentrations in late fall and winter.

Time	R square
Oct to Dec,2011	0.69
Nov to Jan, 2012	0.70
Oct to Nov, 2013	0.74
Dec to Feb, 2014	0.73

There could be a possibility that the SOC produced is not well dispersed because of the weak wind in summer and the geographical features prevent SOC from escaping the Kananaskis Valley. The stable ratio of SOC/OC could be explained by the co-emission of SOC and OC during all four seasons (Figure 5-5). Precipitation removal was expected to remove OC and SOC components of particulate carbon preferentially. However, these effects would be transitory and not long lasting if local sources of OC, EC and SOC replenish the atmosphere with organic matter. Therefore, the ratio of SOC/OC and OC/EC are stable throughout the seasons.

This method (Equation (1)) to estimate SOC has only been applied to OC and EC aerosol components in previous studies (Hallquist et al., 2009; Alfarra et al., 2004). However, it is interesting to consider how this might apply to dry deposition and /or precipitation. Two factors

that are important to consider are 1) aerosol size and 2) dry deposition velocity. OC and EC typically are not uniform across aerosol size distributions. Aerosol deposition velocity also varies with aerosol diameter. Therefore (OC/ EC) $_{min}$ may differ considerably for aerosol, dry deposition and precipitation. This is an interesting avenue of research, but it goes beyond the scope of this particular thesis to explore this concept in depth. Instead, it is interesting to contemplate for future research.
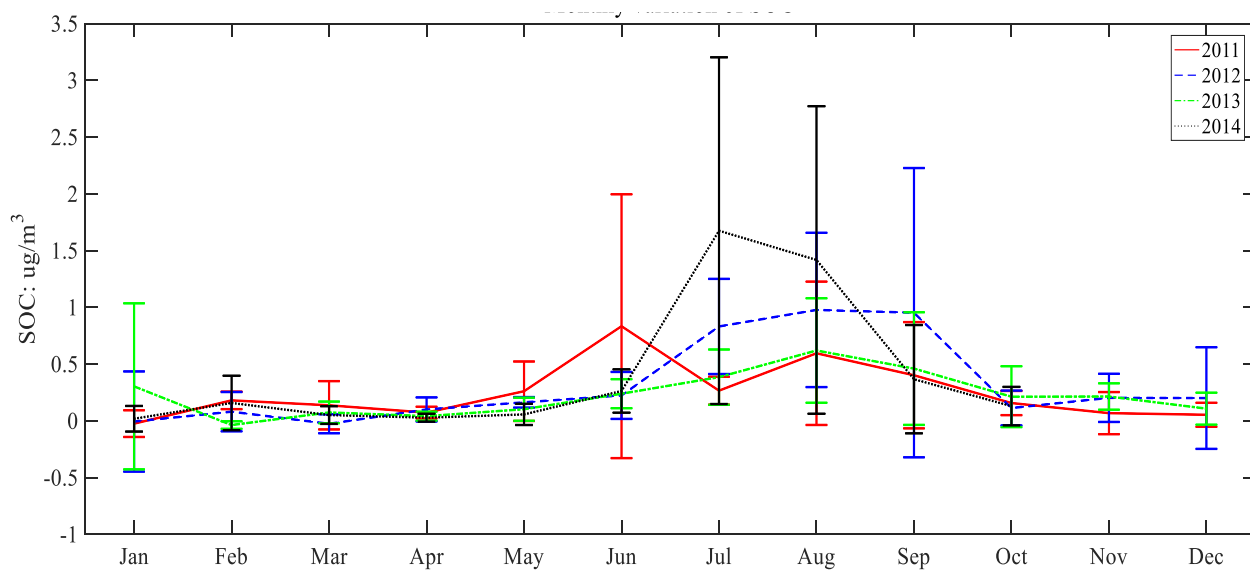
Figure 5-4 Calculated concentration of secondary organic carbon in IMPROVE dataset.
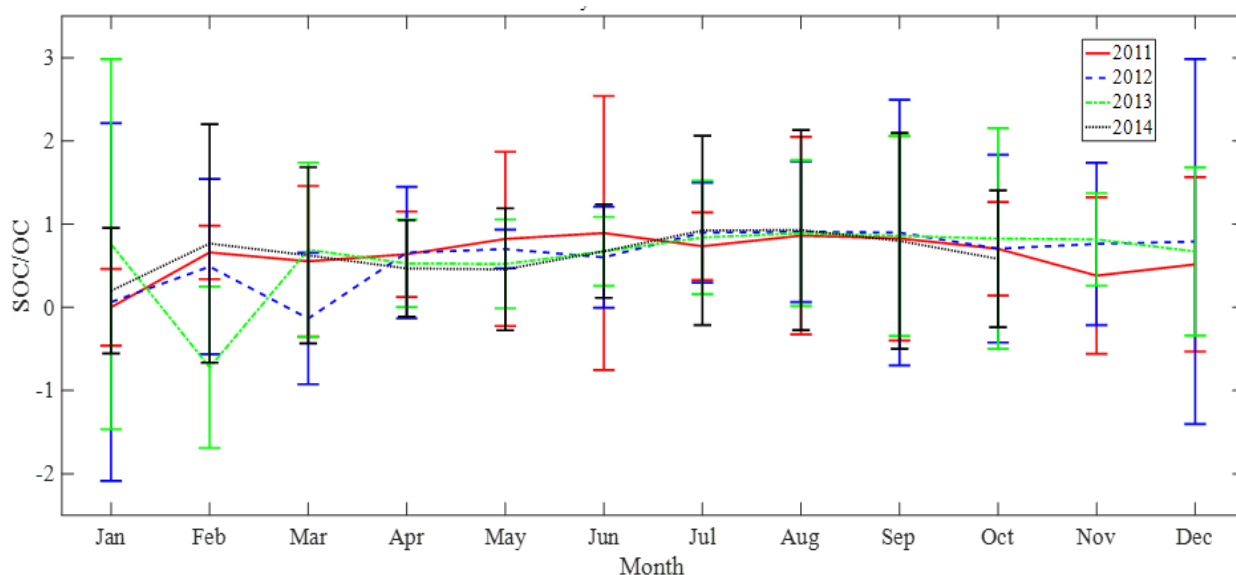
Figure 5-5 Ratio of calculated secondary organic carbon to measured organic carbon in IMPROVE dataset. Note that negative values are possible since an average of three data points is used to calculate (OC/EC) min.

5.1.3 Comparison between IMPORVE Dataset and results in our experiment

The IMPROVE Dataset showed that PM 2.5 and PM 10 in rural areas are from the same or similar sources since the ratio of PM 2.5 to PM 10 remained stable throughout 2011 to 2014 (Figure 2-2). The fraction of TC in PM 2.5 was also stable varying around 0.2 ± 0.1 (Figure 2-5). However, the concentrations of TC and PM 2.5 displayed seasonal features of slightly higher values in autumn and lower values in winter, implying an enhanced autumn source for TC and PM2.5. The concentrations of aerosol EC and OC reached their maximum average values from late spring to early autumn (Figure 2-3, 2-4). A seasonal maximum TC, EC and OC flux in nighttime dry deposition in autumn at Kananaskis (Figure 4-1) that was absent during the day

(Figure 4-2) suggests a local source of carbon was present in Kananaskis during the autumn and at night. Further this source of dry deposition maintained the same ratio of OC/EC in autumn as it does throughout the year (Figure 4-7). This source was likely not firewood (high EC) as we might expect a seasonal signal in OC/EC either as camping takes place in autumn or heating of local buildings using wood during cold winter weather (a very localized source of carbon). This would be distributed throughout the valley. Our observations for dry deposition captured the feature that TC, EC and OC at night are high in autumn and low in winter consistent with a non-firewood source (smoke from campfires or firewood heating). Further, the lack of evidence for this increase in OC and EC in Calgary suggests emissions of OC and EC were local and did not undergo transport to Calgary. In September, traffic was observed to double each year at Kananaskis (http://www.ucalgary.ca/ensc/files/ensc/k-traffic-sept06-ensc-report-july07revsept07.pdf).   This increase in traffic volume, was related with an increasing variation in EC1 and OC3, which were indicators of gasoline exhaust (Figure 2-7 and 2-8).

The precipitation samples did not demonstrate obvious seasonality in TC, EC or OC concentrations in Kananaskis (Figure 4-4), even though the carbon concentrations in the atmosphere (PM2.5 and dry deposition at night) reached peaks mainly in summer (Figure 2-2, 4-4). This indicates that the removal of particulate carbon by precipitation in Kananaskis does not vary much during the year, but dry deposition does.

The OC/EC in the IMPROVE aerosol dataset displayed that a high ratio of 4.1 in winter and a low ratio of 2.1 in autumn (Figure 2-6). The yearly average OC/EC ratio was about 2 which was far lower than our observations for both dry deposition (OC/EC ranges between 11.9 and 33.4)

and precipitation (OC/EC ranges between 11.8 and 46), implying that OC was much more easily removed than EC via deposition due to its larger surface area and larger size (Jurado et al., 2008).

The IMPROVE dataset together with our observations in Kananaskis, indicates that the particulate carbon (TC, EC and OC) in the atmosphere in rural areas had a seasonal feature that suggested a higher deposition rate of TC, OC and EC at night during autumn was possibly associated with vehicle exhaust and higher traffic in the valley in autumn than winter. OC is much more easily deposited via dry deposition and precipitation than EC. This result is supported by previous measurements of dry deposition and precipitation OC and EC in the literature (Jurado et al., 2008). Comparing these results for those in Calgary, it is notable that seasonality was absent in the Calgary dataset (Figure 4-1 and 4-2). A vehicle source that is higher in autumn at Kananaskis but not Calgary is a reasonable explanation.

5.2 Dry Deposition and Precipitation in Kananaskis and Calgary

In Section 2.4 we described our expectations for sources of TC, EC and OC in our study for Kananaskis and Calgary, which represent continental rural and a relatively unpolluted urban environment. Here we explore whether our expectations for these datasets were met regarding to source identification.

5.2.1 Dry deposition

5.2.1.1 Both locations

1. Particulate carbon from vehicle exhaust was shown to exist through the year in both rural and urban locations with an OC/EC ratio of around 22 in dry deposition (Appendix 2).

Even though the concentrations of EC and OC varied during the year at night, the OC/EC ratio remained around 22 throughout the year (Figure 4-7 A). Seasonality that may be caused by biomass burning for heating or biological activities was not observed. Particulate carbon from vehicle exhaust can be the only contributor that has a stable OC/EC ratio throughout the year at night in the Kananaskis. Also, in Calgary, the OC/EC ratio in dry deposition had a value of about 22 in the day and is uniform all year round (Figure 4-7 B). Therefore, particulate carbon from vehicle exhaust could be identified with an OC/EC ratio of about 22.

2. Biological emissions occur only in summer and have no EC component, which will cause high OC/EC ratios.

There was an increase in OC at the Kananaskis site in summer for dry deposition (Figure 4-1), but EC also experienced an increase. The OC/EC ratio for a biogenic source was expected to be extremely high (no EC emitted) and much higher than 22 for vehicle

exhaust. The biogenic source of OC in summer was absent in Calgary with no extremely high OC/EC values. The results are consistent with our expectation that vehicle exhaust exists as the dominant source of particulate carbon for both Kananaskis and Calgary. The increase in OC and EC in summer at Kananaskis was suggested to be due to higher traffic volumes. The Kananaskis site sits about 200 meters southeast of Highway 40 (Kananaskis Trail), and about 9 km south of the Trans-Canada Highway. Highway 40 was estimated to have an Average Annual Daily Traffic (AADT) of 640 and an Average Summer Daily Traffic (ASDT) of 780 in 2016. The Trans-Canada Highway close to the Barrier Lake station was estimated to have an AADT of 1230 and a high ASDT of 1480 in 2016 (Government of Alberta ministry of Transportation, 2017). This interpretation is supported by the consistent OC/EC value for nighttime dry deposition in Kananaskis of around 22.

3. Biomass burning happens both in winter and summer, predominantly in Kananaskis associated with recreation and tourism.

EC is expected to lower the OC/EC ratio due to the incomplete burning of biomass burning. EC concentrations at nighttime in Kananaskis increased sharply in summer, which indicates a local source of EC. In Kananaskis (Figure 5-6 and Figure 5-7), wind speed was lowest in summer at night; 40% of which was classified as calm conditions (less than 0.3 m/s). These low wind conditions correspond to the sudden increase in EC and OC concentrations at nighttime in late spring and summer. Lower OC and EC values for the remainder of the year may be explained by higher wind speeds that to help disperse particulate carbon in Kananaskis. During daytime, winds for all four seasons were similar

in direction, and comparatively had a higher speed than winds at night. Meanwhile, southeast winds at night, blocked by mountainous terrain, obstructed the distribution of EC and OC. Winds mainly from southwest in the day, and aligned with valley, assisted the transport of EC and OC out of the valley. The OC/EC ratio of around 18 (lower than 22) in the day throughout the year also provides evidence that a small portion of local biomass burning contributes to dry deposition.
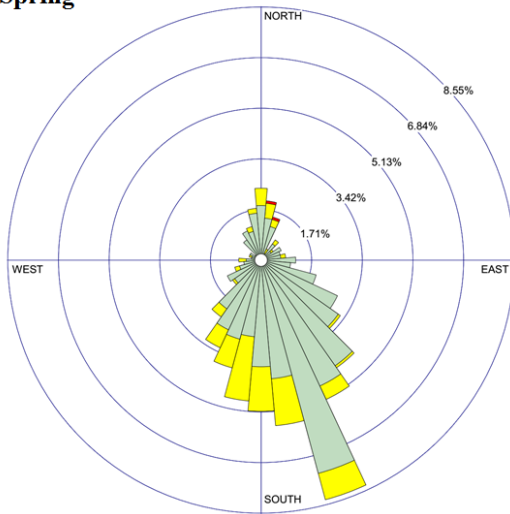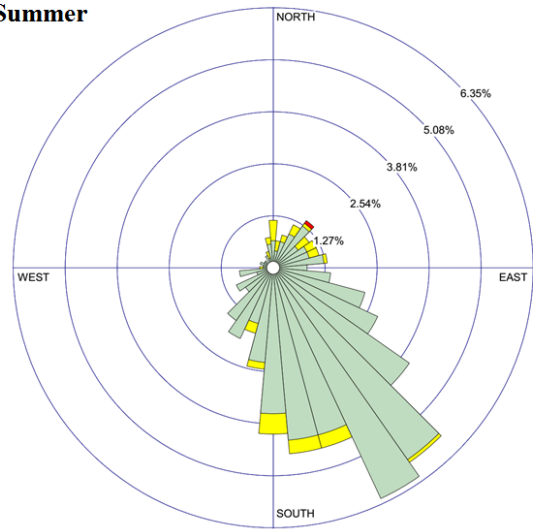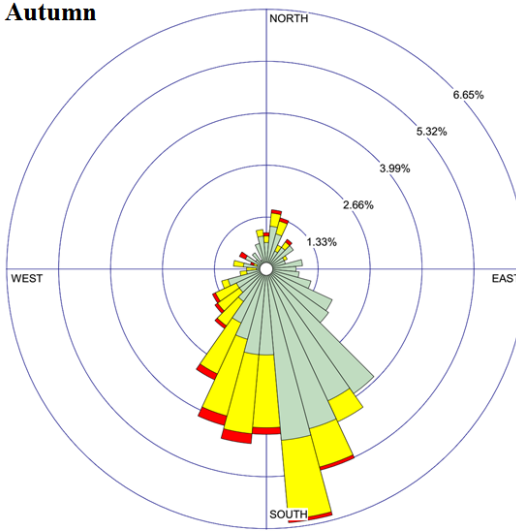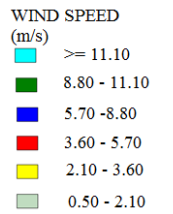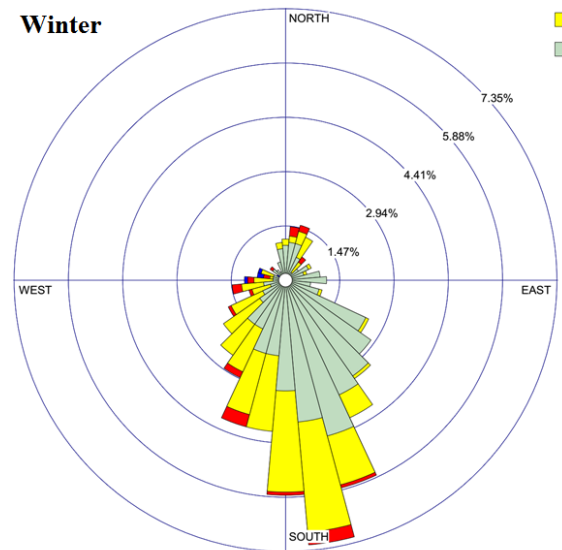
Figure 5-6 Wind rose plot at nighttime in Kananaskis.
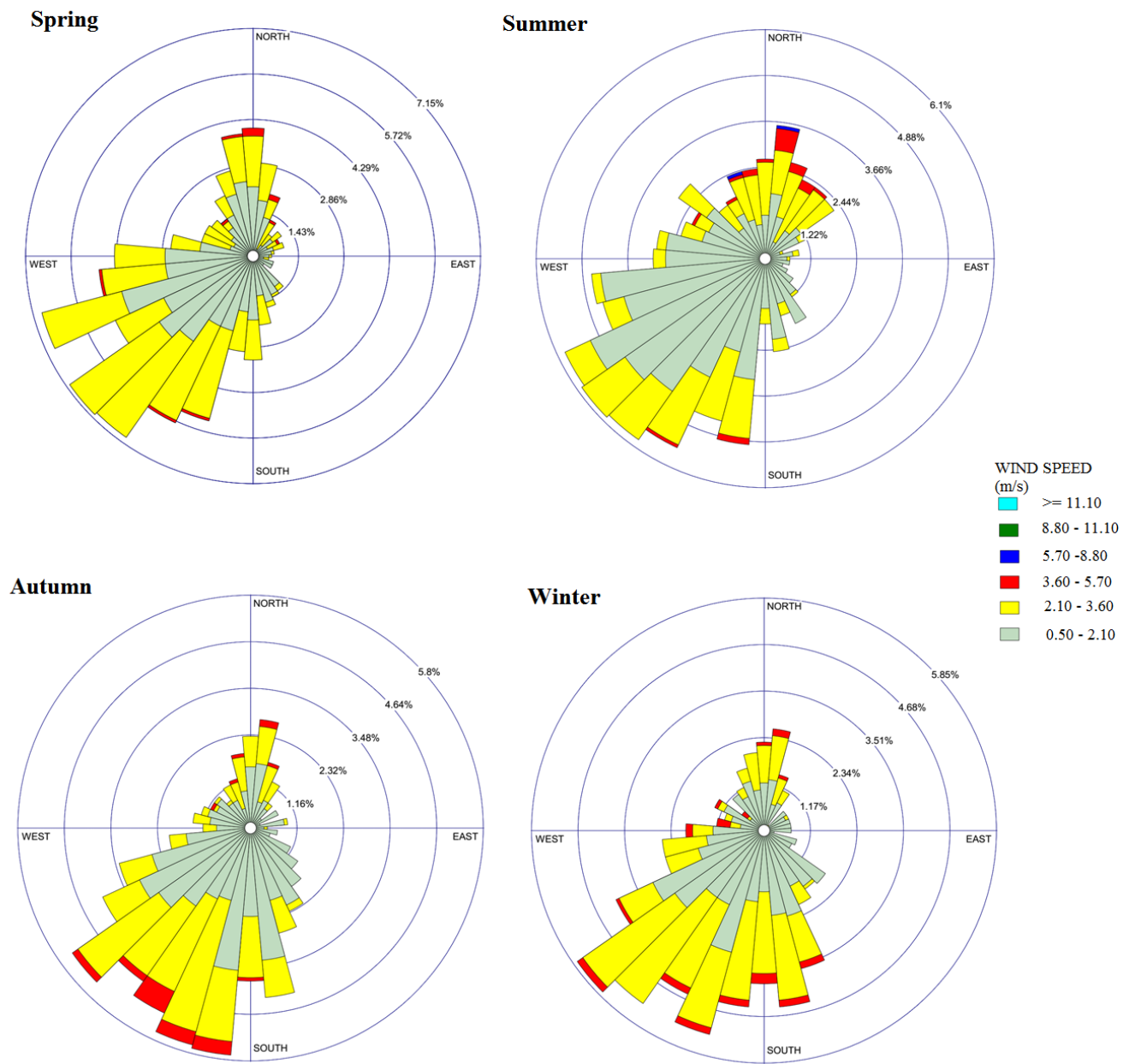
Figure 5-7 Wind rose plot at daytime in Kananaskis.

In Calgary (Figure5-8 and Figure 5-9), average wind speed was much higher than that in Kananaskis. EC from recreation like outdoor barbeques in the day exist in summer, however the winds in daytime in summer helps the dispersion of particulate carbon and does not influence the OC/EC ratio as much as vehicle exhaust does. In winter, biomass burning for heating houses proportionally contributes more to particulate carbon than biomass burning does in Kananaskis in summer (Figure 4-7).
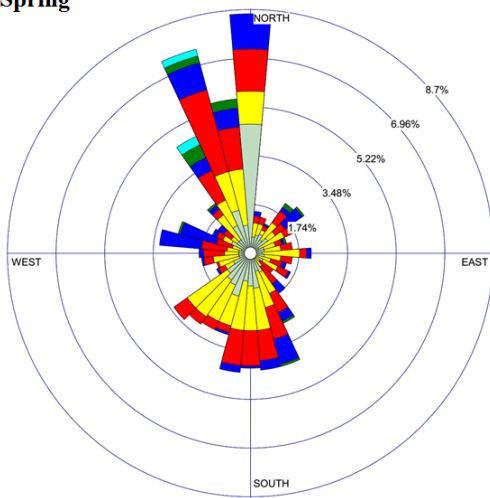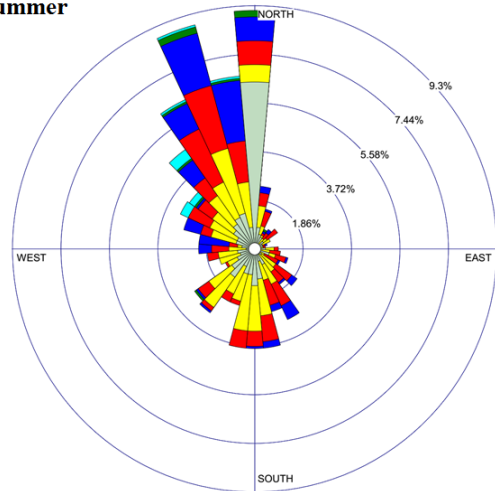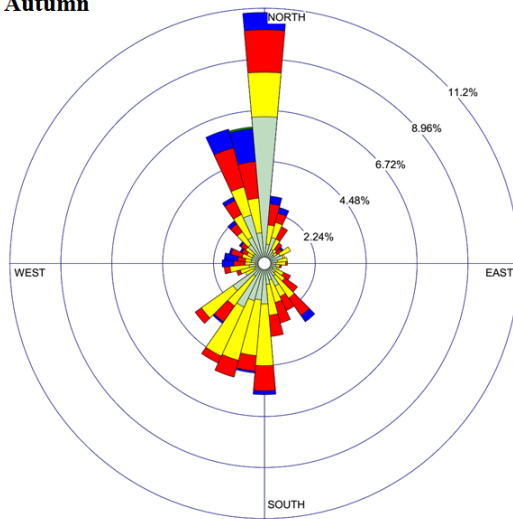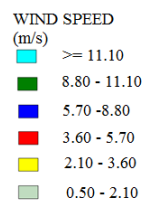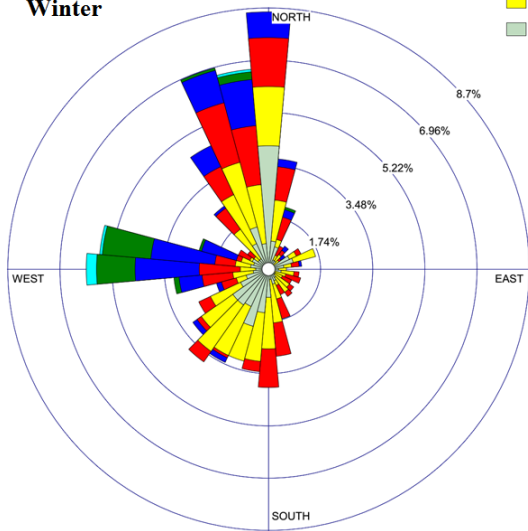
Figure 5-8 Wind rose plot at nighttime in Calgary.
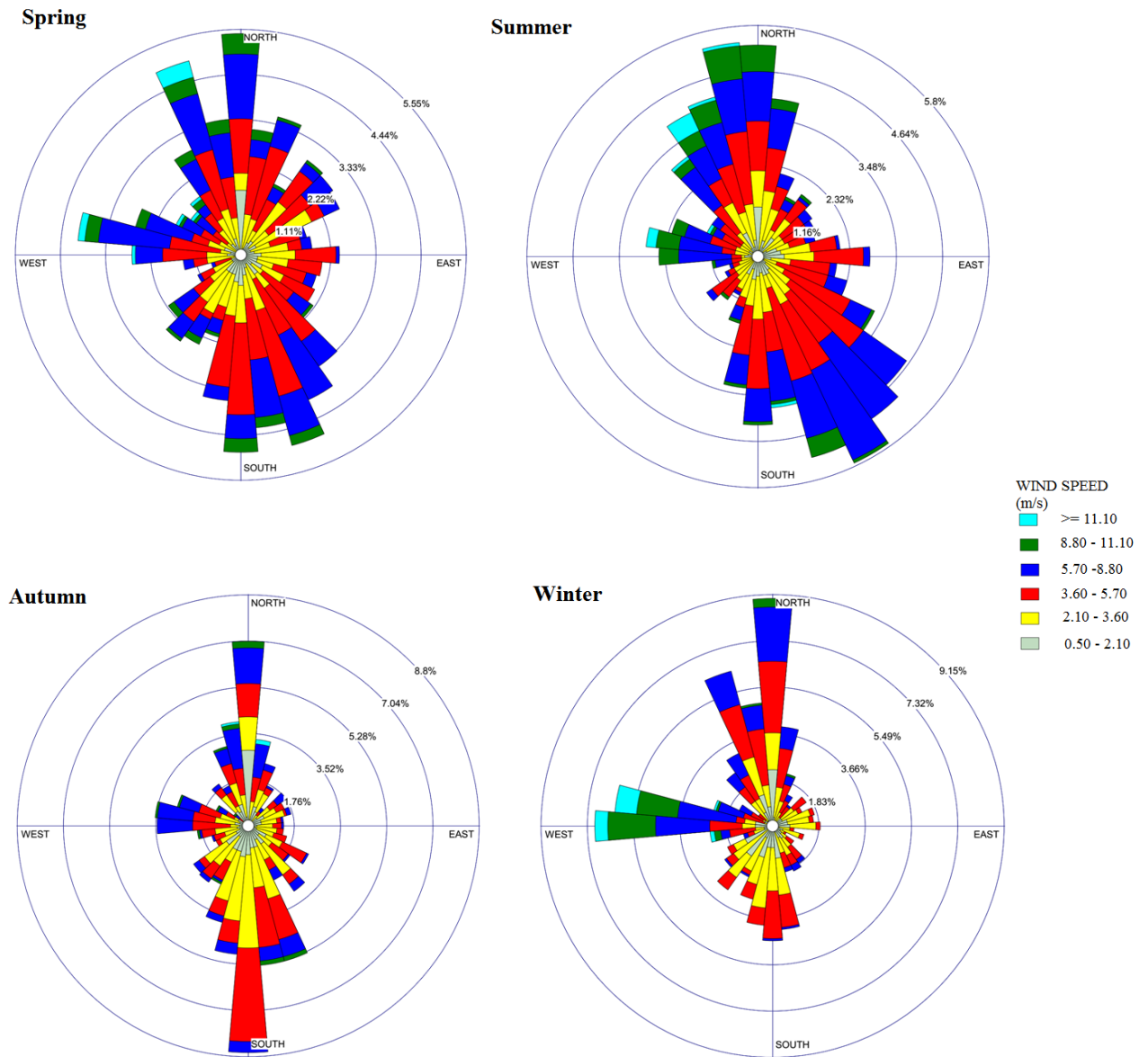
Figure 5-9 Wind rose plot at daytime in Calgary.

4. Sources from long-range transport are expected to impact both locations simultaneously.

The IMPROVE dataset indicates each carbon fraction can be used for the source apportionment of carbonaceous aerosol (Kim et al., 2003; Kim and Hopke, 2004). Yu's group extracted OP by dissolution of carbon in water to identify polar organic compounds (Yu et al., 2002). The OP fraction showed that substantial water-soluble polar compounds might be present in the local atmosphere and were related with long range transport. Both in Kananaskis and Calgary, the OP fraction was found in dry deposition samples. Table 5-3 shows the concentrations of OP in dry deposition at two locations. Little variation with day or night (Table 5-3) or with seasons (not shown) was observed at both locations.

Table 5-3 OP concentrations in dry deposition in Kananaskis and Calgary

Time & Location	Kananaskis $\mu g/\ (m^2 \cdot 8hrs)$	Calgary $\mu g/\ (m^2 \cdot 8hrs)$
Nighttime	1.0 ± 0.5	0.5 ± 0.4
Daytime	1.6 ± 0.4	0.7 ± 0.5

5. A lower boundary layer at night increases PM concentration and a higher boundary layer in the day lowers the concentration at both locations.

In Kananaskis, the concentration of EC during the day, which was not related with biological emissions, is higher than that at night throughout the year (Figure 4-1 B and

Figure 4-2 B). This is opposite to what might be expected for local fire wood burning since the lower boundary layer is expected to increase the EC concentrations in Kananaskis. Instead, traffic emissions are consistent with increasing TC and OC in the day.

5.2.1.2 Calgary

1. Vehicle exhaust was suggested to be the dominant source of carbon in Calgary due to the lack of significant urban industrial activities with an identical OC/EC ratio of 22 in the day.

2. A morning and evening peak in particulate matter is expected due to higher traffic volumes.

No difference between nighttime and daytime was observed in TC, OC and EC concentrations in Calgary since daytime dry deposition captured morning peak traffic and nighttime dry deposition captured evening peak traffic.

3. More EC from biomass burning at night would lower the OC/EC ratio.

OC/EC ratios that decreased at night in Calgary is consistent with biomass burning. Although most houses in Calgary use natural gas for heating, the number of houses in Calgary burning wood is still larger than that in Kananaskis. Wood burning in Calgary is expected to produce a fairly large proportion of EC, which would cause lower OC/EC

values in winter. In contrast, propane is used for winter heat in the Kananaskis and this is expected to have higher combustion efficiency, so a lower proportion of EC would be produced relative to woodfires. Therefore, OC/EC in Calgary at night (around 13) was lower that for the Kananaskis (around 22).

5.2.2 Precipitation

With regard to precipitation, we have demonstrated the expectation described in Section 1.4 that in both locations OC is much more easily removed by precipitation than EC because OC mostly is hydrophilic while EC (especially fresh EC is homophobic). When EC gets aged (there is SOC and inorganic sulfate or nitrate coating), it becomes hydrophilic and easy to remove by precipitation. The average OC/EC ratios at both locations were much higher than those for dry deposition and aerosols (Figure 5-10).
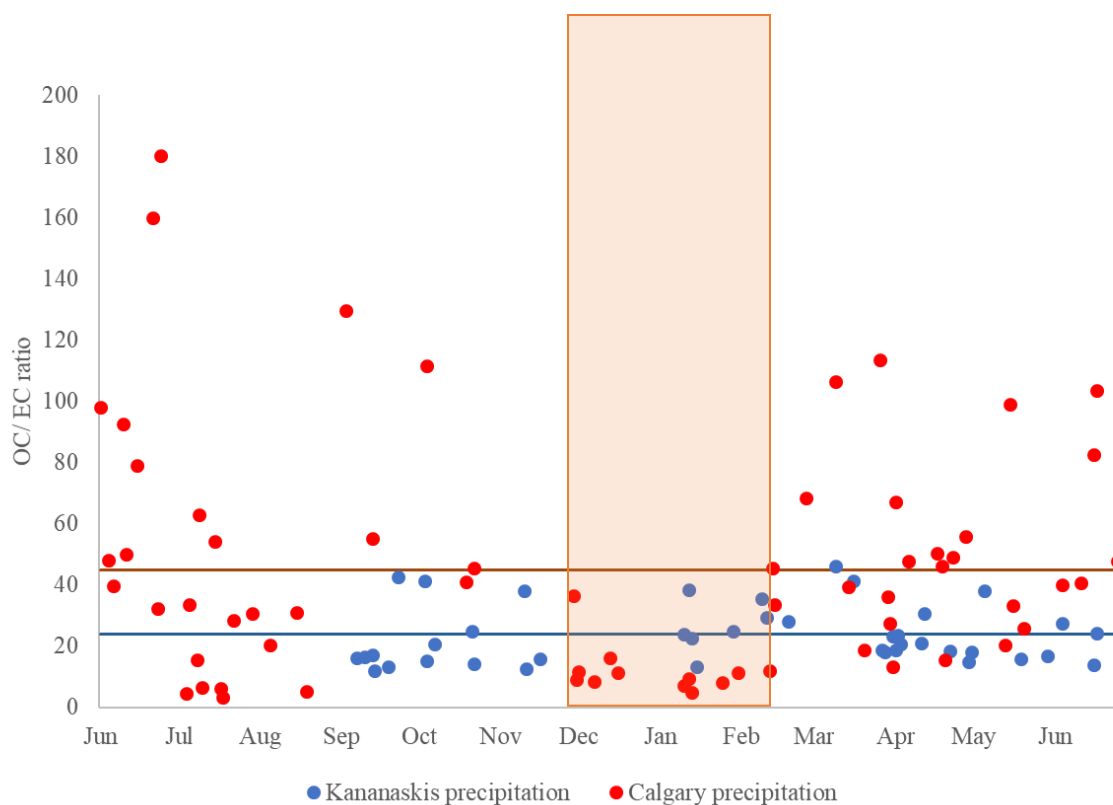
Figure 5-10 OC/EC ratio in precipitation in Kananaskis and Calgary. The red line indicates the average of OC/EC ratio in Kananaskis; the blue line indicates the average of OC/EC ratio in Calgary; the orange box covers the period when OC/EC ratio are extremely low.

However, there are questions related to the TC, EC and OC concentrations and OC/EC ratios at these two locations:

1. Why were there no seasonal obvious peaks in EC or OC in Kananaskis showing biomass burning or biological activities?

2. Why were there low OC/EC ratios observed in winter in Calgary?

To answer these questions, first we applied a principal component analysis (PCA) (Thurston and Spengler, 1985) to identify and quantify the major source contributors in precipitation in Kananaskis and Calgary based on the potential sources we find in Table 5-1. Then we used air quality data to distinguish sources from possible industrial events.

5.2.2.1 Principal component analysis in Kananaskis

Following the PCA process described in Chapter 3, three main components were extracted from analyzed carbon fractions in Kananaskis. Results for summer and winter are summarized in Tables 5-4 and 5-5. In summer, Component 1 was highly loaded with OC2, OC3, OC4, OP and EC1. This component is related with gasoline exhaust, road dust profile and long-range-transport. Component 2 in summer, was highly loaded with EC2 and EC3, which represent diesel exhaust and recreation events (Table 5-1). The high loading of OC1 in Component 3 in summer, reflected the contribution of biomass burning (woodfire burning/forest fires). In winter, Component 1 was highly loaded with OC2, OC3, OC4 and EC1, which reflected gasoline exhaust, road dust profile and long-range-transport. Component 2 in winter was highly loaded with OC1 and OP, which stood for biomass burning and long-range transport. The high loading of EC2 and EC3 in Component 3 in winter reflected the contribution of diesel exhaust and recreation events.

Table 5-4 Principal component analysis for summer in Kananaskis. Note that only results over 0.65 are presented.

| | Component Matrix | | |
	1	2	3
OC1			0.87
OC2	0.82		
OC3	0.81		
OC4	0.90		
OP	0.85		
EC1	0.82		
EC2		0.90	
EC3		0.83	
	Gasoline &Road dust &Long-range transport	Diesel & Recreation events	Biomass burning

Table 5-5 Principal component analysis for winter in Kananaskis. Note that only results over 0.65 are presented.

	Component Matrix		
	1	2	3
OC1		0.90	
OC2	0.92		
OC3	0.76		
OC4	0.82		
OP		0.75	
EC1	0.84		
EC2			0.91
EC3			0.82
	Gasoline &Road dust	Biomass burning & Long-range transport	Diesel &Recreation events

Source contributions can be resolved for summer and winter samples (Figure 5-11). Obviously, vehicle exhaust (gasoline and diesel) dominates the TC emission in both summer and winter. Here we answer the first question: volume of traffic emission dominates EC and OC emissions as well as OC/EC ratios even in rural continental locations. Note that only three major components were extracted using PCA analysis in Kananaskis. The second major source related with diesel exhaust and recreation events is uniform in summer and winter, indicating a stable

carbon contribution from diesel vehicles and recreation events. Biomass burning is likely local in

summer (no OP) but is regionally emitted in winter (Tables 5-4 and 5-5).
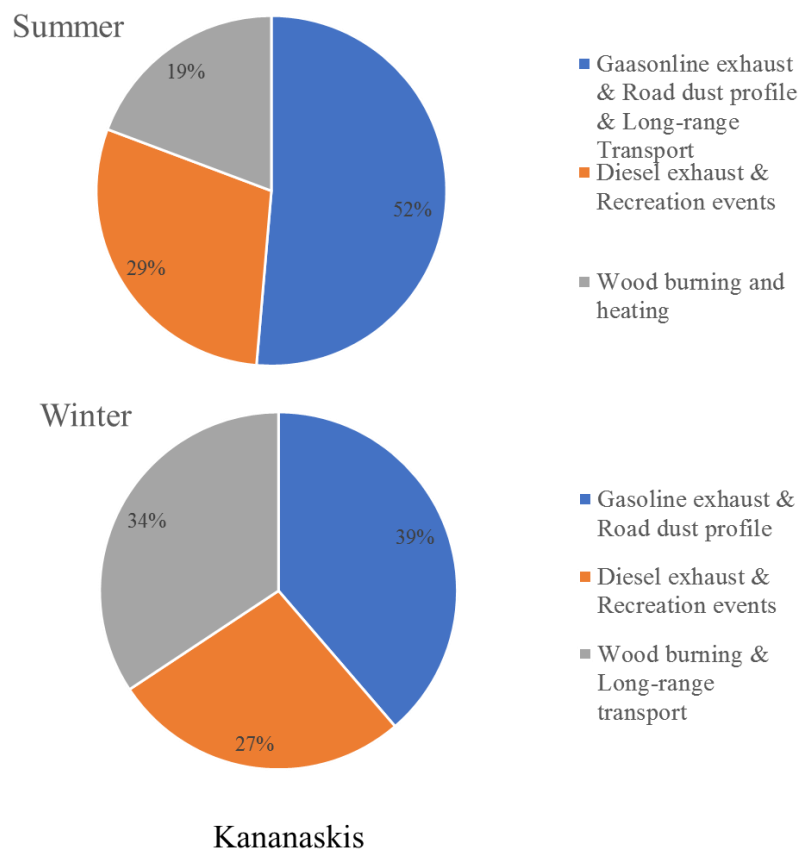
Figure 5-11 Relative contributions of major sources to particulate carbon during summer

and winter in Kananaskis.

5.2.2.2 Principal component analysis in Calgary

Together with ion concentration results, PCA was also conducted for Calgary data to understand the different carbon components (Tables 5-6 and 5-7). Five major source contributors were extracted via PCA: gasoline exhaust and road dust profile, diesel exhaust, recreation events, wood burning and heating and long-range transport (Figure 5-12). It is not surprising that more components were identified than Kananaskis as diverse emissions influence the Calgary site. Similar to what was found for the Kananaskis, vehicle exhaust is the main contributor to particulate carbon in Calgary; about 60% both in summer and winter (Figure 5-12). The percentage of gasoline exhaust and road dust profile increased in winter (41%) compared to summer (34%) in Calgary. Fewer recreation events take place in winter, which is likely due to the cold weather. Other contributors do not vary much throughout the year.

Sodium and Sulfate are associated with OC1 in both summer and winter. Magnesium is not associated with any component using 0.65 as the criteria. Potassium and Calcium appear to be associated with diesel exhaust in winter but not in summer. Vehicle emissions from diesel exhaust are expected to contain more sulfur than gasoline combustion since the anti-knock agent MoS_2 is added to diesel engines (Norman et al., 2004). Instead Sulfur is associated with lighter hydrocarbon fraction (identified as gasoline here). Gasoline likely encompassed the light hydrocarbon emissions associated with sulfur-rich oil and gas activities upwind of Calgary (Norman et al., 2004). Alberta's oil and gas are associated with geological formations that represent an ancient inland sea. Therefore, sodium is unexpected along with sulfur in the light hydrocarbon fraction. Magnesium and Calcium are typically emitted together from lithosphere. However, two separate

industries emitting Magnesium (High River) and Calcium (Greystone) are present to the west of Calgary near the hamlet of Exshaw. The influence of these emissions is evident by the lack of correspondence between Magnesium and Calcium. Potassium is typically considered a component of biomass burning. However, in this PCA analysis, it is associated with diesel emissions in winter but not in summer. The reason for this is unresolved.

Table 5-6 Principal component analysis for summer in Calgary. Note that only results over 0.65 are presented.

	Component Matrix				
	1	2	3	4	5
OC1				0.83	
OC2	0.78				
OC3					
OC4	0.76				
OP					0.84
EC1	0.72				
EC2		0.85			
EC3			0.88		
Sulfate	0.76				
Sodium	0.67	0.65			
Potassium					
Magnesium					
Calcium					
	Gasoline &Road dust profile	Diesel	Recreation events	Wood burning & heating	Long-range transport

Table 5-7 Principal component analysis for winter in Calgary. Note that only results over 0.65 are presented.

	Component Matrix				
	1	2	3	4	5
OC1			0.76		
OC2	0.89				
OC3	0.90				
OC4	0.70				
OP					0.68
EC1	0.68				
EC2		0.93			
EC3				0.81	
Sulfate	0.77				
Sodium	0.81				
Potassium		0.80			
Magnesium					
Calcium		0.73			
	Gasoline &Road dust profile	Diesel	Wood Burning and heating	Recreation events	Long-range transport
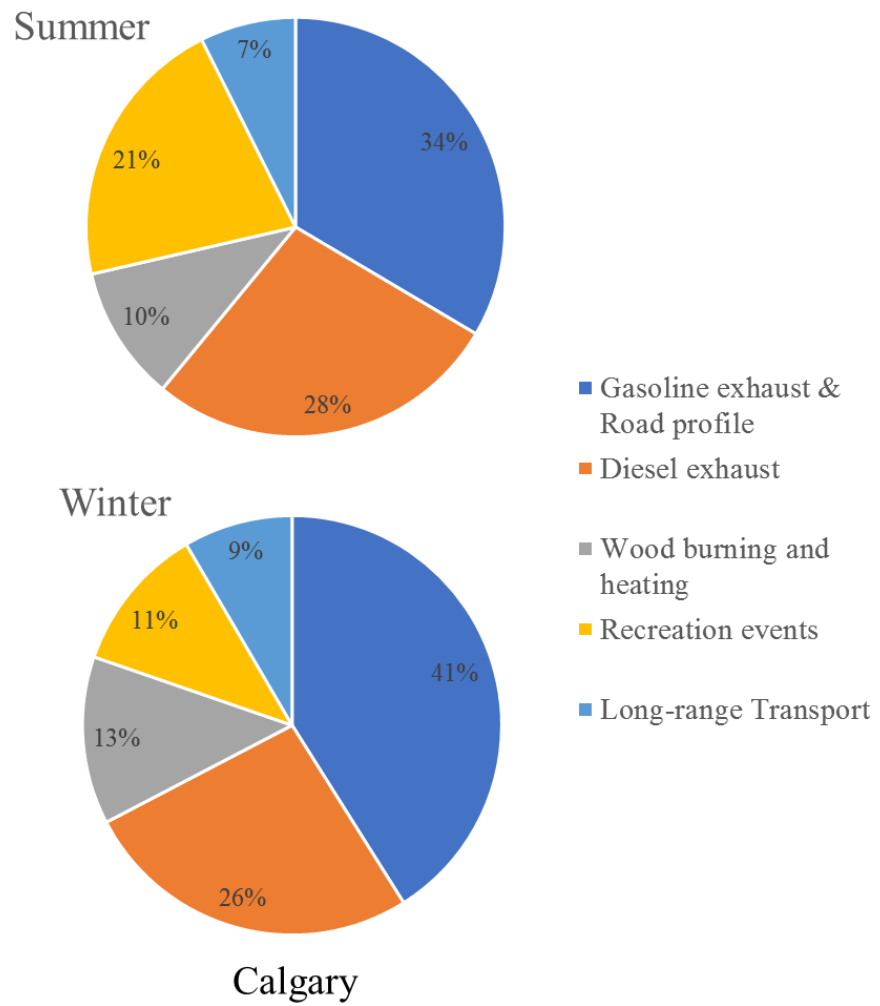
Figure 5-12 Relative contributions of major sources to particulate carbon during four seasons in Calgary

5.2.2.3.1 EC, SOC and SO₄ in winter precipitation

Very interesting results were observed for EC versus SO_4 in winter (Figure 4-8). Further if equation (Chapter 4(1)) is used for precipitation with an (OC/EC) $_{min}$ =12, then a strong correlation between SOC and SO_4 was observed (Figure 5-13). When individual OC and EC components for winter are plotted against SO_4, either no relationships or poor relationships results exist.
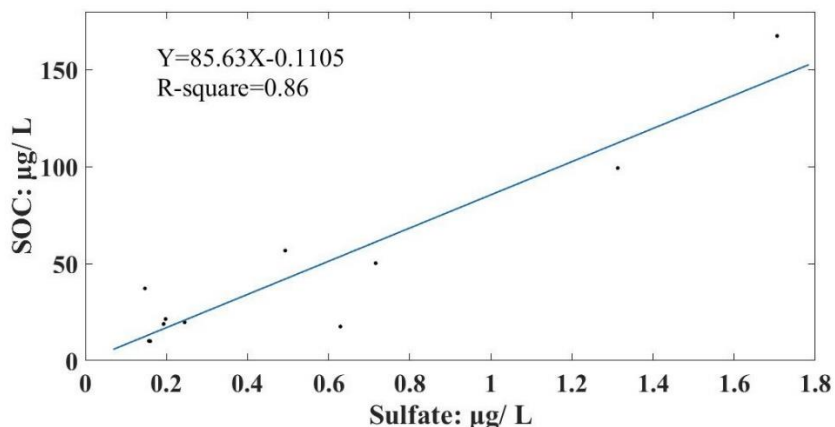
Figure 5-13 Correlation between SOC and sulfate in winter in Calgary.

In an effort to understand whether a particular upwind source was responsible for this correlation in winter in Calgary, air quality from NW Calgary and SE Calgary stations were studied.

5.2.2.3.2 Air quality data in Calgary

The air quality is dependent on the rate at which pollutants are emitted into the atmosphere and the ability of the atmosphere to disperse these pollutants. The movement and dispersion of

pollutants is controlled by wind, temperature, turbulence and the changes in these elements caused by local topography. Using source apportionment, the carbon sources were roughly divided into four categories: gasoline exhaust, diesel exhaust, biomass burning and long-range transport. With the assistance of air quality data, the major pollution events can be captured from industrial regions upwind that may change the measured concentration of particulate carbon at our sampling site.

Three pollutants (NO_X, PM and SO_2) were discussed to identify pollution events due to their properties related with industrial production. NO_X, is produced by the high temperature combustion of fossil fuels and will increase significantly when pollution events occur. PM consists of a mixture of particles of varying size and chemical composition and is usually related with increased total carbon as discussed in section 5.1. SO_2 is generated both naturally and anthropogenically, including the processing and combustion of fossil fuels containing sulfur. The latter process is found to have a positive correlation with elemental carbon as mentioned in 5.2.4.

Two air quality monitoring stations are situated in the southeast and northwest of the city. Our sampling site in Calgary sits close to the northwest monitoring station. Therefore, when high values of the same pollutant occur at both monitoring stations, this pollutant can be identified as being derived from upwind industrial facilities. Applying the criteria that PM at both locations were over 12 µg/m^3 (average + standard deviation), we were able to find those days with high-values for particulate matter, which likely includes a significant proportion of particulate carbon. Among these days, NOx monitored over 0.04 ppm (average + standard deviation) at the SE station and over 0.03 ppm at NW station was considered as high NOx events. These were related with high temperature combustion of fossil fuels, potentially from industrial facilities. Another indicator

of upstream industrial activities was high SO_2. Since only the SE station monitored SO_2, we were not able to compare SO_2 results at the NW and SE Calgary stations. The SO_2 concentration usually remained at 0 and increased to 0.001 ppm when industrial events were suspected.

Figure 5-14 presents the events identified with our criteria: 39 events with high PM values; 27 events with both high PM and NO_x values; 16 events with high PM, NOx values and presence of SO_2. Comparing these days with "industrial events", we would be able to explain most of the very high OC and EC concentrations measured in autumn and winter, especially in dry deposition since less precipitation fell in winter than in summer that year. The high OC and EC concentrations in summer were not considered to come from industrial sources since the NO_x and SO_2 did not appear in the air quality data.
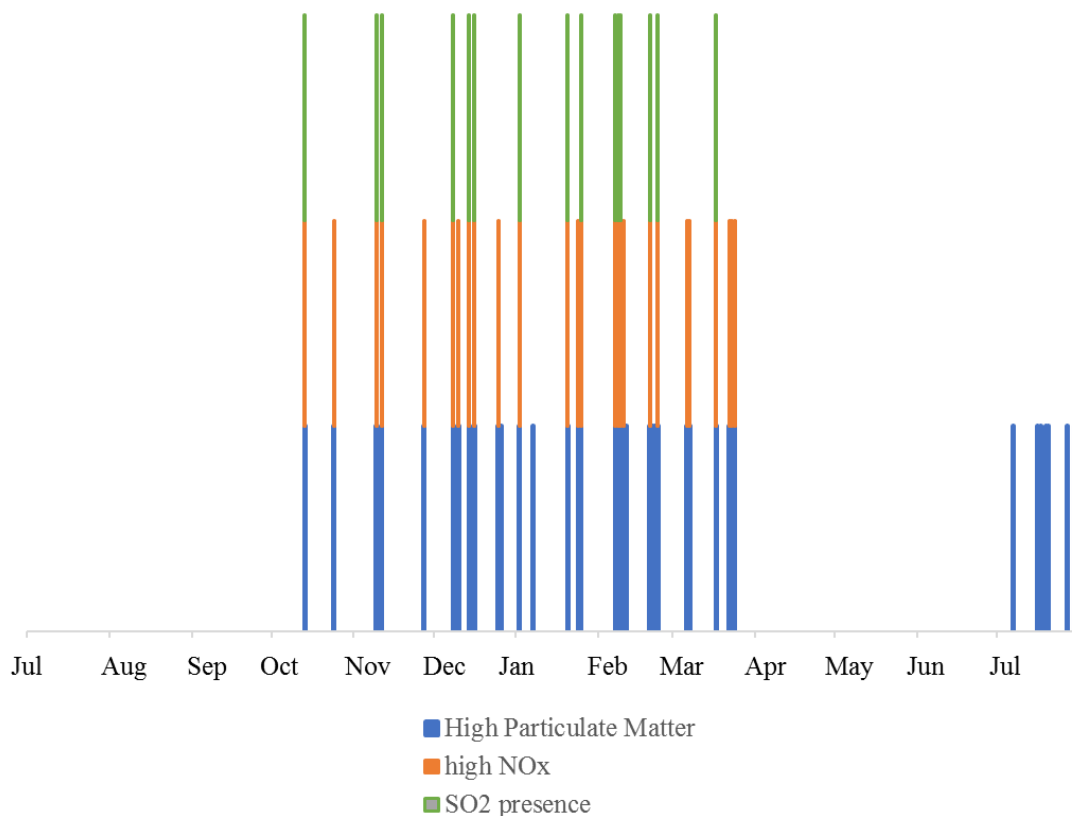
Figure 5-14 Events distinguished by pollution factors

The high pollution events covered the period in winter when OC/EC ratios were low, which was also the period when SO_4 and EC has a positive correlation. During this period, dominantly northwest winds had an average of 4.3 km/hr, which was lower than the year-average wind speed of 7.8 km/hr for the NW Calgary station. Such lower wind speed did not favor the dispersion of the pollutants near our sampling site, which increased the concentrations of particulate carbon. The concentration of SO_4 also increased due to the slow process of oxidation of the upwind SO_2 produced anthropogenically from the industrial facilities (Brook et al., 1993). Despite being inert, EC is known to play an important chemical role, particularly its ability to catalyze the oxidation

of SO_2 to SO_4 in aqueous solution such as precipitation (Chang et al., 1982). Governed by the physical processes of coagulation or diffusion in the atmosphere, EC may act as a cloud condensation nucleus and be coated with ambient particles like H_2SO_4 with adequate time. Such coated EC can have a lifetime range from less than 40 hours in rainy climates to over one week in dry climates (Ogren and Charlson, 1983). With the meteorological conditions of slow winds and infrequent precipitation winter, EC has the possibility to have a positive correlation with SO_4 in winter in Calgary. Therefore, EC coated with SO_4 can be removed from the atmosphere effectively via precipitation, lowering the OC/EC ratio in precipitation. However, EC concentration and OC/EC did not appear correlated with wind direction or wind speed in this experiment.

Chapter Six Summary and Recommendation

6.1 Summary

This is the first study of elemental carbon(EC), organic carbon(OC) and total carbon(TC) from dry deposition and precipitation in a rural area (Kananaskis) and an urban area (Calgary) in southwestern Alberta. It revealed results that can be anticipated together with some unexpected findings. This study, with the IMPROVE dataset, demonstrates that the EC, OC concentrations of dry deposition and precipitation are valuable in determining the contribution from a selection of organic pollution sources. The results will be evaluated in this section in terms of the expectations described in section 1.4.

<u>Both locations</u>

1. Particulate carbon from vehicle exhaust exists thorough the year in both rural and urban locations. Even though the concentrations of EC and OC varied during the year at night, the OC/EC ratio remains around 22 throughout the year. Biomass burning for heating or biological activities, which may cause seasonality, was not observed in aerosols. Vehicle exhaust was the dominant contributor to particulate carbon with a stable OC/EC ratio throughout the year at night in the Kananaskis. The OC/EC ratio in Calgary in dry deposition also had a value of about 22 in the day and is uniform all year round. Therefore, particulate carbon from vehicle exhaust can be identified with an identical OC/EC ratio of about 22.

2. The organic component of biological emissions occur only in summer. This is expected to cause high OC/EC ratios since no EC is emitted from vegetation. An increase in OC was apparent in the IMPROVE dataset and in dry deposition in Kananaskis in summer, but EC also experienced an increase. The OC/EC ratio for a biogenic source was expected to be extremely high without EC emission and much higher than the value of 22 for vehicle exhaust. The increase in OC and EC in summer at Kananaskis was likely due to higher traffic volumes from Highway 40 (Kananaskis Trail) and the Trans-Canada Highway. The biogenic source of OC in summer was absent in Calgary, with a uniform OC concentration throughout the year. This interpretation strengthens our first expectation that vehicle exhaust is the dominant source for particulate carbon at both locations.

3. Biomass burning happens both in winter and summer, predominantly in Kananaskis associated with recreation and tourism, and especially at night. This is expected to result in low OC/EC ratios. EC is expected to lower the OC/EC ratio due to the incomplete burning of biomass burning. EC concentrations at nighttime in Kananaskis increased sharply in summer, which indicates a local source of EC. In Kananaskis, wind speed was lowest in summer at night. These low wind conditions corresponded to the sudden increase in EC and OC concentrations at nighttime in late spring and summer. Lower OC/EC values for the remainder of the year might be explained by higher wind speeds that to help disperse particulate carbon in Kananaskis. Meanwhile, southeast winds at night blocked by mountainous terrain obstructed the distribution of particulate carbon while winds mainly from southwest in the day, and aligned with valley, assisted the transport of particulate carbon out of the valley. A small portion of local biomass burning also contributed to dry

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deposition with the evidence that OC/EC was reduced to about 18 when biomass burning emissions are present. In Calgary, EC from recreation like outdoor barbeques in the day exist in summer, however the high-speed winds in daytime in summer helps the dispersion of particulate carbon and does not influence the OC/EC ratio as much as vehicle exhaust does. In winter, biomass burning for heating houses proportionally contributed more to particulate carbon than biomass burning does in Kananaskis in summer (OC/EC values for Calgary were as low as around 10 in dry deposition and around 3 in precipitation).

4. Sources from long-range transport are expected to impact both locations simultaneously. The IMPROVE dataset indicates each carbon fraction can be used for the source apportionment of carbonaceous aerosol (Kim et al., 2003; Kim and Hopke, 2004). OP was extracted by dissolution of carbon in water to identify polar organic compounds (Yu et al., 2002). Both in Kananaskis and Calgary, the OP fraction was found in dry deposition samples, which shows that particulate carbon from long-range transport is present in the local atmosphere.

5. A lower boundary layer at night increases PM concentration and a higher boundary layer in the day lowers the concentration at both locations. In Kananaskis, the concentration of EC during the day, which is not related with biological emissions, was higher than that at night throughout the year. This was opposite to what might be expected for local fire wood burning since the lower boundary layer was expected to increase the EC concentrations in Kananaskis. Instead, traffic emissions were consistent with increasing TC and OC in the

day. In Calgary, both EC and OC decreased in the day, which was evidence that the higher boundary layer lowered the concentration of locally emitted TC.

Calgary

1. Vehicle exhaust was suggested to be the dominant source of carbon in Calgary due to the lack of significant urban industrial activities with an identical OC/EC ratio of 22 in the day.

2. A morning and evening peak in particulate matter was expected due to higher traffic volumes. Since daytime dry deposition captured morning peak traffic and nighttime dry deposition captured evening peak traffic, no difference between nighttime and daytime was observed in TC, OC, and EC concentrations in Calgary. This also indicates that our sampling methods to distinguish day and nighttime emissions could be improved in the future.

3. More EC from biomass burning at night would lower the OC/EC ratio. Yes, OC/EC values that decreased at night in Calgary were consistent with biomass burning. More houses in Calgary burn wood for heating than that in Kananaskis where propane is the major heating fuel, therefore OC/EC in Calgary at night (around 13) was lower than that in Kananaskis (around 22).

4. Pollutants from rural industrial activities from upstream oil and gas exploration and production can be transported into the city and influence the carbon concentration in conjunction with aerosol SO_4.

6.2 Recommendation for future works

This study examined particulate carbon in precipitation and dry deposition for the first time in Southern Alberta. There are plenty of opportunities for future work. Limitations of the study, that were identified after data collection and analysis, and recommendations for improvement for future studies were provided to solve these limitations as following.

1. A problem related with the sampler was that no cover was used on the funnel. The particles on the surface of the funnel could be blown away during high-wind days. To solve this problem, a deep and rigid-surface funnel could be used to reduce the wind effect.

2. Samples in Kananaskis were not collected at the beginning two months of our experiment period, therefore we were not able to compare the results during that time. In future work, a standardized sampling schedule should be decided before starting the experiment and more samplers should be distributed at more locations besides University of Calgary and Kananaskis station.

3. Small volumes of samples and the long time required for sample processing increase the chance for sample contamination. An improvement, such as faster processing using sealed sampler, to the sampling procedure could reduce contamination and increase data quality.

4. Though we discussed the influence of the Rockies, an in-depth study of local topography and air mass trajectories of particulate carbon sources should be conducted assist identify point source emitters that mostly influence the city of Calgary.

5. Biogenic emissions, which would be expected to be evident as high OC/EC values in growing seasons with a larger signal in the Kananaskis than Calgary, were notably absent in both dry deposition and precipitation in the Kananaskis. The reason for this lack of signal is not clear. However, one possible explanation could be that biogenic particles are larger than 11 microns and were removed by Whatman filtration. In future, the effect of Whatman No. 1 filters on biogenic organic components should be examined: for example, larger summer samples from forested continental sites could be split into two with one portion filtered through Whatman No.1 filters to compare with the unfiltered portion.

6. Though propane is a relatively clean fuel comparing with coal or wood burning, OC and EC can be formed from propane burning. Characterizing emissions from propane combustion would be an important topic to help understand the source of OC and EC in this study.

There are several choices for additional work in analysis. For example: due to the scope of our study, we have not examined if we can apply the estimation method of SOC to dry deposition or precipitation. It could be an interesting topic in future work; Though we have evidence that long-range transport exists at both rural and urban locations, we are not sure about the potential oxidation routes and transport of particulate carbon; and we could evaluate the carbon and ion sources from industries directly by sampling at oil and sands areas in the future.

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Appendix

1. Concentration of acids and salts as coagulants in solution (Torres et al., 2014).

Acids/Salts in solution	Concentration(mole/L)	Ionic strength(mole/L)	pH
Control A	0	0	7.00
Control B	0	0	7.00
NH_4NO_3	0.12	0.12	5.07
HNO_3	0.60	0.60	0.22
H_2SO_4	0.94	2.81	0.02
HCl	0.29	0.29	0.54
H_3PO_4	0.82	4.91	1.14
$(NH_4)_2SO_4$	0.08	0.23	5.42
$NH_4H_2PO_4$	0.09	0.09	4.70
NaCl	0.17	0.17	7.00
$Al_2(SO_4)_3$	0.03	0.44	5.86

2. Ranges of carbon concentration in Chapter Four

Sample types	Locations	TC	EC	OC	OC/EC
Nighttime Dry Deposition Unit: μg/(m²·8hrs)	Kananaskis	4.2-92.5 (25 ± 25)	0.4-25.3 (8 ± 12) Max(summer):25 ± 12	2.8-51.7 (17 ± 14) Max(summer): 36 ± 12	11.9-33.4 (22 ± 5)
	Calgary	70.5-121.9 (95 ± 13)	3.0-11.1 (7 ± 2) Max(autumn): 8 ± 2	65.0-115.7 (89 ± 12) Max(summer): 95 ± 7	8.5-23.6 (13 ± 4)
Daytime Dry Deposition Unit: μg/(m²·8hrs)	Kananaskis	48.1-65.5 (56 ± 5)	2.1-4.1 (3 ± 1)	45.0-62.9 (53 ± 3)	12.9-28.9 (18.2 ±4)
	Calgary	69.8-116.2 (91 ± 11)	1.2-8.8 (5 ± 1)	64.5-108.4 (86 ± 8)	9.8-70.5 (22 ± 14)

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Sample types	Locations	TC	EC	OC	OC/EC
Precipitation Unit: µg/L	Kananaskis	335.7-922.6 (540 ± 163) Max(winter): 2249 ± 2125 Min(summer): 626 ± 204	11.0-31.5 (23 ± 6)	312.9-899.1 (540 ± 163)	11.8-46.0 (24 ± 10)
	Calgary	219.6-14432.9 (2249 ± 2125) Min(winter): 883 ± 340 Max(summer): 2982 ± 2827	4.8-235.0 (65 ± 42)	189.3-14278.5 (2248 ± 2125)	3.3-180.2 (45 ± 38)