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Kelowna PM_{2.5} Characterization Monitoring Project 2006–2007

Final Report

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Meteorological Service of Canada
Environment Canada
Pacific and Yukon Region
November 2012

Canada

Cat. No.: En56-248/2014E-PDF
ISBN: 978-1-100-23716-9

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Summary

Kelowna, in the Okanagan region of British Columbia, is the third largest metropolitan area in the province, having a population of approximately 180 000. A number of actions targeting residential wood smoke, burning and mobile sources have been initiated in recent years to address particulate matter (PM) pollution in Kelowna, and while PM_{2.5} levels remain below the Canada-wide Standard and provincial objectives, Kelowna still experiences episodes of elevated levels of PM, particularly in the cold season and during forest fire events.

In order to characterize PM_{2.5}, determine and quantify its sources and assess its impact on visibility, a speciation sampling program was initiated in Kelowna in September 2006 as a follow-up study to a PM speciation study the year prior. Particulate samples were taken every sixth day for approximately one year at Okanagan College and subsequently analyzed by Environment Canada following National Air Pollution Surveillance network protocols. In addition, previous studies in Kelowna had identified organic carbon as an important contributor to PM_{2.5} mass, so an effort was made to further speciate this fraction, including the measurement of diagnostic and tracer species (n-alkanes, polycyclic aromatic hydrocarbons [PAHs] and petroleum biomarkers) on a weekly basis from October 2006 to March 2007, to gain insight into sources at three sites in the Kelowna area.

PM_{2.5} concentrations measured at the Okanagan College site during this study ranged from 1.5 to 22.1 µg/m³, and average/median concentrations were 6.6/4.7 µg/m³ (n=55), which is similar to the long-term annual average PM_{2.5} for Kelowna and slightly lower than the annual average measured during a PM speciation study the previous year. The 10 days having the highest PM_{2.5} were all observed during the cold season (Oct.-Mar.) and had light winds ranging from the northeast to south; however, all PM_{2.5} values measured during this study were below established 24-hour average objectives. A PM_{2.5} mass reconstruction showed that on average over the course of the study, organic matter made up 48% of the mass, followed by elemental carbon and ammonium nitrate at 15%, ammonium sulphate at 8%, particle-bound water at 3%, the category of Other at 2% and sodium chloride at 1%, while 8% was unaccounted for. The top 20% PM_{2.5} days showed similar mass reconstruction, with the exception of ammonium nitrate, which was higher than its average contribution. On a seasonal basis, the most significant difference in relative contributions was the variation of the ammonium nitrate (25% contribution in the winter versus 5% in the summer). The limited number of PM_{2.5} speciation samples precluded a quantitative source apportionment; however, information derived from a principal components analysis and analysis of trace metal concentrations indicated that crustal sources, as indicated by Fe and Mn, were highest on average in the spring and fall seasons, whereas traffic sources, as indicated by Pb and Zn, were higher in the fall and winter, following the trend of PM_{2.5} seasonality. Overall PM_{2.5} speciation results are comparable to those of the PM_{2.5} speciation study the previous year, with the exception of ammonium nitrate, which appears to have been significantly undervalued in the previous study compared with the current study, due to suspected negative biases caused by sampling methodology.

The quantification of several organic tracer compounds provided further information on source contribution, particularly in the cold season. Week-long biweekly (Oct.–Mar.) concentrations (avg.±sd) were 17.2 ± 7.2 ng/m³, 16.1 ± 5.7 ng/m³, 0.90 ± 0.30 ng/m³ and 307 ± 206 ng/m³ for the n-alkanes (C₂₂–C₃₆), 20 PAHs, 12 petroleum biomarkers and levoglucosan, respectively. Alkanes and biomarkers had significant correlation, indicating an overlapping source, namely motor vehicles. Total PAHs did not correlate well with either n-alkanes or biomarkers but did correlate significantly with levoglucosan, indicating that wood smoke is a significant contributor of these compounds in the winter. The carbon preference index value of the alkanes indicated a primarily anthropogenic aerosol source with some influence from biogenic sources. The most abundant PAHs were the lower molecular weight species retene, fluoranthene and pyrene, followed at lower concentrations by benzo(b)fluoranthene and chrysene. High concentrations of retene, which has been identified as a tracer for wood combustion, and strong correlation with levoglucosan, further indicates the significance of wood-burning contribution to PAHs in Kelowna. The average concentration of benzo[a]pyrene measured during this study (0.4 ng/m³) was below the World Health Organization annual average guidance value (1.2 ng/m³). Using the ambient biomarker concentrations and a source profile from a previous tunnel study, the motor vehicle contribution to primary organic carbon ranged from 0.17 to 0.96 µg/m³ and averaged 0.58 ± 0.12 µg/m³ at the Okanagan College site, which corresponded to a percent contribution to primary PM_{2.5} ranging from 5 to 49%, with an average of $23\pm5\%$. By comparing the average levoglucosan:PM_{2.5} ratio of 3.5 ± 1.2 to corresponding values and source apportionment results of previous studies in B.C. and the Yukon, the annual average wood-burning contribution to PM_{2.5} in Kelowna during this study was estimated to be slightly higher than that of Prince George (24%, winter season). The wood smoke contribution in Kelowna in the cold season (Oct.–Mar.) was nearly double the annual contribution, while the warm season (Apr.–Sep.) contribution was approximately one sixth of the annual contribution.

The visibility extinction coefficient estimated during this study ranged from 21 to 192 Mm⁻¹ and averaged 52 Mm⁻¹ (n=54), which is similar to annual average values found in the Lower Fraser Valley. This corresponds to an average visual range of 75 km, with values ranging from 186 km down to 20 km. On an annual basis, the most important contributors to visibility loss in Kelowna, exclusive of Rayleigh scattering, were organic matter at 39%, followed by elemental carbon (39%), ammonium nitrate (19%), coarse mass (9%), ammonium sulfate (7%), nitrogen dioxide (7%) and soil (2%). The largest seasonal shift in relative contribution was in the winter, also the season with the highest observed extinction values, where the importance of ammonium nitrate increased significantly (38% contribution compared with 4% in the summer). Based on an analysis of a limited number of digital images captured during the study, it appears that visibility degradation in Kelowna can occur at PM_{2.5} levels that are well below the existing objectives.

The result of this study showed that while PM_{2.5} levels in Kelowna remained below established 24-hour average objectives, elevated levels do occur in the winter. In the cold season, when PM_{2.5} is the highest, traffic and wood-burning sources were estimated to make up the majority of PM_{2.5}. Efforts to achieve significant reductions of PM_{2.5} during this season, therefore, should consider reductions strategies for these two sources.

1. Introduction

The impact of airborne particulate matter (PM) on human health has been a matter of study for several decades. Fine particulate matter (PM_{2.5}) has the ability to penetrate deeply into the lungs, and associations have been found between increased ambient concentrations and increased mortality and hospitalization and reduced cardiovascular and pulmonary function (Pope and Dockery, 2006). In addition to health impacts, PM_{2.5} is the main contributor to visibility degradation, which is caused by the absorption and scattering of light by particles and gases in the atmosphere. Visibility degradation can lead to loss of enjoyment of scenic vistas, increased healthcare costs (ENVIRON, 2013) and can have negative impacts on revenue from tourism (McNeil and Roberge, 2000) and on Aboriginal cultural and spiritual traditions (Carlson, 2009).

Kelowna, in the Okanagan region of British Columbia, is the third largest metropolitan area in the province, having a population of approximately 180 000 (Statscan, 2012). A number of actions targeting residential wood smoke, burning and mobile sources have been initiated in recent years to address PM pollution in Kelowna (RDCO, 2007). While PM_{2.5} levels remain below the Canada-wide Standard and provincial objectives (Figure 1), Kelowna still experiences episodes of elevated levels of PM, particularly in the cold season and during summer forest fire events (Figure 2). The central Okanagan is one of the fastest growing regions in the country, with a population increase of 10.8% from 2006 to 2011 (Statscan, 2012). In addition, the Thompson Okanagan region has a large tourism sector accounting for 14% of the province's accommodation room revenue (B.C. Government, 2011). These factors are expected to continue to put pressure on the region's air resources, with significant increases in PM_{2.5} emissions forecasted for 2030 (RWDI, 2011).

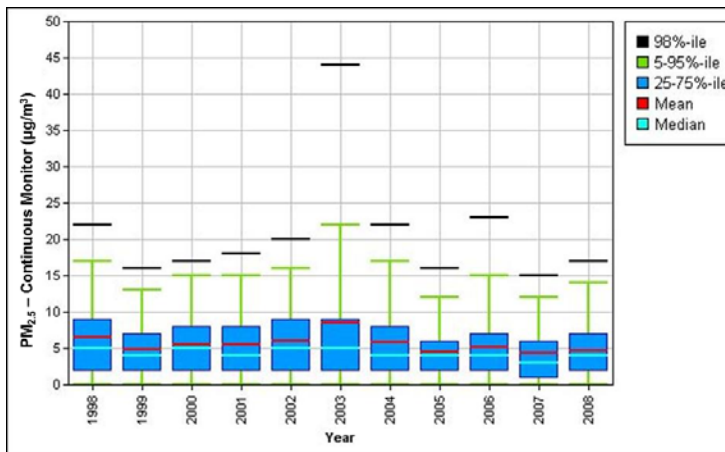


Figure 1: 10-year annual trend for PM_{2.5} in Kelowna

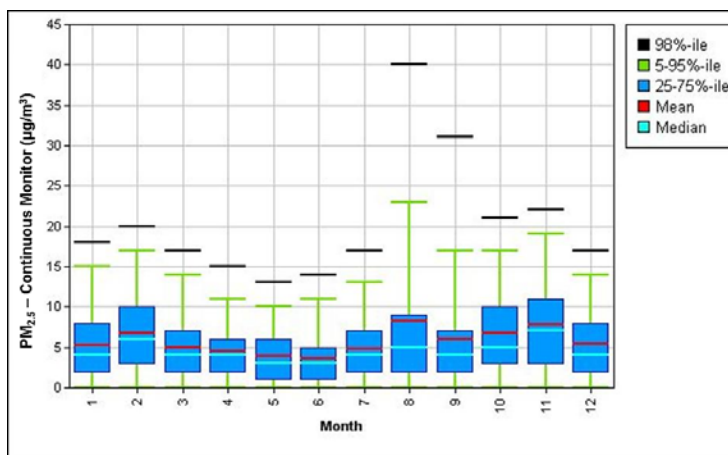


Figure 2: 10-year seasonal trend for PM_{2.5} in Kelowna

An important step in informing air quality management actions to reduce ambient PM levels and improve visual air quality is a speciation sampling program, which allows for the identification and quantification of the individual species contributing to PM mass. Knowledge of the constituents of PM can be combined with knowledge of the emission profiles of common sources to apportion the measured PM to individual source categories. Another commonly used technique to obtain information on PM sources contribution is the measurement of diagnostic and tracer species. The determination of the ambient concentration of tracer compounds that are unique to specific sources, when compared to their emission concentration, can be used to estimate source contribution. The diagnostic and tracer compounds used in this study included various aliphatic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), petroleum biomarkers and levoglucosan.

Aliphatic n-alkanes, which are emitted from plant waxes as well as biomass and fossil fuel combustion, have been used to characterize PM derived from different source categories. By comparing the concentrations of odd-carbon numbered alkanes with even-carbon numbered alkanes, using the carbon preference index (CPI), one can distinguish between PM originating from biogenic and anthropogenic sources (Kalaitzoglou *et al.*, 2004; Cheng *et al.*, 2006; Ding *et al.*, 2009).

PAHs are compounds that are commonly emitted during combustion processes. Diagnostic ratios of the various PAH species have been widely used as source-specific indicators (Ravindra *et al.*, 2008); however, the validity of such techniques is subject to several assumptions that may not hold true (Galarneau, 2008). Nevertheless, determination of PAHs can provide general information on the contribution of various combustion-related sources to ambient PM. In addition, a number of PAHs have been identified as being toxic, and therefore monitoring of their ambient concentrations is important. For example, the United States Environmental Protection Agency has classified seven PAHs (benzo[a]pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene and indeno[1,2,3-cd]pyrene) as probable human carcinogens.

Hopanes and steranes, also known as petroleum biomarkers, are classes of compounds that are emitted from engine lubricating oil in motor vehicles (Rogge *et al.*, 1993a). As they are relatively stable in the atmosphere after emission and primarily emitted

by internal combustion engines, ambient concentrations of these biomarkers, in combination with source profiles, have been used to quantify motor vehicle exhaust contribution to primary PM (Brook *et al.*, 2007). More recent studies have found that hopanes and steranes can degrade in the atmosphere due to reaction with OH radicals, particularly at lower relative humidity (RH) values (Weitkamp *et al.*, 2008; Lambe *et al.*, 2009), and this should be taken into account in quantitative source apportionment studies.

Levoglucosan is a compound that is emitted in large concentrations during the burning of cellulose. Several studies have made use of ambient levoglucosan concentration ratios with PM or organic carbon (OC) to identify biomass burning plumes (e.g. Leithead *et al.*, 2006; Jordan *et al.*, 2006a; Puxbaum *et al.*, 2007); however, emission profiles can vary due to different burning conditions and fuel types, therefore reliance on ambient levoglucosan concentration ratios alone to estimate biomass-burning contribution to PM can be subject to uncertainty (Hedberg *et al.*, 2006). In addition, recent studies have found that levoglucosan is not as stable in the atmosphere as was previously reported, due to reaction with OH radicals (Hennigan *et al.*, 2010; Kessler *et al.*, 2010; Hoffman *et al.*, 2010). Nevertheless, levoglucosan data, when used in combination with other methods of source apportionment, can provide an estimate of relative levels of wood smoke contribution.

In order to characterize PM_{2.5} in Kelowna, determine and quantify its sources and assess its impact on visibility, a speciation sampling program was initiated in Kelowna in the fall of 2006. Previous studies in Kelowna had identified OC as an important contributor to PM_{2.5} mass (Allen, 2009; J. Brook, pers. comm.), so an effort was made to further speciate the OC fraction of the PM to gain insight into its sources. The intent was for this to be a two-year follow-up study to a PM speciation study in Kelowna the year prior (Allen, 2009); however, funding cuts partway through the study led to only a year of PM_{2.5} speciation data and six months of organic compound speciation data being collected. This precluded the use of a quantitative source apportionment technique, such as positive matrix factorization. Nevertheless, useful information was derived from the data and is presented in this report.

2. Methodology

2.1 Sampling Sites

All sampling and data collection was conducted in and around the city of Kelowna, within the Central Okanagan Regional District between September 2006 and September 2007 (Figure 3). The main sampling site was located at Okanagan College, less than 3 km from the city centre. Sampling took place on the rooftop of the four-storey science building approximately 130 m north of K.L.O. Road ($49^{\circ}51'45''\text{N}$, $119^{\circ}28'40''\text{W}$). This location is also a B.C. Ministry of Environment and National Air Pollution Surveillance (NAPS) air quality monitoring site. Two additional sampling sites were located on the rooftop of the two-storey Kelowna City Hall ($49^{\circ}53'16''\text{N}$, $119^{\circ}29'46''\text{W}$) building and on the deck of a private residence in Westbank ($49^{\circ}50'43''\text{N}$, $119^{\circ}37'7''\text{W}$). The Okanagan College site was located in a primarily residential and light commercial area, the City Hall site was in the primarily commercial downtown area, and the Westbank site was in a residential neighbourhood.

The National Pollutant Release Inventory lists three asphalt/cement plants and four wood processing plants that reported emissions of PM for the years 2006 and 2007 in the Kelowna area. In addition, Kelowna is served by a major six-lane highway running through its centre (Highway 97/Harvey Avenue) 2.3 km north of the Okanagan College sampling site. The 2005 annual average daily traffic counts 3.4 km to the northwest of the sampling site were approximately 47 000; traffic is ~12% heavier in the summer (BC Ministry of Transport).



Figure 3: Location of the sampling sites (image from Google Earth)

2.2 Sampling and Analysis

PM_{2.5} samples were taken every sixth day for approximately one year at Okanagan College and subsequently analyzed by Environment Canada following NAPS network protocols. In addition, samples for OC diagnostic and tracer species (n-alkanes, PAHs and petroleum biomarkers) were taken at three sites during the cold season. Sampling methodologies are discussed in detail below.

2.2.1 PM_{2.5} Speciation

Ambient aerosol samples were collected at the Okanagan College site using a Thermo Fisher Partisol Model 2300 Speciation Sampler, for a 24-hour period every sixth day from September 14, 2006, to September 17, 2007. The sampling program was interrupted from February 11 to March 15 due to sampler problems.

The Partisol 2300 Speciation Sampler used three Harvard designed Chemcomb cartridges, the configuration of which is summarized in Table 1. A 10 litre per minute flow rate was used on all cartridges, and flows were audited with an independent flow standard at the beginning, mid-point and end of the study. All audited flows for all channels agreed within $\pm 10\%$.

Table 1: Speciation cartridge configuration

Module	Media	Analytes
Cartridge A	Quartz filter	Organic and elemental carbon, levoglucosan
Cartridge B (two components)	Teflon filter	PM _{2.5} mass and metals
	Quartz filter	Organic carbon artifact
Cartridge C (four components)	Carbonate coated denuder	Sulfur dioxide and nitric acid
	Citric acid coated denuder	Ammonia
	Teflon filter	Anions, organic acids and cations
	Nylon filter	Nitrate, sulfate

All sampling media were prepared at Environment Canada's Analysis and Air Quality Division at the Environmental Technology and Science Centre (ETSC) in Ottawa, Canada. ETSC shipped all sampling media to the field already installed in the sampling cartridges. New sampling cartridges were loaded onto the sampler, and sampled cartridges were unloaded and sealed by a site operator on a weekly basis and subsequently shipped to ETSC for analysis as follows:

Cartridge A

The quartz filters were used to measure carbon content using a DRI Model 2001 thermal/dual-optical carbon analyzer (Atmoslytic Inc Calabasas, CA) and the IMPROVE (Interagency Monitoring of Protected Visual Environments) analysis protocol. A ~ 0.5 cm² punch of a sample quartz filter is heated stepwise at temperatures of 120°C (OC1), 250°C (OC2), 450°C (OC3) and 550°C (OC4) in a non-oxidizing helium (He) atmosphere, and 550°C (EC1), 700°C (EC2) and 800°C (EC3) in an oxidizing 2% O₂/98% He atmosphere. The carbon that evolves at each temperature is oxidized to carbon dioxide (CO₂) in a manganese dioxide (MnO₂) oxidizer at 900°C. The CO₂ is then reduced to methane (CH₄) in a nickel catalyst methanator at 420°C. Finally, the CH₄ is quantified with a flame ionization detector.

Levoglucosan was determined on the archived portions of the quartz filters in February 2012 because this analysis was not available at ETSC at the time of the study. Although its stability during storage was not determined as part of this study, levoglucosan has been shown to be stable on quartz filters after storage for 10 years at -50°C (Ma *et al.*, 2010). The filters for this study were stored at -20°C, which should have minimized biological and chemical degradation. Filters were extracted in de-ionized water and analysed for levoglucosan and seven other sugar compounds by ion chromatography using pulsed amperometric detection.

Cartridge B

The Teflon filters were used to determine PM_{2.5} mass by gravimetry followed by extraction by microwave acid digestion and analysis of 20 elements by Inductively-Coupled Plasma – Mass Spectrometry (ICP-MS).

The back-up quartz filters were used to measure carbon content using the method discussed above. The OC results from Cartridge B were used to correct OC results from Cartridge A for any positive OC artifacts resulting from absorption of semi-volatile OC during the sampling period.

Cartridge C

The Teflon filters were extracted in de-ionized water and analyzed for 21 anions, organic acids and cations by ion chromatography.

The nylon filters were extracted in de-ionized water and analyzed for nitrate and sulphate by ion chromatography. The nitrate from the nylon filter is used to correct nitrate results from the Teflon filter for any negative sampling artifacts.

Denuders were extracted in de-ionized water and analyzed for nitrate, sulphate and ammonium by ion chromatography to approximate gas concentrations (NH₃, SO₂ and HNO₃) for the sampling period.

In addition to the laboratory quality control procedures carried out as part of routine NAPS speciation analysis, six field blank samples were taken for each channel on the speciation sampler. The average of the six field blanks was subtracted from each data point for six ion species whose average field blank value exceeded twice the method detection limit.

2.2.2 PM_{2.5} Mass Reconstruction

PM_{2.5} mass was reconstructed from the sum of measured species using a modified equation, based on the formula used by the NAPS network (Dabek-Zlotorzynska *et al.*, 2011):

Reconstructed Fine Mass: RCFM=ASO₄+ANO₃+OM+EC+TEO+OTHER+NaCl+ PBW

Where:

Ammonium nitrate (ANO₃) = 1.29*[NO₃⁻]

Ammonium sulphate (ASO₄) = [SO₄²⁻] + [NH₄⁺] - 0.29[NO₃⁻]

Organic Matter (OM) = k*[OC]

Elemental Carbon: EC=EC

Other: 1.5*[Fe]

Trace Element Oxides (TEO) =

1.47*[V]+1.29*[Mn]+1.27*[Ni]+1.25*[Cu]+1.24*[Zn]+1.32*[As]+1.08*[Pb]+1.2*[Se]+
1.37*[Sr]+1.31*[Cr]

Sodium Chloride: (NaCl) = [Na] + [Cl]

Particle-bound water (PBW) = 0.32*([SO₄²⁻] + [NH₄⁺])

Due to X-ray fluorescence (XRF) analysis not being available for the sampling configuration used in this study, the elements Si, Ca, K and Ti, which make much of the crustal matter mass, could not be measured, therefore rather than having a “soil” component, Fe was included in the “Other” fraction. In addition, P could not be measured and was therefore omitted from the TEO component. A factor (k) of 1.6 was to convert OC to OM, which has been recommended for urban aerosols (Turpin and Lim, 2001). The “Unaccounted” component of the reconstructed mass is the difference between the total measured concentration and the RCFM.

2.2.3 Organic Carbon Speciation

Samples for n-alkanes, PAHs, hopanes and steranes were collected using a GPS-1 polyurethane foam (PUF) high-volume sampler (General Metal Works) for a seven-day period every second week from October 5, 2006, to March 20, 2007, at the Okanagan College site. The PUF sampling head contained a 102 mm quartz filter and PUF/XAD4 resin/PUF “sandwich” downstream to capture gaseous volatilization off the filter, thereby reducing negative sampling artifacts of the particle phase. A PM_{2.5} inlet was not available for the PUF sampler, so total suspended particulate (TSP) was collected at an approximate flow rate of 250 litres per minute for a total sampling volume of approximately 2500 m³ per sampling event. Flow rates were measured at the beginning and end of the seven-day sampling period, and an average of the two readings was used to determine the volume of air collected. Flow rates on the PUF sampler were calibrated every two months over the course of the six-month sampling period.

In addition, a URG-2000-25A Personal Pesticide Sampler (URG) (URG Corporation, Chapel Hill, NC) was used to collect n-alkanes, PAHs, hopanes and steranes for seven-day periods starting on October 5, 2006, November 14, 2006, and January 9, 2007, at all three sites. A fourth URG sampling event in March 2007 had to be discarded due to

pump problems. The URG sampler contained a 25 mm quartz filter as well as a PUF-XAD4-PUF sandwich downstream. The URG sampler operated with a PM_{2.5} inlet and a flow rate of 4 litres per minute, achieved by use of an external pump, for a total sampling volume of approximately 40 m³ per sampling event. Flow rates were measured at the beginning and end of the seven-day sampling period, and an average of the two readings was used to determine the volume of air collected.

A denuder upstream of the filter to capture gaseous organic species was not used for either sampler, so volatile and semi-volatile gaseous species may have been captured on the PUF plug and by condensation on the quartz filter, making the sampling technique susceptible to positive artifacts (Mader and Pankow, 2001). For n-alkanes, it has been found that compounds <C₂₅ can be subject to a significant positive artifact (Sihabut *et al.*, 2005). In order to allow comparison with previous studies in B.C., n-alkanes >C₂₁ are reported here (Cheng *et al.*, 2006), although it is noted that positive artifacts could be present for the lower molecular weight compounds. Similarly, only the PAHs with 4, 5 and 6 aromatic rings are reported here. PAHs with 5 or 6 aromatic rings have low vapour pressures and are associated with the particle phase, whereas 4-ring PAHs can be emitted in both the gas and particle phases (Schauer *et al.*, 1999, 2001, 2002), and their partitioning in the atmosphere will be dependent on their concentration, the temperature and the concentration and composition of the ambient PM matrix (Baek *et al.*, 1991). It is recognized, therefore, that some positive sampling artifacts may be present for some of the 4-ring PAHs reported here. However, it is informative that Eiguren-Fernandez *et al.* (2004) found that 4-ring PAHs were predominantly in the particle phase in a sampling campaign in southern California. Petroleum biomarkers from motor vehicle exhaust have been shown to exist primarily in the particle phase (Schauer *et al.*, 1999, 2002; Sihabut *et al.*, 2005).

All sampling media were prepared at ETSC: quartz filters were baked at 900 °C for four hours and stored sealed in a freezer until use. The sampling heads were assembled at ETSC and sent to the sampling site in coolers on ice and refrigerated until being loaded onto the sampler. Sampling cartridges were unloaded by a site operator immediately following the one-week sampling period and stored in a fridge until being shipped to ETSC in coolers on ice within two weeks.

The filters and absorbent cartridges were extracted at ETSC together as a single sample for each sampling event, following a procedure described previously (Brook *et al.*, 2007). Briefly, the samples were extracted initially with dichloromethane after which the extract was concentrated, exchanged to hexane and cleaned-up/separated on a deactivated silica column. Fraction 1, eluted with hexane, was sent to Natural Resources Canada CANMET Energy Technology Centre in Ottawa for analysis of 28 alkanes (14 compounds >C₂₁ are reported here) and 67 biomarkers (a selection of 12 common compounds are reported here) by gas chromatograph mass spectrometry as described in Brook *et al.* (2007). Fraction 2, eluted with hexane/acetone, was analyzed for 32 PAHs (20 compounds with 4, 5 and 6 aromatic rings are reported here) at ETSC by gas chromatograph mass spectrometry following standard NAPS methodology for analysis of PAHs collected on a filter/PUF. All alkane, PAH and biomarker compounds reported in this study are listed in Table 2.

Table 2: List of alkane, PAH and biomarker species reported in this study

Alkanes	PAHs	Biomarkers
Docosane (C22)	Fluoranthene (Flt)	C27 Trisnorhopane Tm (H15)
Tricosane (C23)	Pyrene (Pyr)	C29 $\alpha\beta$ -30-norhopane (H17)
Tetracosane (C24)	Retene (Ret)	C30 $\alpha\beta$ -hopane (H19)
Pentacosane (C25)	Benzo[a]fluorine (BaFl)	C30 $\beta\alpha$ -hopane (H20)
Hexacosane (C26)	Benzo[b]fluorine (BbFl)	C27 20R- $\beta\alpha\alpha$ -cholestane (S11)
Heptacosane (C27)	1-methylpyrene (Mpy)	C27 20S- $\alpha\alpha\alpha$ -cholestane (S12)
Octacosane (C28)	Benzo(ghi)fluoranthene (BgHiF)	C27 20R- $\alpha\beta\beta$ -cholestane (S13)
Nonacosane (C29)	Benzo[a]anthracene (BaA)	C27 20R- $\alpha\alpha\alpha$ -cholestane (S15)
Triacontane (C30)	Triphenylene (Tri)	C29 20S- $\alpha\alpha\alpha$ -ethylcholestane (S22)
Hentriacontane (C31)	Chrysene (Chry)	C29 20R- $\alpha\beta\beta$ -ethylcholestane (S23)
Dotriacontane (C32)	Benzo[b]fluoranthene (BbFlt)	C29 20S- $\alpha\beta\beta$ (20R-Baa)-ethylcholestane (S24)
Tritriacontane (C33)	Benzo[k]fluoranthene (BkFlt)	C29 20R- $\alpha\alpha\alpha$ -ethylcholestane (S25)
Tetratriacontane (C34)	Benzo(e)pyrene (BeP)	
Hexatriacontane (C36)	Benzo[a]pyrene (BaP)	
	Perylene (Per)	
	Indeno(1,2,3-cd)]fluoranthene (IF)	
	Indeno(1,2,3-cd)]pyrene (IP)	
	Dibenzo[a,h]anthracene (DahH)	
	Benzo(b)chrysene (BbC)	
	Benzo[g,h,i]perylene (BgHiP)	

Field blank samples were taken for both the PUF and URG samplers. The PUF field blank had quantifiable levels of alkanes at approximately an order of magnitude less than typical sample loadings, so samples were blank corrected. For an unknown reason, the URG field blank had high levels of alkanes: higher than some sample loadings, so URG alkane data are not reported here. Field blank levels for PAHs and biomarkers on the PUF and URG samplers were non-detectable or orders of magnitude below sample concentrations, so no blank correction was performed. Each sample extract was spiked with a surrogate standard, and all results were corrected based on surrogate recovery. Average recovery for 4 deuterated alkanes was 86%; for 11 deuterated PAHs, 99%; for $\beta\beta$ -hopane, 72%; and for α -androstane, 97%. In addition, NIST SRM 1649a was included for analysis of 16 PAHs, and average recovery was 93%. Dibenzo[a,h]anthracene, which had an average SRM recovery of 135%, was the only species with average recoveries not within $100 \pm 20\%$.

2.2.4 Visibility Measurements

The extinction coefficient, b_{ext} , was reconstructed from particle speciation, nitrogen dioxide (NO_2) and meteorological data based on the revised IMPROVE algorithm (Pitchford *et al.*, 2007):

$$\begin{aligned} b_{\text{ext}} \approx & 2.2 f_{\text{S}}(\text{RH}) [\text{ASO}_4]_{\text{S}} + 4.8 f_{\text{L}}(\text{RH}) [\text{ASO}_4]_{\text{L}} \\ & + 2.4 f_{\text{S}}(\text{RH}) [\text{ANO}_3]_{\text{S}} + 5.1 f_{\text{L}}(\text{RH}) [\text{ANO}_3]_{\text{L}} \\ & + 2.8 [\text{OM}]_{\text{S}} + 6.1 [\text{OM}]_{\text{L}} \\ & + 10 [\text{EC}] + [\text{Fine Soil}] + 0.6 [\text{CM}] + 1.7 f_{\text{SS}}(\text{RH}) [\text{Sea Salt}] \\ & + 0.33 [\text{NO}_2 \text{ (ppb)}] + \text{Rayleigh scattering (site specific)} \end{aligned}$$

A few modifications to the IMPROVE algorithm were applied for this data set. For consistency with mass reconstruction procedures, the formulas outlined in section 2.2.2 were used to calculate ASO_4 , sea salt (NaCl) and OM. Also, as the Fine Soil (FS) and Course Mass (CM) components were not available for this study, seasonal FS:PM_{2.5} and CM:PM_{2.5} ratios were determined from the previous study in Kelowna (Allen, 2009), and these seasonal ratios were then used to calculate a FS and CM based on measured PM_{2.5} for each sampling event. While not determined from directly measured species, the FS and CM derived by this method should provide a good estimate of FS and CM contribution to b_{ext} , which as we will see is minor compared with other components. All $f(\text{RH})$ factors were determined individually for each sampling event, first on an hourly basis from hourly RH measurements at the site and then averaged to 24-hour values. This is different than the IMPROVE method, which uses climatological mean $f(\text{RH})$ values in determining b_{ext} because the goal is to assess long-term trends. A Rayleigh scattering value of 11 Mm^{-1} was used for all data, which was calculated using the following formula, which incorporated the average temperature (T) and pressure (P) over the course of the study (Watson, 2002):

$$\text{Rayleigh Scattering (550nm) (Mm}^{-1}\text{)} = 11.4(293/T(^{\circ}\text{K})) * P(\text{atm})$$

In addition, a digital camera was installed at the Okanagan College site oriented in a northerly direction and automatically captured images twice an hour during daylight hours for the duration of the study. The camera was down for intermittent periods throughout the study, with the largest gap being July and August 2007.

2.2.5 Other Measurements

Data from a number of parameters routinely reported at the Okanagan College NAPS site on an hourly basis and maintained by the B.C. Ministry of Environment were utilized in this study, including CO , NO_2 , PM_{2.5} measured by a Tapered Element Oscillating Micro-balance (TEOM) and meteorology (temperature, relative humidity and wind speed/direction).

3. Results and Discussion

3.1 Meteorology

Temperature data over the course of the study are shown in Figure 4. The summer maximum temperature was 35°C, and the winter low was -20°C. Seasonal average temperatures over the 12-month period were 10°C (Sep.–Nov.), 0°C (Dec.–Feb.), 11°C (Mar.–May) and 21°C (Jun.–Aug.).

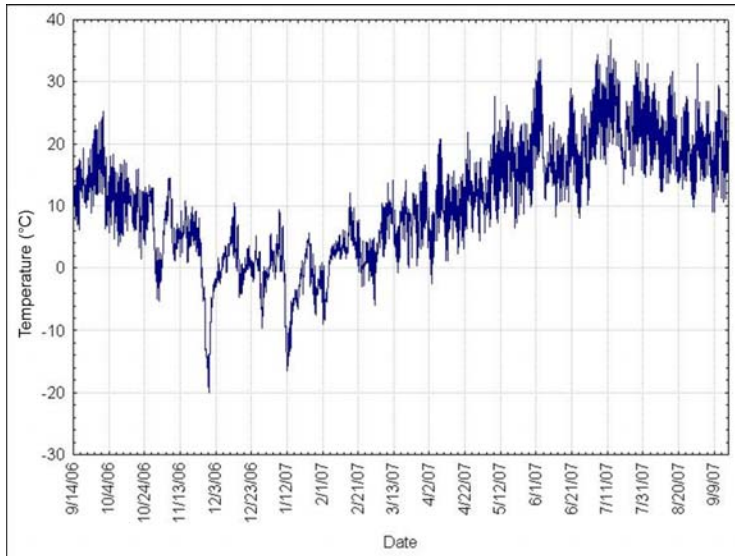


Figure 4: Hourly temperature at the Okanagan College site during the study

The wind roses shown in Figure 5 illustrate predominant seasonal and diurnal wind direction and speed during the study. The predominant direction of the wind in Kelowna tends to be along a northeast-southwest transect, which follows the topography of the Okanagan Valley at the sampling site. In all seasons, the strongest winds tend to be predominantly from the southwest as opposed to the northeast. Wind direction and speed were more varied in summer and winter, while spring winds tended to be stronger and from a predominantly southwesterly direction. Wind speeds in the fall were lower and predominantly from the northeast and east. There was a distinct diurnal pattern, with daytime winds predominantly from the southwest and nighttime winds from the northeast.

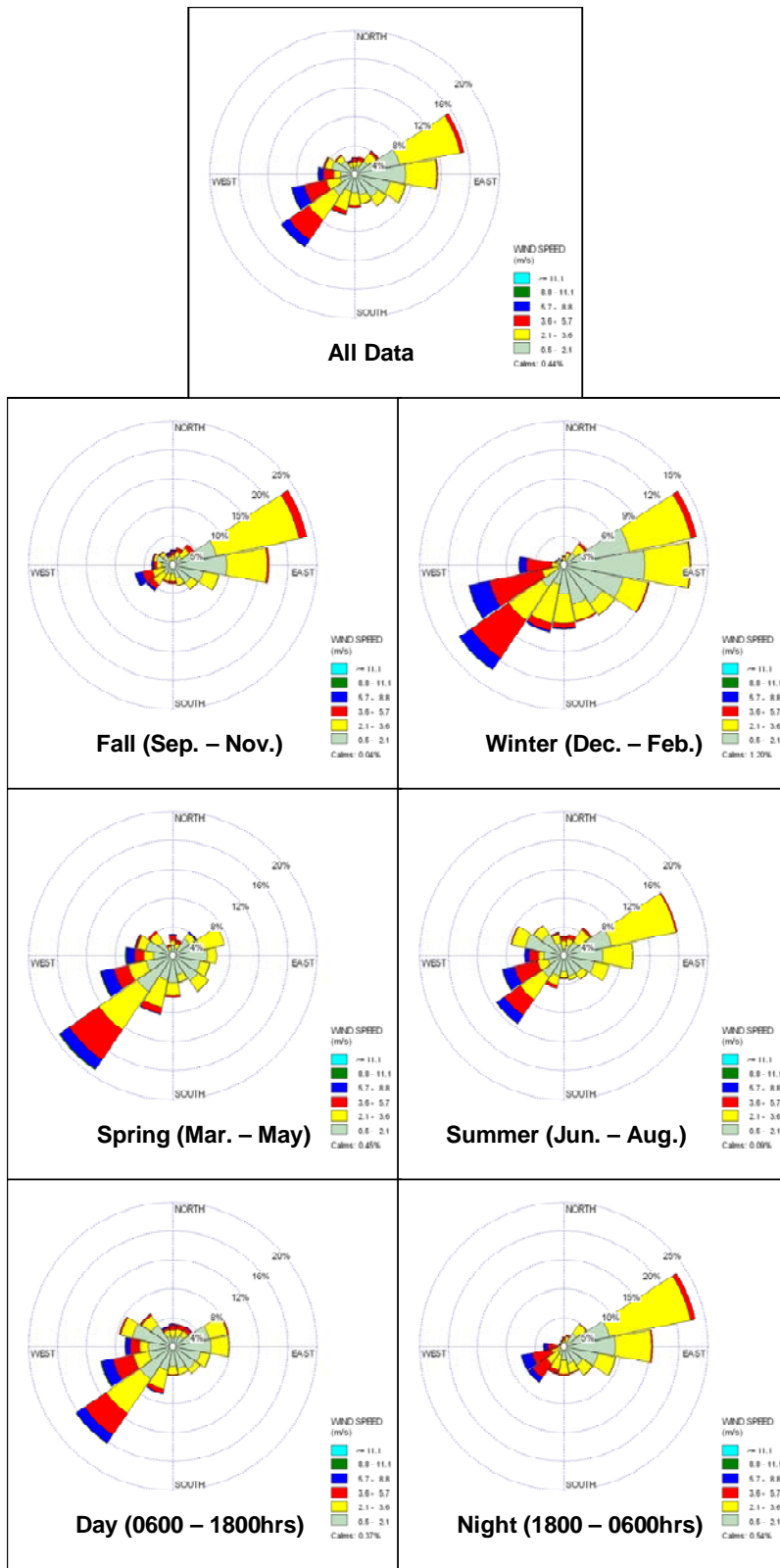


Figure 5: Wind roses showing the wind speed and direction at the Okanagan College site during the study

3.2 PM_{2.5} Speciation

3.2.1 PM_{2.5} Characterization

A time series of the PM_{2.5} concentration from the speciation sampler is shown in Figure 6. Eight sampling events were missed due to sampler problems, with the largest gap being five samples from mid-February to mid-March. Average/median concentrations were 6.6/4.7 µg/m³ (n=55). For comparison, 24-hour average values from the collocated TEOM are also shown in Figure 6. It can be seen that the TEOM tracks the speciation sampler quite well but has a significant negative bias during the cold season, which is commonly seen due to the loss of volatile PM on the TEOM (Allen *et al.*, 1997; Dann *et al.*, 2006).

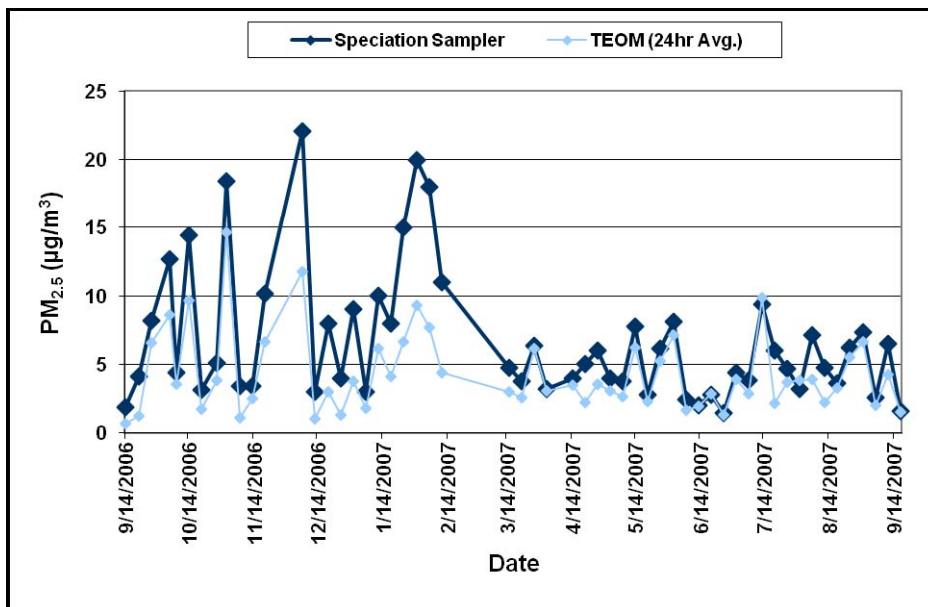


Figure 6: Time series of PM_{2.5} measured by the speciation sampler and TEOM at the Okanagan College site

Overall, PM_{2.5} concentrations measured during this study ranged from 1.5 µg/m³ to a maximum of 22.1 µg/m³ (December 7, 2006). The Canada-wide Standard for 24-hour average PM_{2.5} is 30 µg/m³, based on the 98th percentile, averaged over 3 consecutive years, while British Columbia has established a 24-hour average PM_{2.5} objective of 25 µg/m³ and an annual average objective of 8 µg/m³. All PM_{2.5} values measured during this study were below the above 24-hour average objectives. Average PM_{2.5} results from this study are comparable to the long-term average of 5.6 µg/m³, measured with a TEOM in Kelowna (see Figure 1) and slightly lower than that measured during the previous year's study (Allen, 2009). Also, for comparison, average PM_{2.5} concentrations for a selection of B.C. locations during the same time period using filter-based sampling are shown in Table 3.

Table 3: Average filter-based PM_{2.5} at selected B.C. locations (Sep. 2006 – Sep. 2007)

Location	Average PM _{2.5} (µg/m ³)	Average PM _{2.5} (µg/m ³) Oct.–Mar.	Average PM _{2.5} (µg/m ³) Apr.–Sep.
Abbotsford	6.1	5.9	6.1
Burnaby	5.7	5.4	6.0
Kelowna (this study)	6.6	9.2	4.7
Port Moody	5.8	5.5	6.1
Victoria	8.0	8.1	7.7

The seasonal pattern of PM_{2.5} concentration is shown Figure 7. It can be seen that the winter season had the highest PM_{2.5} levels.

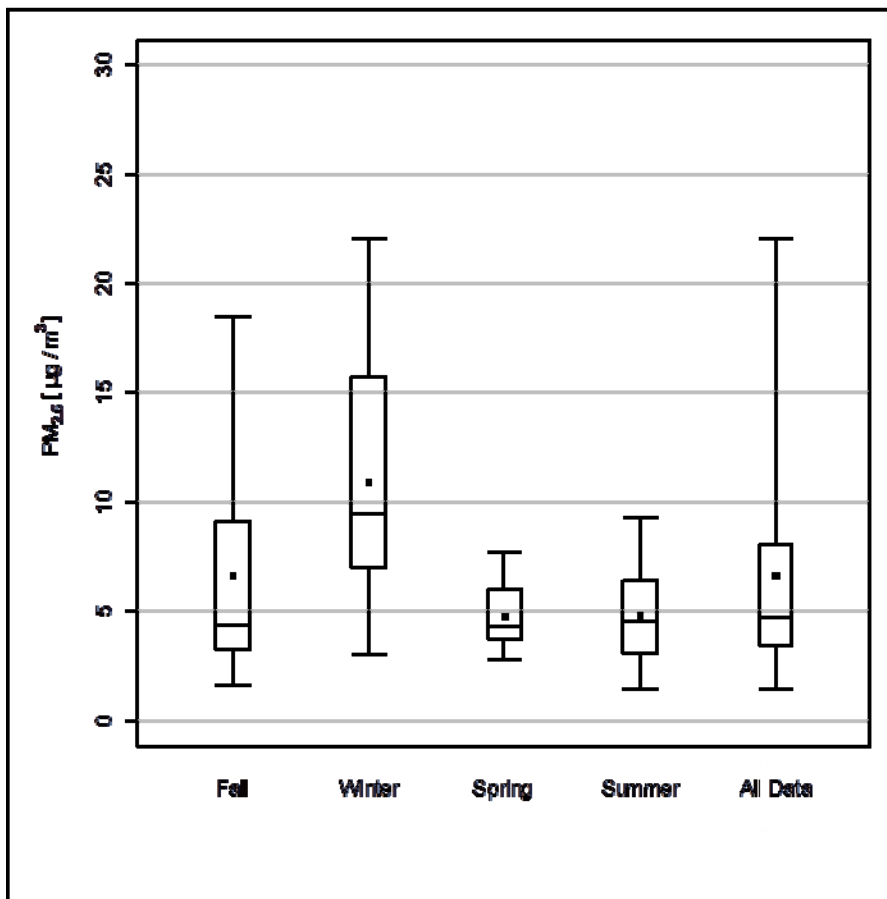


Figure 7: Seasonal trend of PM_{2.5} at the Okanagan College site (whiskers = max/min; box = 25th/75th percentile; line = median; point = mean)

A pollution rose (Figure 8) shows that while largest frequency of daily average wind directions (calculated from hourly data using vector averaging) were from the south to southeast, days having the highest $PM_{2.5}$ levels during this study tended to be from the south to northeast. The 10 days having the highest $PM_{2.5}$ were all during the cold season and are associated with light winds (Table 4).

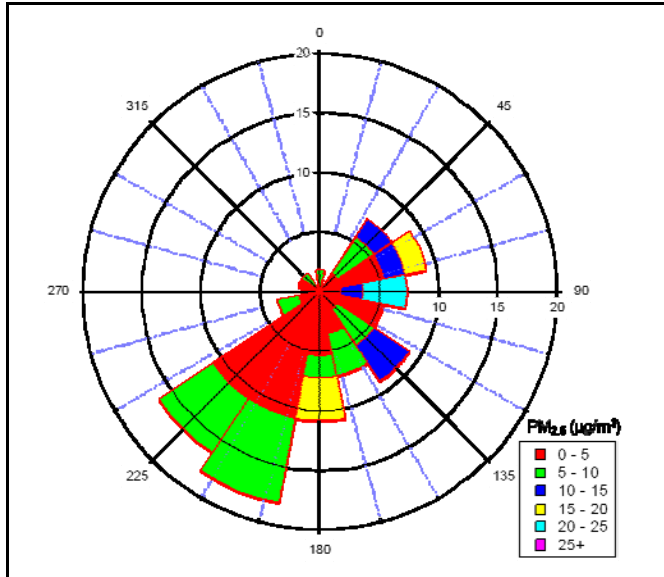


Figure 8: $PM_{2.5}$ and wind direction rose plot

Table 4: Meteorological data from days with the highest $PM_{2.5}$

Date	$PM_{2.5}$ ($\mu\text{g}/\text{m}^3$)	Temperature ($^{\circ}\text{C}$)	Wind Speed (m/s)
19/11/2006	10	4.7	3.2
12/1/2007	10	-17.4	2.6
11/2/2007	11	1.0	1.2
5/10/2006	13	7.9	1.9
14/10/2006	14	8.5	2.0
24/1/2007	15	1.4	1.8
1/11/2006	18	-4.9	2.2
5/2/2006	18	-0.2	2.2
30/1/2007	20	-4.1	1.8
7/12/2006	22	-0.7	1.6

By summing all measured $PM_{2.5}$ components and comparing it to the measured $PM_{2.5}$ mass, we can assess the “mass closure.” The correlation between measured and reconstructed $PM_{2.5}$ shows that the mass closure is very good, with a slope of 0.96 and correlation r^2 of 0.93 (Figure 9). The relative contribution of various species to total $PM_{2.5}$ is displayed in Figure 10. The data is separated by season as well as the 20% of days having the highest concentration of $PM_{2.5}$ (11 days). With the exception of the spring season, the reconstructed $PM_{2.5}$ slightly underestimates the total measured $PM_{2.5}$, with

the “Unaccounted” fraction being positive, but $\leq 1 \mu\text{g}/\text{m}^3$. This fraction would be made up, at least in part, of the soil components that were not measured. There was a slight overestimation of the mass in the spring season ($0.1 \mu\text{g}/\text{m}^3$). On average over the course of the study, OM made up 48% of the mass, followed by EC and ANO_3 at 15%, ASO_4 at 8%, PBW at 3%, Other at 2%, NaCl at 1% and TEO at $<1\%$, while 8% was unaccounted for. On a seasonal basis, the most significant difference in relative contributions is the variation of the ANO_3 (25% contribution in the winter versus 5% in the summer), which is due to its reactivity and volatilization at warmer temperatures. The mass contribution results from this study are comparable to those from Burnaby, Abbotsford and Golden: other sites in B.C. where NAPS speciation sampling has taken place in recent years, with OM being the largest contributor to $\text{PM}_{2.5}$ mass (Dabek-Zlotorzynska *et al.*, 2011).

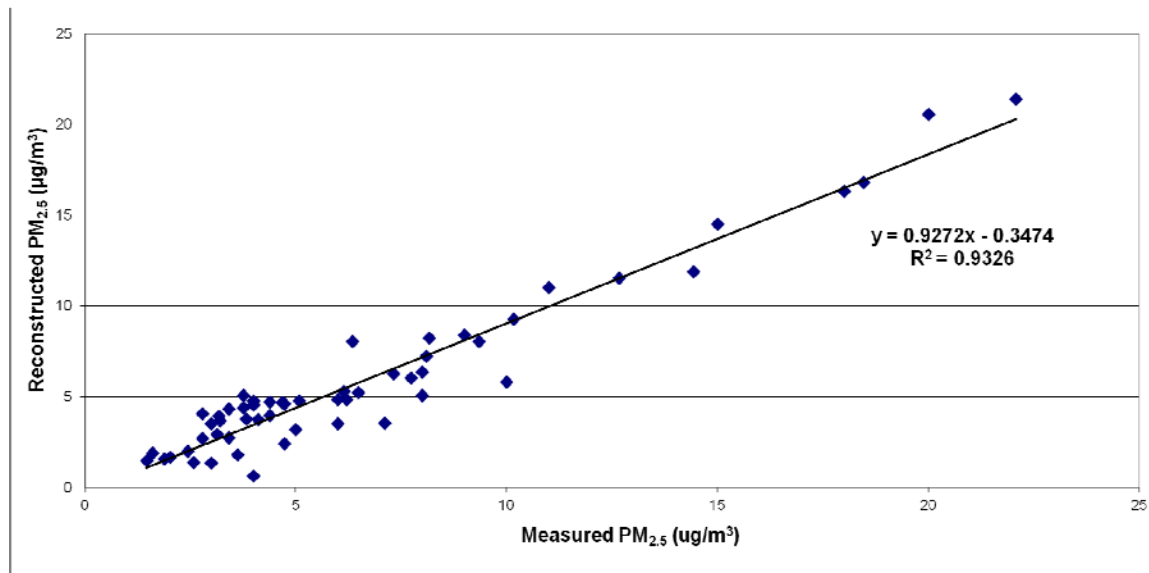


Figure 9: $\text{PM}_{2.5}$ mass closure – measured vs. reconstructed $\text{PM}_{2.5}$

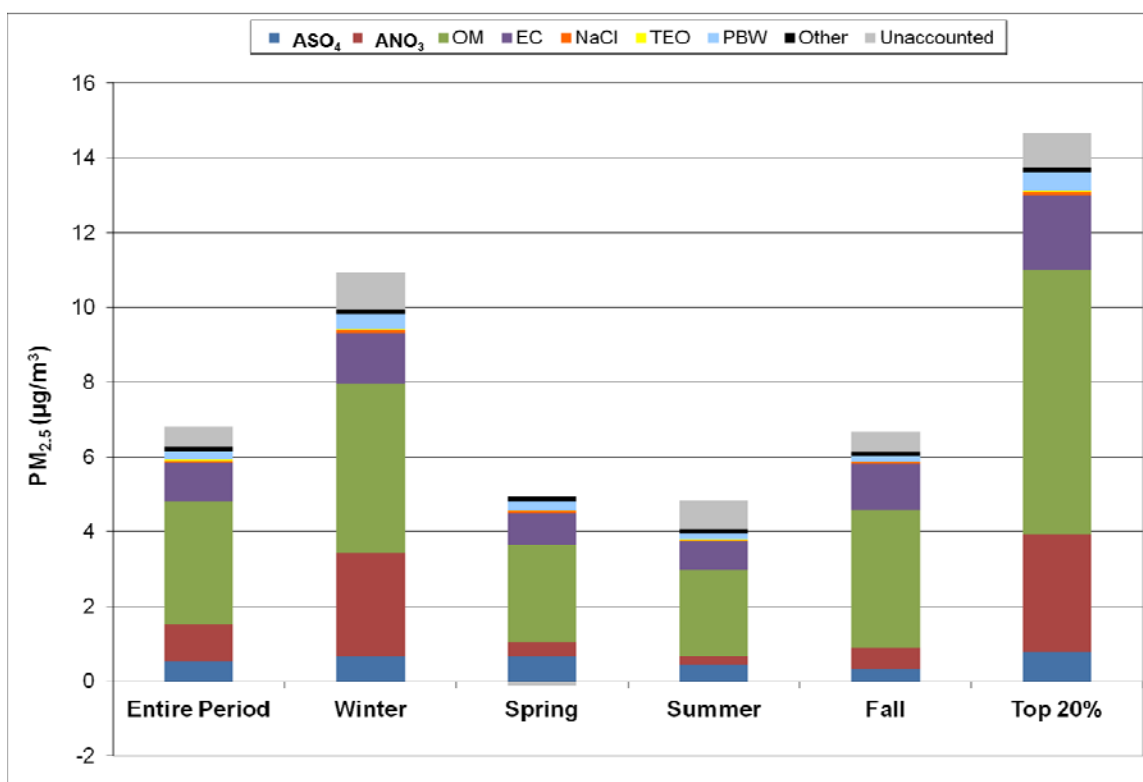


Figure 10: PM_{2.5} mass reconstruction

A principal components analysis (PCA) was performed on the speciation dataset; however, the major sources (e.g. traffic, wood smoke and secondary aerosol) appear to have been lumped into one factor (high correlations of OC, EC, NO₃⁻, NH₄⁺, K⁺, Zn, Pb, Ba, levoglucosan, CO and NO₂) due to the insufficient number of samples available. Other significant factors included one with high correlations of Ca, Fe and Mn (likely crustal material), another highly correlated with Na (likely road salt) and another highly correlated with Cu (unknown).

Trace metal data (Figure 11) can also be used to provide some indication of source specificity. The elements Ba, Cu, Fe, Mn, Pb and Zn were measured at significant levels while all other metals had average concentrations of <1 ng/m³. Seasonal variation of Ba, Cu, Fe, Mn, Pb and Zn are shown in Figure 12. Both Fe and Mn are likely associated with suspended fine crustal material as these elements were highly correlated with Ca in the PCA. Both Fe and Mn showed slightly higher levels in the spring and fall season. Given the lack of significant industrial metal refining and processing or incineration sources in the region, traffic emissions are likely the major source of Pb and Zn; tire wear is a source of Zn, and road dust can be a source of Pb. These two elements were highly correlated with the combined PCA factor, which included the traffic source and had their highest average concentrations in the fall and winter, following the trend of PM_{2.5} seasonality. Ba was found to be strongly correlated with the combined PCA factor and moderately correlated with the crustal factor and had highest average concentration in the fall, likely indicating a mixed source as Ba can come from both crustal material and traffic sources (brake wear). Cu showed a different seasonal pattern with the highest average concentrations in the summer and winter; however, this is largely driven by the existence of two sampling days

(Jan. 12 and Jun. 13, 2007), having abnormally high Cu concentrations of 18 and 11 ng/m³, respectively. Winds on both these days were light (<3.6 m/s) and were from the east and west, respectively. When these two points are removed, the seasonal pattern shows little seasonality with just slightly higher values in the fall and winter. Cu can be emitted from break wear; however, it was not found to correlate with the combined PCA factor, potentially indicating a local unknown source of Cu emissions.

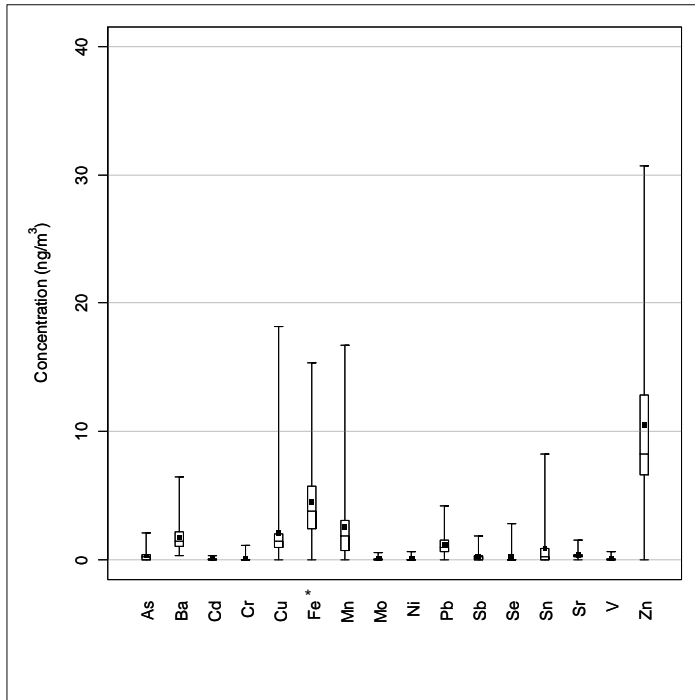


Figure 11: Trace metals concentrations in PM_{2.5} (whiskers = max/min; box = 25th/75th percentile; line = median; point = mean)

*Fe concentrations have been multiplied by 0.1.

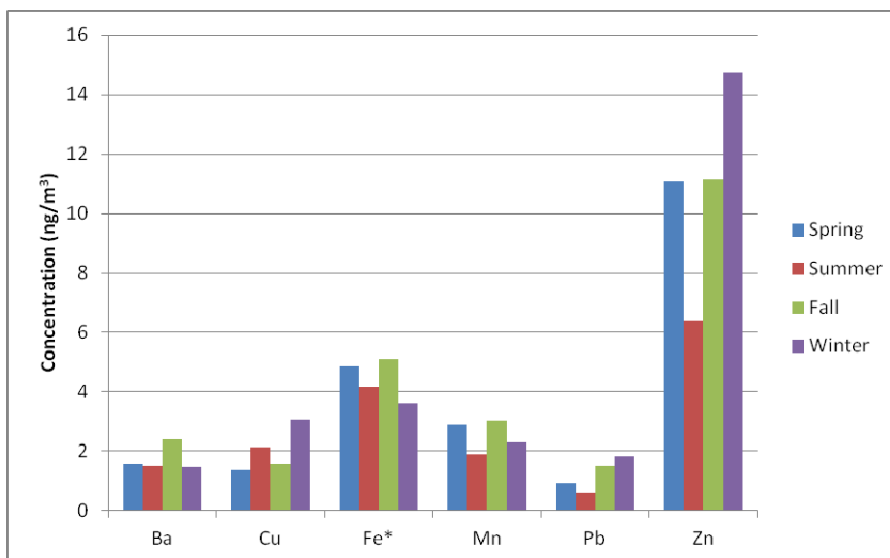


Figure 12: Seasonal average concentrations of the major trace metals

*Fe concentrations have been multiplied by 0.1.

3.2.2 Comparison with Previous Study

As the current Environment Canada study was intended to be a follow-up study to a study conducted at the same location by the B.C. Ministry of Environment (MoE) (Allen, 2009), it is useful to assess the two datasets for comparability and compatibility. The existence of three sampling days in September 2006 when the two sampling programs overlapped allows for a rudimentary comparison. A number of differences in the sampling and analysis methodology could affect the comparability; these are summarized in Table 5. Apart from the use of different samplers, methodology for the collection and analysis of PM_{2.5} mass and OC/EC were the same between the two studies. Methodology differs, however, for the ions and metals. The previous study used a single Teflon filter to collect PM for subsequent analysis for ions and metals, with no nylon backup filter or denuders in place. In addition, the current study used acid digestion ICP-MS to quantify Metals, whereas the previous study used XRF.

Table 5: Methodology comparison for the current study and previous study

	Environment Canada Study	Ministry of Environment Study
Samplers	Partisol 2300 Speciation Sampler (three channels used)	Partisol 2000 and 2x Partisol 2025 (three channels used)
Laboratory	ETSC	ETSC
Mass	Teflon filter #1 (Gravimetric)	Teflon filter #1 (Gravimetric)
OC/EC	Quartz filter Quartz back-up filter (DRI Method)	Quartz filter Quartz back-up filter (DRI Method)
Ions	Teflon filter #2 (IC) Nylon back-up filter (IC) Denuders for removal/collection of NH ₃ /HNO ₃ /SO ₂	Teflon filter #1 (IC)
Metals	Teflon filter #1 (ICP-MS acid digestion)	Teflon filter #1 (XRF)

Comparison results from the three overlapping sampling days are shown in Table 6. Bulk PM_{2.5} concentrations from the two studies are comparable, with the exception of the previous study's Sep. 14 sample, which appears to be erroneously low when compared with the reconstructed mass for that day. For the latter two samples, the MoE PM_{2.5} is approximately 10% lower than this study's results. The carbon values, again with the exception of the Sep. 14 sample, are comparable; however, the MoE samples tended to read higher than those found in this study for OC but lower for EC. This might indicate that it was the split between OC/EC during analysis that was the cause; however, it is unclear why this would be, given the same methodology was used. Also, we should be careful not to read too much into this limited comparison. Overall, given the detection limits, the ions agree quite well between the two studies, with the exception of NO₃⁻, where the MoE results are lower; significantly in the case of Sep. 20 and 26. This is not

unexpected, given the differences in sampling and analysis methodology. The use of a denuder and back-up filter are important when sampling for particulate nitrate, as their use can reduce sampling artifacts. The denuder captures and removes HNO₃, which could otherwise lead to a positive NO₃⁻ artifact caused by HNO₃ absorption onto the filter. The back-up nylon has a high affinity for gaseous nitrate, which can volatilize off the front Teflon filter, therefore its use reduces negative sampling artifacts. In addition, the use of one filter for both metals analysis by XRF followed by ions analysis could result in volatilization of nitrate. Although the XRF analysis is non-destructive to the filter, it is done under vacuum, which may lead to loss of volatiles. It appears, based on this limited comparison, that the loss of nitrate or negative sampling/analysis artifacts may have been a factor in the MoE data. Overall, the agreement between the trace elements was relatively good, given the different analysis methodology and detection limits. Mass closure was slightly better in this study.

Table 6: Comparison of results from three overlapping samples of the current study and previous study

	Sep. 14, 2006		Sep. 20, 2006		Sep. 26, 2006	
Species (µg/m ³)	Current	Previous	Current	Previous	Current	Previous
PM _{2.5}	1.8	0.4	4.1	3.8	9.1	8.2
OC	0.35	1.43	1.33	1.79	3.23	3.54
EC	0.72	0.36	0.99	0.64	1.74	0.99
SO ₄ ²⁻	0.16	0.12	0.31	0.33	0.33	0.35
NO ₃ ⁻	0.08	0.07	0.17	0.08	0.41	0.13
NH ₄ ⁺	nd	0.03	0.06	0.13	0.09	0.11
K ⁺	nd	0.01	nd	0.02	0.07	0.06
Na ⁺	nd	nd	nd	nd	0.03	0.03
Mn	0.0007	Nd	0.001	nd	0.017	0.016
Fe	0.020	0.027	0.025	0.038	0.154	0.173
Cu	0.0008	0.009	0.001	0.009	0.004	nd
Zn	0.006	nd	0.006	nd	0.009	0.005
Pb	0.001	0.0001	0.0005	0.0018	0.0015	0.001
Mass closure (Measured – Reconstructed)	+0.3	-2.4	+0.3	-0.4	-0.2	+1.3

nd = not detected above the method detection limit

Over the course of the current study, the average PM_{2.5} of 6.6 µg/m³ was slightly lower than the annual average of 7.6 µg/m³ found during the MoE study. A forest fire event in the Kelowna region in late summer 2006 could be one contributing factor to the higher average value found in the previous study. The seasonal pattern of PM_{2.5} is also very similar between the two studies, with winter showing the highest values, followed by fall and then lower and nearly equal average values for spring and summer (Figure 10 above, and Figure 5.11 in Allen (2009)). The mass reconstruction, however, shows slightly different results between the two studies. Similar to the current study, OM is by far the dominant contributor to PM_{2.5} in the MoE study, but this is followed by EC and SOIL at relatively equivalent levels, and then ASO₄, “Unidentified,” “Other” and ANO₃, as opposed to the order of OM > EC ≈ ANO₃ > ASO₄ > Unaccounted > PBW > Other > NaCl > TEO found in the EC study. The most evident difference is the contribution of

ANO₃, which is significantly undervalued in the MoE study compared with the current study, even in the winter season when it is expected to be higher. This is, in all likelihood, due to the differences in methodology discussed above. Loss of ANO₃ due to volatilization during the XRF analysis in the MoE study could explain the large increase of the “Unidentified” fraction in the winter.

3.3 Organic Compound Speciation Results

A time series of total n-alkanes, PAHs and biomarkers for each of the PUF samples at the Okanagan College site are shown in Figure 13. Also shown here are the one-in-six-day levoglucosan results for the day(s) falling within each of the PUF sampling periods. In addition, the corresponding weekly average PM_{2.5} calculated from hourly TEOM data are displayed. As discussed above, the TEOM tends to read low during the winter season, so values shown here are underestimates; linear regression of TEOM PM_{2.5} vs. speciation PM_{2.5} for the October to March period had a slope of 0.54 and r^2 of 0.81. Both the n-alkanes and biomarkers tended to peak towards the end of the winter, with the four highest samples in February and March, whereas the PAHs peaked earlier, from late December to early February, potentially indicating that PAH concentrations were affected by residential heating, which would be highest during the coldest months of the year (Dec.–Feb.). Pearson correlation coefficients are shown in Table 7 below. Alkanes and biomarkers had significant correlation, indicating an overlapping source, namely motor vehicles. Total PAHs did not correlate well with either n-alkanes or biomarkers but did correlate significantly with levoglucosan, indicating that wood smoke is a significant contributor of these compounds in the winter. Additionally, both PAHs and levoglucosan were correlated with PM_{2.5}, indicating the importance of wood smoke sources on cold season PM in Kelowna. The results of the organic compound speciation and information on source contribution are discussed in more detail below.

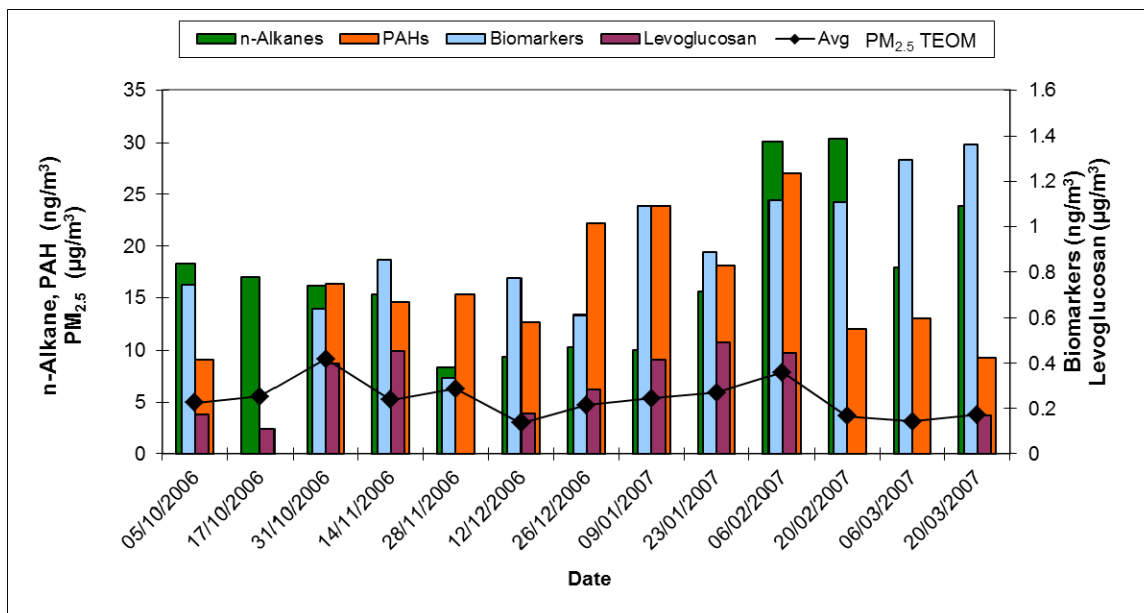


Figure 13: Organic compound speciation results at the Okanagan College site

**Table 7: Pearson correlation coefficients for organic compound species
(correlations greater than 0.6 are in bold)**

	n-Alkane	PAHs	Biomarkers	Levoglucosan
PAHs	-0.07			
Biomarkers	0.62	-0.06		
Levoglucosan	0.06	0.66	-0.01	
PM _{2.5}	0.04	0.52	-0.38	0.56

3.3.1 n-Alkanes

Results for n-alkanes in TSP samples collected by the PUF sampler are summarized in Table 8 along with results from recent studies in B.C. for comparison. Total weekly n-alkanes ranged from 8.4 to 30.4 ng/m³ and averaged 17.2 ± 7.2 (Avg. \pm SD). These concentrations are in good agreement with previous studies at urban locations in B.C. The CPI, calculated as the sum of odd-carbon numbered alkanes divided by the sum of even-carbon numbered alkanes, can be an indicator of source contribution to alkanes. Anthropogenic sources, such as automobile exhaust, display a CPI close to unity whereas biogenic sources show preference for odd-numbered alkanes and therefore show a CPI >1, with vascular plant wax having CPI values from 6–10 (Rogge *et al.*, 1993b; Simoneit, 1989). CPI values in this study ranged from 1.13 to 2.13 and averaged 1.45, showing a slight preferential presence of the odd-carbon numbered alkanes. This indicates a primarily anthropogenic aerosol source with some influence from biogenic sources. The average CPI was slightly higher for the fall (Oct.–Nov.) samples (1.56) compared with the winter (Dec.–Feb.) samples (1.36).

Table 8: n-Alkane results from the PUF sampler at the Okanagan College site

Location	Season	Site	Total n-Alkanes Min – Max (Avg \pm SD) (ng/m ³)	CPI ^a Min – Max (Avg \pm SD)	C _{max}	Reference
Kelowna	Fall– Winter	Urban	8.4 – 30.4 (17.2 \pm 7.2)	1.13 – 2.13 (1.45 \pm 0.28)	C ₂₅ , C ₂₇ , C ₂₉	This study
Golden	Fall– Winter	Urban	4.5 – 74.4 (14.5 \pm 7.8)	(1.31)	–	Ding <i>et al.</i> , 2006
	Spring– Summer	Urban	4.9 – 29.7 (5.1 \pm 2.8)	(1.71)	–	
Lower Fraser Valley	Summer	Urban	3.3 – 30.8 (14.8 \pm 10.3)	1.17 – 2.38 (1.74 \pm 0.52)	C ₂₅ , C ₂₇ , C ₂₉	Cheng <i>et al.</i> , 2006
		Tunnel	45.5 – 111.6 (83.9 \pm 24.6)	0.98 – 1.32 (1.15 \pm 0.11)	C ₂₅	
		Forest	2.0 – 16.4 (10.6 \pm 4.7)	1.92 – 3.15 (2.39 \pm 0.47)	C ₂₃ , C ₂₅ , C ₂₇	

^a C₂₂–C₃₃ alkanes were used to calculate CPI for Kelowna and Golden, whereas C₁₄–C₃₃ were used for the Lower Fraser Valley.

3.3.2 PAHs

Results for PAHs in TSP samples collected by the PUF sampler are summarized in Table 9 along with results from two other locations in Canada for comparison. It is important to note that, due to the reactivity of PAHs with oxidants such as ozone and OH, losses can occur over the course of a sampling period, the degree to which depends on the ozone concentration, sampling time, proximity to source and specific PAH reactivity (Tsapakakis and Stephanou, 2003; Schauer *et al.*, 2003; Goriaux *et al.*, 2006). Many of the ambient concentrations of PAHs reported in the literature (including those in Table 9) are derived from samplers not equipped with denuders to remove oxidants (Ravindra *et al.*, 2008); however, the sampling time used in this study (one week) is longer than normal and could conceivably have resulted in further losses to reactivity, although further research would be required to assess the extent of the issue. Results reported here can, therefore, be considered as conservative estimates. Despite this, results are comparable with results from a previous study in Golden, B.C., and somewhat higher than results from Toronto, which is not unexpected, given that Kelowna is expected to be more impacted by wood burning emissions in the winter.

Table 9: PAH results from the PUF sampler at the Okanagan College site

Location	Season	Site	Total PAHs ^a Min – Max (Avg \pm SD) (ng/m ³)	Reference
Kelowna	Fall–Winter	Urban	9.1 – 27.0 (16.1 \pm 5.7)	This study
Golden	Fall–Winter	Urban	0.7 – 100 (17.6 \pm 15.0)	Ding <i>et al.</i> , 2009
	Spring–Summer	Urban	0.3 – 8.3 (1.0 \pm 1.4)	
Toronto (Gage)	Fall–Winter	Urban	1.7 – 11.7 (4.3 \pm 1.9)	NAPS, 2012
	Spring–Summer	Urban	0.4 – 19.5 (4.8 \pm 3.3)	

^a Kelowna and Toronto studies are based on the same suite of PAH species and total suspended particulate, whereas the Golden study reported fewer PAH species and were PM_{2.5} samples.

The average concentrations of the individual PAH species are shown in Figure 14. The most abundant PAHs were the lower molecular weight species retene, fluoranthene and pyrene, followed at lower concentrations by benzo(b)fluoranthene and chrysene. High concentrations of retene, which has been identified as a tracer for wood combustion (Ramdahl, 1983), and correlation with levoglucosan ($r = 0.76$), further indicates the significance of wood burning contribution to PAHs in Kelowna. Fluoranthene and the heavier PAHs including CRHY, B(b)FLT, B(k)FLT, B(e)P, B(a)P, IP and B(ghi)P have been identified as being associated with fossil fuel combustion (Sofowote *et al.*, 2011) and are found at significant levels in Kelowna. The World Health Organization has recommended an annual average guidance value of 1.2 ng/m³ for benzo[a]pyrene in

ambient air. Concentrations of benzo[a]pyrene ranged from 0.2 to 0.7 ng/m³ and averaged 0.4 ng/m³ during this study.

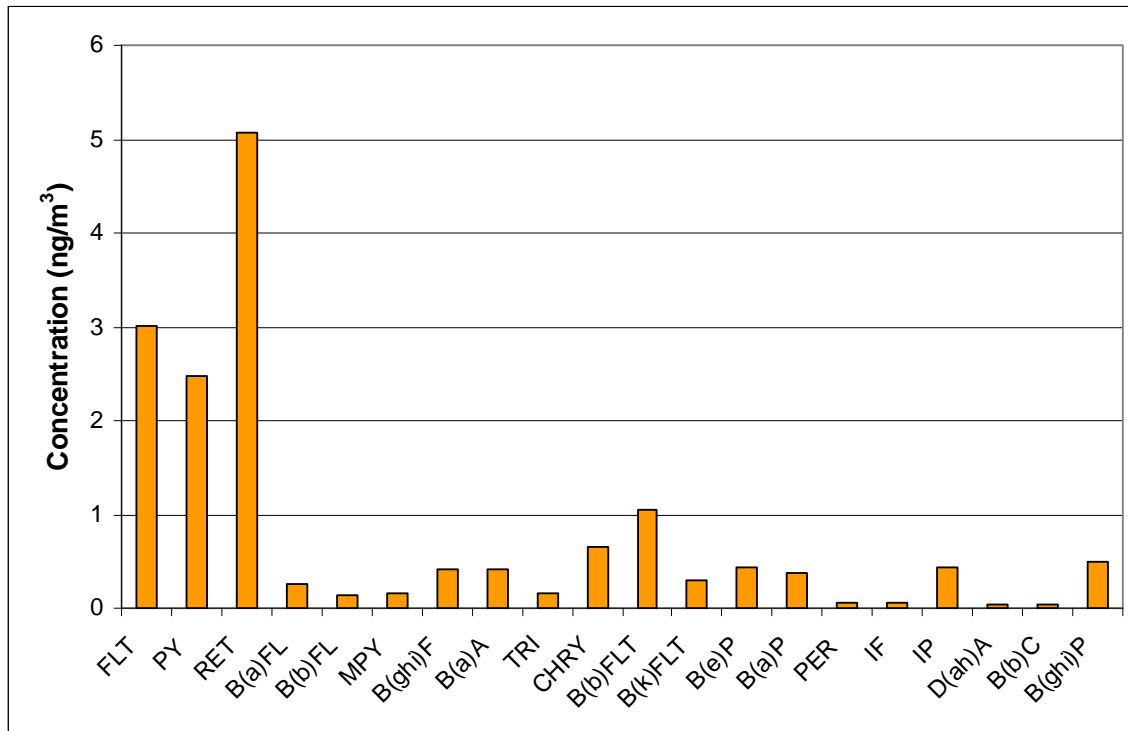


Figure 14: Average concentrations of individual PAH species at the Okanagan College site

The spatial variation of total PAHs collected with the URG samplers at the three sampling sites is shown in Figure 15 along with the collocated PUF sampler results for comparison. For all three sampling periods, the concentration of total PAHs is higher at the College and Downtown sites compared with the Westbank site, which is further from the areas of densest combustion related emissions. The October sample shows higher concentrations at City Hall compared with the College, whereas the reverse is true for the November and January samples. This is likely due to the increased impact of wood smoke during the latter two sampling periods, which is expected to be higher in residential neighbourhoods surrounding the college. Indeed the % contribution of retene to total PAHs is 2.5x higher during the latter two sampling periods and is higher at the College and Westbank sites (~34%) compared with the City Hall site (~28%). It can be seen that the PUF results are higher than the URG for all three sampling periods, which could be due to coarse particle-bound PAHs, which would have been captured by the PUF sampler but not the URG sampler.

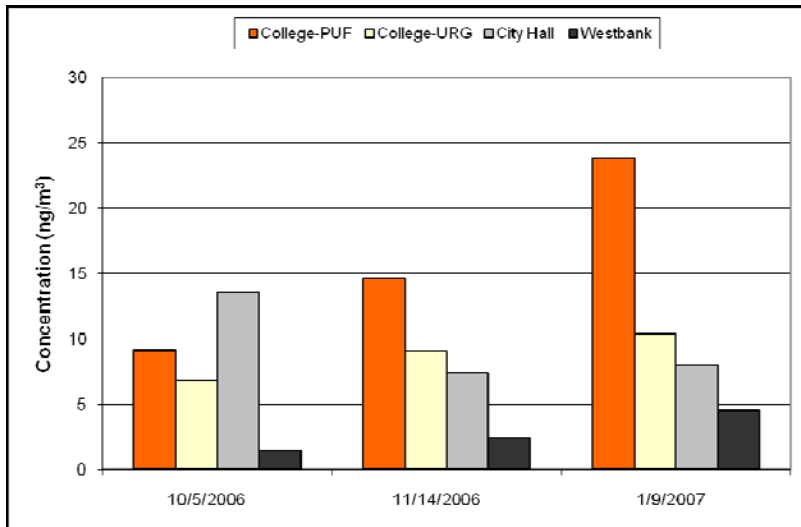


Figure 15: Spatial variation of total PAH concentrations at the three sampling sites

3.3.3 Petroleum Biomarkers

Results for 12 biomarkers collected by the PUF sampler are summarized in Table 10 along with results from recent studies in B.C. for comparison. Total weekly biomarkers ranged from 0.34 to 1.4 ng/m³ and averaged 0.90 ± 0.30 (Avg. \pm SD). These concentrations are within the range of values found elsewhere in Canada and confirm the importance of traffic emissions as a contributor to PM at this site.

Table 10: Petroleum biomarker results from the PUF sampler at the Okanagan College site

Location	Season	Site	Total Biomarkers ^a Min – Max (Avg \pm SD) (ng/m ³)	Reference
Kelowna	Fall–Winter	Urban	0.34 – 1.4 (0.90 \pm 0.30)	This study
Golden	Fall–Winter	Urban	(1.3 \pm 0.82)	Ding <i>et al.</i> , 2009.
Toronto Area	Spring–Summer	Urban Heavy Traffic	(1.0 Weekend) (2.0 Weekday)	Brook <i>et al.</i> , 2007.
		Urban Moderate Traffic	(0.5 Weekend) (0.7 Weekday)	
		Rural	(<0.1 Weekend) (0.2 Weekday)	

^a Kelowna study is based on total suspended particulate whereas the Toronto and Golden studies were based on PM_{2.5} only. The same suite of biomarker species were measured in the Kelowna and Toronto studies whereas the Golden study reported a slightly different biomarker mix.

The spatial variation in biomarker concentrations at the three sampling sites is shown in Figure 16. The October sampling date had no quantifiable concentrations of biomarkers

on the URG samplers, which have higher detection limits than the PUF due to the lower flow rate. Improvements to detection limits were made by the lab so that subsequent URG sampling events were detectable. The November sample showed the highest concentration of biomarkers at the City Hall site and the lowest at Westbank, indicating the relative impact of traffic emissions at the sites. However, the January sample showed higher concentrations at City Hall and Westbank, which may at times be influenced by traffic emissions from the city centre, as there is large contribution of winds from the east and east-northeast in the winter season.

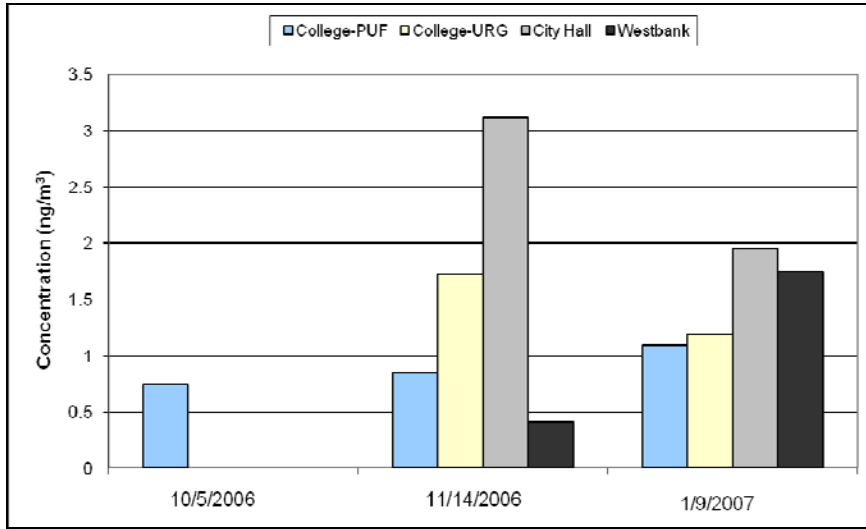


Figure 16: Spatial variation of total biomarker concentrations at the three sampling sites

The contribution of primary particulate OC emissions from motor vehicles to $PM_{2.5}$ concentrations were estimated following the method of Brook *et al.* (2007). Ambient concentrations (in ng/m^3) for each of the 12 biomarkers were regressed against an emission profile of the same biomarkers (in ng/ng carbon) derived from several hours of measurements over multiple days inside the Cassiar Tunnel in Vancouver (Graham *et al.*, 2002). The slope of the line provides an estimate of the ambient OC from motor vehicles in $ng C/m^3$ (MV-OC); however, to convert this into a percent contribution to $PM_{2.5}$, the concentration of OC is needed. This was not available for the weekly PUF samples, so instead it was estimated using TEOM $PM_{2.5}$ data as a surrogate. The daily OC from the speciation sampler was regressed against the daily average TEOM $PM_{2.5}$ for all sampling dates between October and March ($n=24$), yielding an r^2 of 0.85. The equation of this regression line was then used to convert weekly average TEOM $PM_{2.5}$ to weekly average OC concentrations, which based on standard error of the slope had standard errors of ~8%.

Using the method of Brook *et al.* (2007), the average correlation (r^2) between the biomarker profile and ambient concentrations was 0.71 ± 0.03 . The results of the contribution calculation are shown in Figure 17, with the error bars representing the upper and lower limits based on the standard error of the slopes for the estimation of OC and MV-OC. It can be seen that MV-OC ranged from 0.17 to $0.96 \mu g/m^3$ and averaged $0.58 \pm 0.12 \mu g/m^3$, which corresponded to a contribution to primary OC ranging from

5 to 49%, with an average of $23 \pm 5\%$. OC contributed 31% to total $PM_{2.5}$ on average during the October to March period. Assuming that secondary production of OC is minimal during this cold season, the primary MV-OC contribution to total $PM_{2.5}$ is $\sim 7\%$. It is important to note that total impact of motor vehicle emissions on $PM_{2.5}$ will be higher, however, as the methodology used here does not take into account primary emissions of EC or the contribution of secondary PM derived from gaseous NO_x , SO_2 and OC emissions from vehicles.

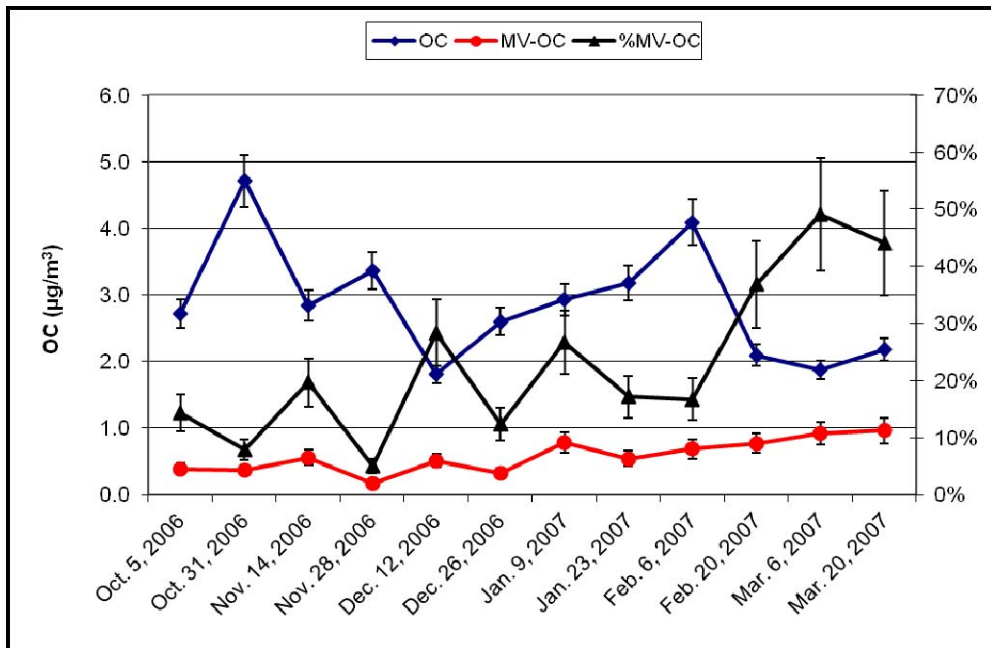


Figure 17: Estimation of the motor vehicle contribution to primary $PM_{2.5}$ at the Okanagan College site

A number of assumptions are involved in the estimate of MV-OC. One is that the vehicles and driving conditions used to derive the profile are representative of those during the current sampling period. Given that the profile was measured in Vancouver a few years prior, it is reasonable to assume that the fleet composition would be similar. The emission profile used here was collected in the summer under steady state vehicle operation, whereas the ambient sampling was done in the winter and would have been impacted by vehicles operating under a variety of conditions. As discussed in Brook *et al.* (2007), these considerations may result in the results calculated here as representing a conservative estimate of motor vehicle contribution. Another important assumption is that biomarkers exist only in the fine particle phase, as biomarker results from the PUF sampler reported here were TSP samples, whereas OC estimates were obtained from fine particle data. It has been found that biomarkers emitted from motor vehicles peak in the ultrafine mode ($<0.18 \mu m$) (Phuleria *et al.*, 2006) and remain in the fine mode at receptor sites (Fine *et al.*, 2004). In addition, the study done a year previously found no significant contribution of motor vehicle emissions to coarse fraction PM in Kelowna (Allen, 2009). The fact that biomarkers collected with the PUF sampler were lower than those collected by the collocated URG sampler (Figure 14), which had a $PM_{2.5}$ cut off, also support this assumption. Finally, it is assumed that the biomarker compounds are chemically stable from source to receptor. It has been found that hopanes and steranes can degrade in the

atmosphere due to reaction with OH radicals (Weitkamp *et al.*, 2008; Lambe *et al.*, 2009). While it is expected that OH radical activity would be relatively low during the wintertime, given the potential for reactive loss, these results would again represent a conservative estimate of motor vehicle contribution. The fact that the previous study estimated that vehicle emissions contributed 19% to PM_{2.5} using positive matrix factorization, albeit averaged over a year (Allen, 2009), supports the argument that results from this study represent a conservative estimate of motor vehicle contribution.

3.3.4 Levoglucosan

Results for levoglucosan collected by the speciation sampler are summarized in Table 11 along with results from recent studies in B.C. and the Yukon for comparison. Levoglucosan ranged from 0 to 133 ng/m³ and 84 to 869 ng/m³ in the warm and cold seasons, respectively. These concentrations are within the range of values found previously and confirm the importance of biomass-burning emissions as a contributor to cold season PM_{2.5} at this site.

Table 11: Levoglucosan results from the speciation sampler at the Okanagan College site

Location	Season	[Levoglucosan] (ng/m ³) (avg ± sd)	[Levo]/[PM _{2.5}] (%) (avg ± sd)	Wood-burning Contribution to PM _{2.5}	Reference
Kelowna	Full year	145 ± 194	1.9 ± 1.7	–	This study
	Apr.–Sep.	26 ± 29	0.6 ± 0.7		
	Oct.–Mar.	307 ± 206	3.5 ± 1.2		
Golden	Dec.–Feb.	1020 ± 478	5.1 ± 1.1	74% (PMF) ^a	Jeong <i>et al.</i> , 2008
Prince George	Dec.–Feb.	255 ± 249	1.6 ± 0.9	24% (PMF)	STI, 2008
Whitehorse	Jan.–Mar.	724 ± 752	6.0 ± 2.4	70-84% (¹⁴ C)	Jones <i>et al.</i> , 2011

^a Note: Estimated includes both wood burning and winter heating factors (which may include some gas furnace heating).

While the use of ambient levoglucosan concentration ratios alone to estimate biomass-burning contribution to PM can be subject to large uncertainties, they can be used to give an approximation of wood smoke contribution. It can be seen that the average levoglucosan:PM_{2.5} ratio from this study was 1.9, slightly higher than that of Prince George, where the wood-burning contribution to PM_{2.5} was found to be 24% using positive matrix factorization. Assuming that the fuel type, burning conditions and atmospheric processing of levoglucosan are consistent between studies, it would follow that the average annual contribution of wood smoke in Kelowna during this study is slightly higher than that of Prince George in the winter. The wood smoke contribution in Kelowna in the cold season (Oct.–Mar.) was nearly double the annual contribution, while the warm season (Apr.–Sep.) contribution was ~6x lower than the annual contribution. The levoglucosan results from this study appear to be in general agreement with the finding of the previous study that residential wood burning contributed 27% to PM_{2.5} averaged over a year (Allen, 2009).

3.4 Visibility Assessment

A time series of reconstructed b_{ext} along with daily average RH is shown in Figure 18. It can be seen that the six sampling days having $b_{\text{ext}} > 100 \text{ Mm}^{-1}$ are all associated with high RH ($> 75\%$). It has been shown in the Chilliwack region area of the Lower Fraser Valley that at RH values greater than 75%, visual air quality, that is, how well one can see a distant vista, can be significantly impacted by meteorological phenomena such as clouds and fog (Sakiyama and Kellerhals, 2011); however, such an analysis was not carried out for this study.

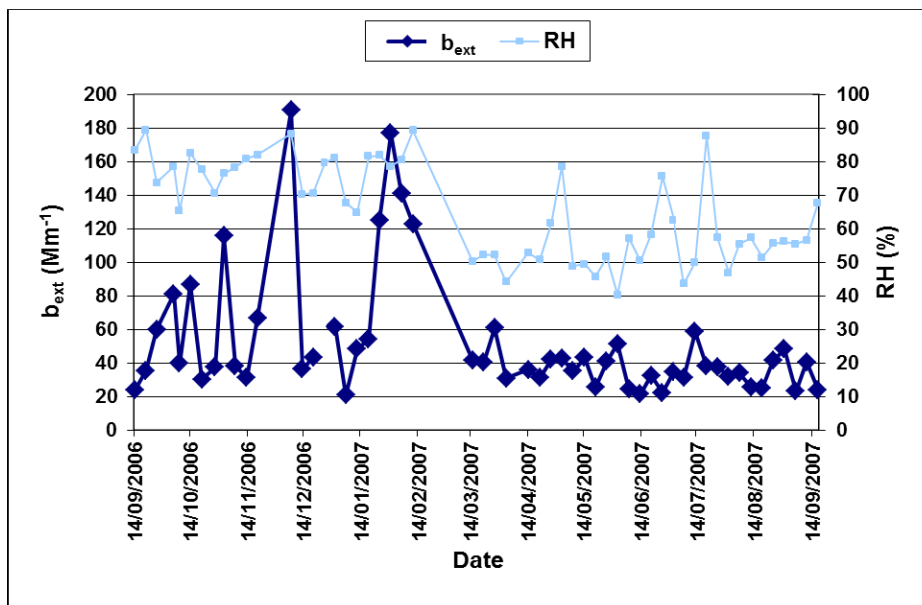


Figure 18: Time series of visibility (b_{ext}), reconstructed from speciation measurements at the Okanagan College site

The seasonal variation in visibility is shown in Figure 19. It is evident that visibility was worse in the fall and winter months compared with the spring and summer. This is due to both higher PM concentrations and RH levels in these seasons. Overall b_{ext} estimated during this study ranged from 21 to 192 Mm^{-1} , and average/median values were $52/39 \text{ Mm}^{-1}$ ($n=54$). This corresponds to an average visual range of 75 km with values ranging from 186 km down to 20 km. For comparison, the 2003–2008 average reconstructed b_{ext} at both Burnaby and Abbotsford was 56 Mm^{-1} with higher values in the fall and winter as seen in this study (So *et al.*, 2012).

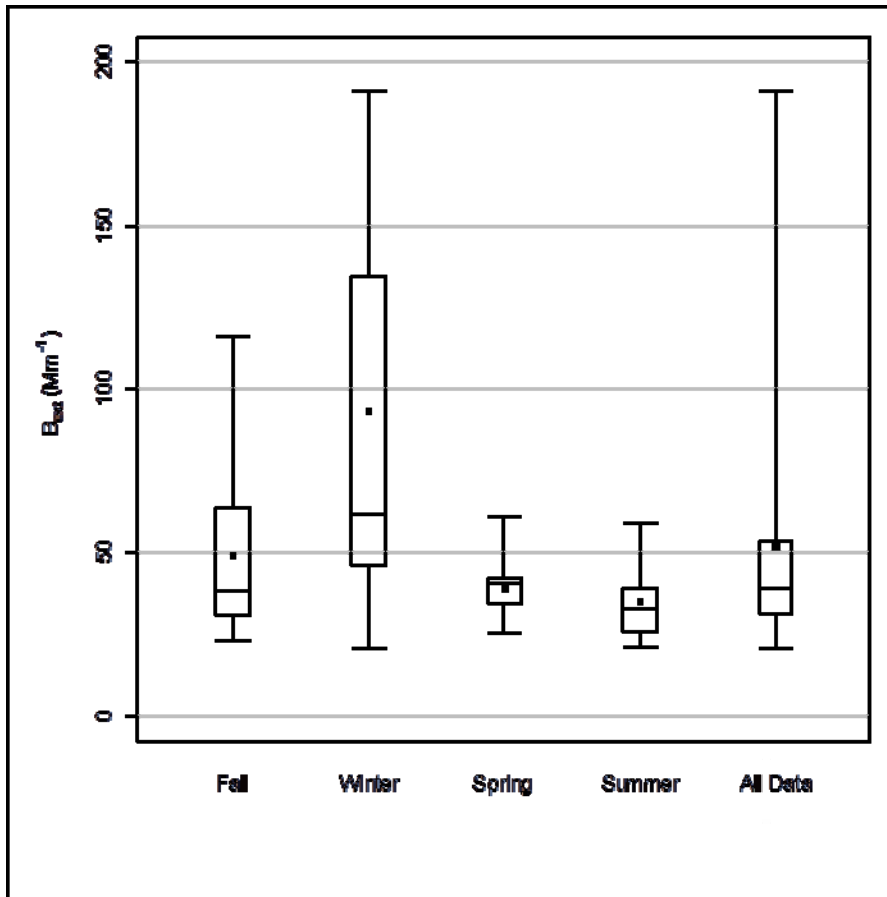


Figure 19: Seasonal trend of reconstructed b_{ext} at the Okanagan College site
(whiskers = max/min; box = 25th/75th percentile; line = median; point = mean)

The relative contributions of the components to total extinction annually, seasonally and for the highest 20% are displayed in Figure 20. On an annual basis, the most important contributors to visibility loss in Kelowna excluding Rayleigh scattering are $\text{OM} > \text{EC} > \text{ANO}_3 > \text{CM} > \text{ASO}_4 \approx \text{NO}_2 > \text{Soil} > \text{Sea salt}$. The relative contribution of components remains fairly consistent through the spring and summer. In the fall, OM increases somewhat while CM decreases. The largest shift in relative contribution is in the winter, where the importance of ANO_3 increases significantly (38% contribution compared with 4% in the summer), following the pattern seen in the $\text{PM}_{2.5}$ mass reconstruction. The worst 20% of days had a similar breakdown to winter as most of the poor visibility days were during this season.

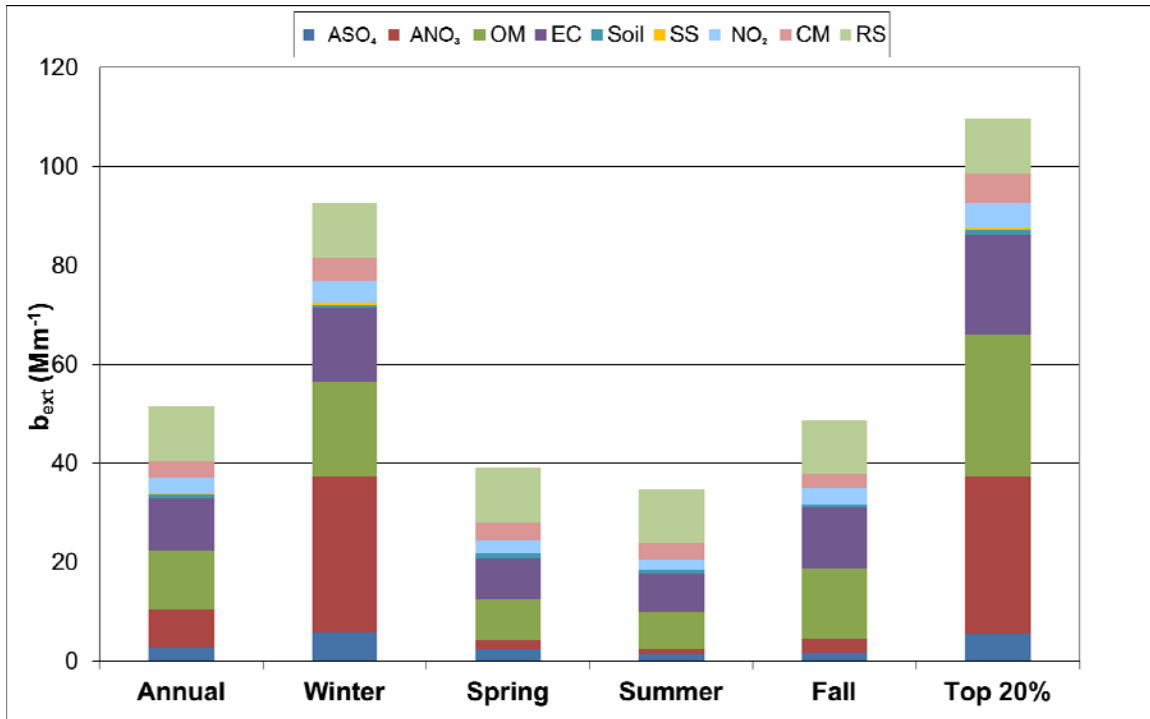


Figure 20: Contribution of individual species to visibility loss at the Okanagan College site (ASO₄ = ammonium sulfate; ANO₃ = ammonium nitrate; OM = organic mass; EC = elemental carbon; Soil = fine soil; SS = sea salt; CM = coarse mass; NO₂ = nitrogen dioxide; RS = Rayleigh scattering)

Digital images can provide a qualitative indication of visual air quality at differing levels of extinction. Four images along with associated b_{ext} , visual range (VR), PM_{2.5} and RH are shown in Figure 21. It is important to note that while the PM_{2.5} and RH are hourly average measurements, the b_{ext} and visual range values are 24-hour averages and are not necessarily the values at the time the photo was taken. However, the picture chosen represented an hour of the day where the hourly PM_{2.5} was equal or very close to the 24-hour average PM_{2.5} for that day. It can be seen that as b_{ext} increases the visual air quality decreases, as illustrated by a reduction in colour, clarity and contrast. The relatively low RH values and absence of clouds obscuring the vista at the time of these photos indicate that air pollution, as opposed to meteorological influences, was primarily responsible for visibility degradation; however, lighting conditions (e.g. sun angle) can also influence perception.

A draft visibility index for the Lower Fraser Valley has been proposed by the B.C. Visibility Coordinating Committee based on a recent study of public perception of visual air quality in Chilliwack, B.C. (Sakiyama and Kellerhals, 2011). The b_{ext} value of 24 Mm⁻¹ or 9 DV associated with image A in Figure 20 would be categorized as “Excellent” visibility according to this draft index, image B (16 DV) would be rated as “Good,” image C (18 DV) would be rated as “Fair” and image D (25 DV) would be rated as “Poor” visibility. The use of an index derived in the Lower Fraser Valley may not be valid here, as it does not necessarily represent public perception in Kelowna. However, based on these limited results, it does appear that visibility degradation in Kelowna can occur at PM_{2.5} levels that are well below the existing objectives.

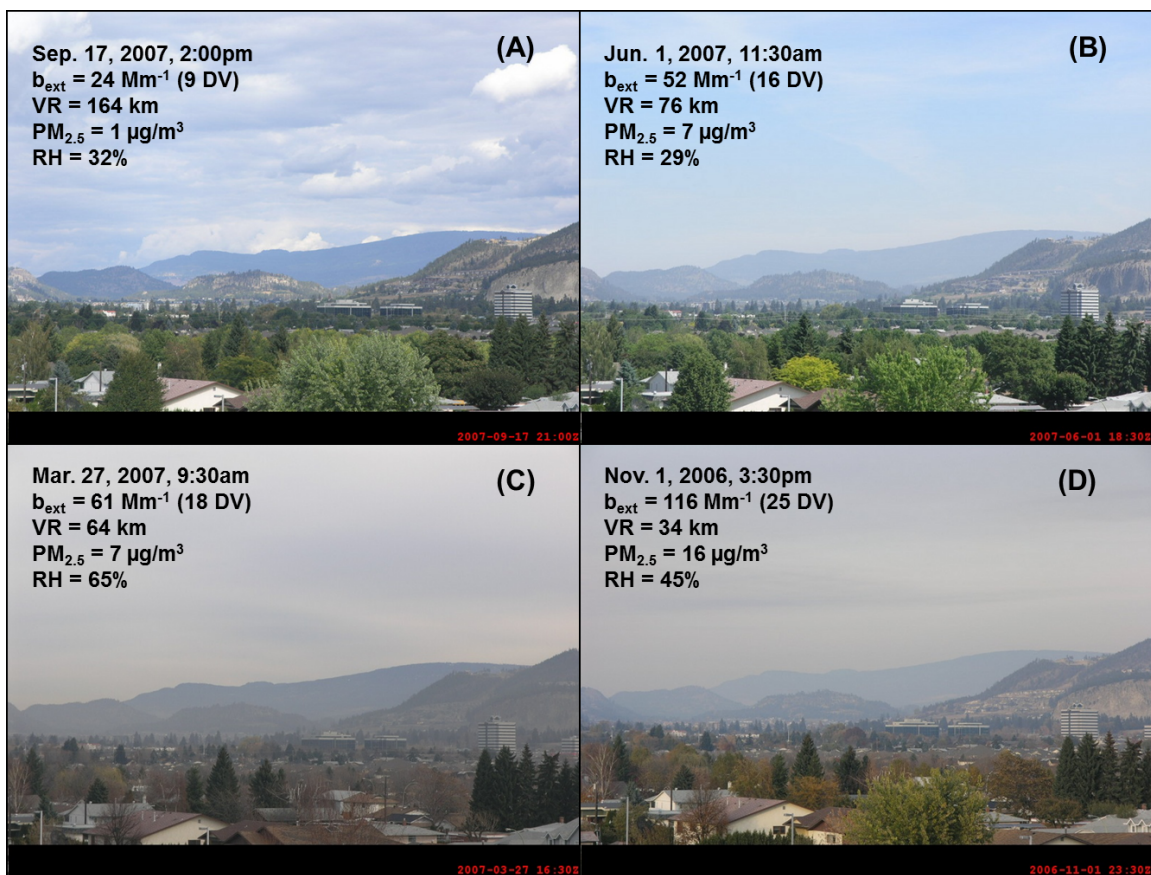


Figure 21: Examples of visual air quality at the Okanagan College site at varying levels of b_{ext} , $\text{PM}_{2.5}$ and RH

4. Conclusions

PM_{2.5} concentrations measured at the Okanagan College site during this study ranged from 1.5 to 22.1 µg/m³, and average/median concentrations were 6.6/4.7 µg/m³ (n=55), which is similar to the long-term annual average PM_{2.5} for Kelowna and slightly lower than the annual average measured during a PM speciation study the previous year. The 10 days having the highest PM_{2.5} were all observed during the cold season (Oct.–Mar.) and had light winds ranging from the northeast to south, however, all PM_{2.5} values measured during this study were below established 24-hour average objectives. A PM_{2.5} mass reconstruction showed that on average over the course of the study, organic matter made up 48% of the mass, followed by elemental carbon and ammonium nitrate at 15%, ammonium sulphate at 8%, particle-bound water at 3%, the category of Other at 2% and sodium chloride at 1%, while 8% was unaccounted for. The days where PM_{2.5} was in the top 20% of measured values showed similar mass reconstruction, with the exception of ammonium nitrate, which was higher than its average contribution. Similarly, on a seasonal basis, the most significant difference in relative contributions was the variation of the ammonium nitrate (25% contribution in the winter versus 5% in the summer). The limited number of PM_{2.5} speciation samples precluded a quantitative source apportionment; however, information derived from a principal components analysis and analysis of trace metal concentrations indicated that crustal sources, as indicated by Fe and Mn, were highest on average in the spring and fall seasons, whereas traffic sources, as indicated by Pb and Zn, were higher in the fall and winter, following the trend of PM_{2.5} seasonality. Overall PM_{2.5} speciation results are comparable to those of the PM_{2.5} speciation study the previous year, with the exception of ammonium nitrate, which appears to have been significantly undervalued in the previous study compared with the current study, due to suspected negative biases caused by sampling methodology.

The quantification of several organic tracer compounds provided further information on source contribution, particularly in the cold season. Week-long biweekly (Oct.–Mar.) concentrations (avg.±sd) were 17.2±7.2 ng/m³, 16.1±5.7 ng/m³, 0.90±0.30 ng/m³ and 307±206 ng/m³ for the n-alkanes (C₂₂–C₃₆), 20 PAHs, 12 petroleum biomarkers and levoglucosan, respectively. Alkanes and biomarkers had significant correlation, indicating an overlapping source, namely motor vehicles. Total PAHs did not correlate well with either n-alkanes or biomarkers but did correlate significantly with levoglucosan, indicating that wood smoke is a significant contributor of these compounds in the winter. The CPI value (Oct.–Mar.) of the alkanes indicated a primarily anthropogenic aerosol source with some influence from biogenic sources. The most abundant PAHs were the lower molecular weight species retene, fluoranthene and pyrene, followed at lower concentrations by benzo(b)fluoranthene and chrysene. High concentrations of retene, which has been identified as a tracer for wood combustion, and strong correlation with levoglucosan, further indicates the significance of wood-burning contribution to PAHs in Kelowna. The average concentrations of benzo[a]pyrene measured during this study (0.4 ng/m³) was below the World Health Organization annual average guidance value (1.2 ng/m³). Using the ambient biomarker concentrations and a source profile from a previous tunnel study, the motor vehicle contribution to primary OC ranged from 0.17 to 0.96 µg/m³ and averaged 0.58±0.12 µg/m³ at the Kelowna College site, which corresponded to a contribution to

primary OC ranging from 5 to 49%, with an average of $23 \pm 5\%$. By comparing the average levoglucosan:PM_{2.5} ratio of 3.5 ± 1.2 to corresponding values and source apportionment results of previous studies in B.C. and the Yukon, the annual average wood-burning contribution to PM_{2.5} in Kelowna during this study was estimated to be slightly higher than that of Prince George (24%, winter season). The wood smoke contribution in Kelowna in the cold season (Oct.–Mar.) was nearly double the annual contribution, while the warm season (Apr.–Sep.) contribution was approximately one sixth of the annual contribution.

The visibility extinction coefficient (b_{ext}) estimated during this study ranged from 21 to 192 Mm⁻¹ and averaged 52 Mm⁻¹ (n=54), which is similar to annual average values found in the Lower Fraser Valley. This corresponds to an average visual range of 75 km, with values ranging from 186 km down to 20 km. The average visibility measured during this study would be categorized as “good” based on a previous visibility perception study in Chilliwack, although use of an index derived in the Lower Fraser Valley may not be valid here, as it does not necessarily represent public perception in Kelowna.

On an annual basis, the most important contributors to visibility loss in Kelowna, exclusive of Rayleigh scattering, were organic matter at 39%, followed by elemental carbon (39%), ammonium nitrate (19%), coarse mass (9%), ammonium sulfate (7%), nitrogen dioxide (7%) and soil (2%). The largest seasonal shift in relative contribution was in the winter, also the season with the highest observed extinction values, where the importance of ammonium nitrate increased significantly (38% contribution compared with 4% in the summer). Based on an analysis of a limited number of digital images captured during the study, it appears that visibility degradation in Kelowna can occur at PM_{2.5} levels that are well below the existing objectives.

The result of this study showed that while PM_{2.5} levels in Kelowna remained below established 24-hour average objectives, elevated levels do occur in the winter. In the cold season, when PM_{2.5} is the highest, traffic and wood-burning sources were estimated to make up the majority of PM_{2.5}. Efforts to achieve significant reductions of PM_{2.5} during this season, therefore, should consider reductions strategies for these two sources.

Acknowledgements

The efforts of the Analysis and Air Quality Section of Environment Canada in the handling and analysis of all particle speciation samples and to Natural Resources Canada CANMET Energy Technology Centre for the alkane and petroleum biomarker analysis are greatly appreciated. The efforts of Steve Josefowich, B.C. Ministry of Environment, Corey Davis, City of Kelowna and Peter Murray in establishing and maintaining the sampling sites for this study are also appreciated. In addition, the advice of Jeff Brook and Gary Poole of Environment Canada and J.P. Charland of Natural Resources Canada on OC speciation sampling and analysis methodologies, and comments on the report by Corinne Schiller, were very helpful.

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