

# 2011

## *The Contribution of Forest Fires to PM<sub>2.5</sub> Burden in Halifax During the Summer of 2011.*



Honours candidate:  
Phuong (Philip) Ong

Direct Supervisor:  
Dr. Mark Gibson

ENVS Course Supervisor:  
Dr. Shannon Sterling

1/1/2011

## **ABSTRACT**

Source apportionment was used to identify the contributing sources to the concentration of  $PM_{2.5}$  in Halifax over the summer of 2011. The source modeling of choice was Positive Matrix Factorization (PMF) because it does not require source profiles. There were 5 factors that were considered: Biomass burning, shipping emission, surface material, long range transportation and sea salt. The PMF result indicated that biomass burning contributed the most to  $PM_{2.5}$  concentration (56.2%). The second prominent source was shipping emission (20.3%). Surface material contributed 12.2% and long range transport of PM contributed 11.3%. Although Halifax is a port city with very close proximity to the ocean, the salt factor did not contribute to concentration of  $PM_{2.5}$ . The  $PM_{2.5}$  showed episodic changes over the sampling period. Combining the episodic change characteristic with the summer sampling time, it is likely that forest fire was the cause of the episodic changes. However, further studies of forest fire inventory, wind direction, and air-mass back track trajectory are needed to confirm that result. Coincidentally, a systematic contamination of nylon filters was identified in this study. The contaminating source, however, was not identified. As a result, it is recommended that nylon filter should be avoided until the contaminating source is identified.

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## ACKNOWLEDGEMENT

*I would like to thank Dr. Mark Gibson for his complete support of my thesis. He has generously provided me with all the resources (laboratory equipment and staff support) in order to finish my thesis. I also want to say thanks to Dr. Shannon Sterling for her sound advises and motivational support. As well, I want to express my great gratitude to Gavin Kings, James Kuchta and Alex Hayes. Without their tireless works in the lab and support for this project, I would have been lost. Last but not least, I want to thank my family, friends and classmates for giving me unconditional motivational and moral help throughout this process*

**Philip Ong**

## **Introduction**

### *Air pollution and public health*

Air pollution has been shown to have both short and long term negative health impacts. Many studies have demonstrated that increased concentrations of particulate matter (PM) correspond to increase in hospital admission rate for cardio vascular illness (Simkhovich et al, 2008). Health effect of air pollutants include, but are not limited to, heart disease, chronic obstructive pulmonary disease, and pneumonia (Simkhovich et al, 2008). Burnett et al (1995) observed over a period of 6 years in Ontario, Canada that an increase of  $13 \mu\text{g}/\text{m}^3$  of ambient particulate sulfate resulted in 3.7% and 2.8% increase in hospital admissions for respiratory and cardiovascular issues. Zanobetty et al (2000) observation in 10 U.S cities during period of 9 years finds similar results in hospital admission for cardiovascular disease and pneumonia for each  $10\mu\text{g}/\text{m}^3$  increase of  $\text{PM}_{10}$  concentration. Schwartz (2001) found that an increase in the level of particulate matter, which has a median aerodynamic diameter of below  $2.5\mu\text{m}$  to  $10\mu\text{m}$ , by  $10\mu\text{g}/\text{m}^3$  was associated with 1.27%, 1.45%, and 2.00% increase in hospital admissions for heart disease, chronic obstructive pulmonary disease, and pneumonia, respectively. As a result, health effects of particulate matter are of concerns for the well-being of the population.

Historically, there have been many events which changed public perception about the danger of air pollutants. One of the most famous examples is the 1952 London black fog event. In December of 1952, a heavy fog composed mainly of atmospheric particles such as black smoke soot and sulfur dioxide ( $\text{SO}_2$ ) from local domestic coal fires and coal-powered power stations were the cause of dramatic increase in mortality (Simkhovich et al, 2008; Davis et al, 2002; Bell & Davis, 2001). This event gave rise to the term smog which comes

from the combination of smoke and fog (smog). Although, the London smog event lasted for two weeks, its effects lasted much longer. It has been suggested that the London smog was responsible for almost 12,000 deaths between December 1952 to February 1953 and afterwards (Simkhovich et al, 2008; Davis et al, 2002; Bell & Davis, 2001).

### *Particulate matter (PM)*

Atmospheric PM is commonly divided into size fractions based on median aerodynamic diameter. PM<sub>10</sub> is used for particles with a median aerodynamic diameter less than 10µm. PM<sub>2.5</sub> is used for particles having a median aerodynamic diameter below 2.5µm and is referred to as fine particulate matter. The size fraction between PM<sub>2.5</sub> and PM<sub>10</sub> is referred to as coarse particulate matter. Ultrafine particles (UFP) are particles having median aerodynamic diameter less than 0.1µm (Simkhovich, 2008; Englert, 2004). PM<sub>10</sub> and below are considered inhalable. Due to their size, these particles can penetrate into the lungs, and trigger an inflammatory related cascade or act as vector carrying other toxic, chemical and biological, agents on their surface or as part of their composition deep into the lung (Simkhovich et al, 2008). The smaller particles are, generally, the more dangerous to cardiovascular and respiratory mortality because they can be deposited deep into lungs and other organs (WHO, 2003). It has been shown that UFP, after being inhaled, can be passed into the bloodstream and be found in remote organ such as the heart (Nemmar et al, 2002)

Sources of particulate air pollutants can be both natural and anthropogenic. Anthropogenic sources of PM<sub>10</sub> include road dust, agricultural dust, tire wear emissions, wood combustion, construction, demolition, and mining operations (Simkhovich et al, 2008). Natural sources of PM<sub>10</sub> include windblown dust and wildfire (Simkhovich et al,



2008). Some of the major anthropogenic sources of PM<sub>2.5</sub> are power plants, oil refineries, metal processing facilities, tailpipe and brake emissions from fuel combustion of vehicles and wildfire. For UFP, the primary contributors are tailpipe emissions from mobile sources such as motor vehicle, aircrafts and marine vessels (Simkhovich et al, 2008). It is clear that anthropogenic sources, especially vehicles emission, are the major contributing source of PM of all type. Therefore many funding and research efforts have been allocated to the understanding of the anthropogenic sources.

In order to gain better understanding about PM, it is necessary to collect and monitor air pollutant variables such as PM concentration, volatile organic compounds (VOCs) and other target species. In Canada, the National Air Pollution Surveillance (NAPS) network is responsible for overseeing the collecting and monitoring of air quality from Provinces, Territories and Municipalities in order to obtain a unified Canada-wide air quality dataset (Dabek-Zlotozynska et al, 2011). Environment Canada, in cooperation with NAPS, provides air monitoring instrumentation and reference standards, operating laboratories for analysis of NAPS samples and many other quality assurance programs. This is to ensure a Canada-wide air quality dataset for criteria pollutants, VOCs, semi-volatiles organic compounds (SVOCs), PM and other target species (Dabek-Zlotozynska et al, 2011). As of 2008, NAPS network has included 14 active sampling sites across Canada with most of them in major urban areas as well as some sites in rural location and smaller communities. The site selection process was designed to ensure that air quality data represent major populated locations of Canada as well as rural areas that are impacted by local and regional industrial sources, specifically of southern Ontario and southern Quebec (Dabek-Zlotozynska et al, 2011).

### *PM in Halifax*

Halifax's sampling sites is located in commercial downtown area impacted by emission from marine vessels, power station and refinery. Some studies have found that in Halifax, PM<sub>2.5</sub> is dominantly contributed by sulfate (Jeong et al, 2011) and sea salt (Dabek-Zlotorzynska, 2011). The sulfate factor was found to have strong summer high pattern while the salt factor has a winter and early spring high pattern (Jeong et al, 2011). Due to its location close to the ocean and the use of road salt during winter, the level of salt factor is significantly higher in Halifax than other Canadian cities (Jeong et al, 2011; Dabek-Zlotorzynska, 2011). Jeong et al (2011) also found that only 35% to 40% of PM<sub>2.5</sub> mass in Halifax comes from local sources such as vehicular emissions, road and sea salt, biomass burning and industrial emission. However, Jeong et al's study did not specify non-local sources. As a result, trans-boundary contributing sources should be investigated, especially in Canadian cities such as Windsor, Toronto and Montreal with close proximity to the industrial regions of the United States (Jeong et al, 2011).

### *Source apportionment:*

In order to evaluate level of exposure of a population or a community to air pollutant, it is necessary to identify the contributing sources (Gibson, 2011). The method of identifying contributing sources is known as source apportionment or receptor modeling. There are four models which are used as standard approaches for conducting source apportionment. The four models are CMB-calculate (Gibson, 2009), CMB v 8.1, Positive Matrix Factorization (PFM), and Principle Component Analysis (CPA) (US EPA, 2011). Each method has its advantage and draw back. Thus, depends on the purposes of the project and data collected, these methods can be used independently or combine with each other or

other method. For example, PMF functions by examining the correlation structure in PM speciation temporal variability using a weighted multivariate statistical approach. Associations between components are found in order to estimate the potential factors (Jeong et al, 2011). Therefore, PMF does not need a source profile database. Another popular standard method of source apportionment is Chemical Mass Balance (CMB). A number of studies have conducted using wood smoke associated chemical species, PM and VOC source profiles coupled to CMB modeling and multivariate models such as PMF (Ward, 2004; Ward, 2006; HellÈn, 2008; Jordan, 2005; Watson, 1997 Bergauff, 2009; Bergauff, 2008; Jeong, 2008; Su, 2008; Ayers, 1999). Ward et al (2006) has confirmed and validated CMB wood smoke source apportionment modeling using radiocarbon-14 ( $^{14}\text{C}$ ) and wood smoke markers that include levoglucosan. Bergauff et al. (2009) and Ward et al. (2008) have used levoglucosan to assess the effectiveness of a wood stove change out intervention in Libby, Montana and to evaluate organic tracers for wood smoke. These studies focus almost exclusively on anthropogenic source such as vessel emission, traffic, residential wood burning, etc. There is a lack of understanding about the contribution of forest burning's emission to the air pollutants, specifically  $\text{PM}_{2.5}$  in Halifax.

*PM and forest fires:*

PM can be produced from natural and anthropogenic biomass burning. Natural sources can be forest fires of which there are between 6000 and 10,000 annually in Canada (Wotawa and Trainer, 2000). Anthropogenic sources can be residential wood burning in wood stoves and wood boilers. More studies have found that residential wood burning for heating during winter is a significant source of air pollutants (Gibson et al, 2010; Jeong et al, 2008; Ward et al, 2006). A study on air quality of the town of Libby, Montana,

demonstrated that residential wood combustion contributed up to 82% of PM<sub>2.5</sub> concentration in the winter months (Ward et al, 2006). ). Similarly, Jeong et al (2008) also found that, at a valley site in rural British Columbia, 74% of PM<sub>2.5</sub> in the winter came from biomass burning. A study in Seattle, United States noted that residential wood smoke (RWS) contributed 16-28% of total PM<sub>2.5</sub> concentrations (Maykut, 2003) while in Christchurch, New Zealand 90% of outdoor wintertime PM<sub>2.5</sub> was found to be attributable to RWS (Naeher, 2007). It has been observed that, on average, 56.2% of the total ambient PM<sub>2.5</sub> is attributable to RWS in the rural Annapolis Valley, Nova Scotia, Canada (Gibson, 2010). These studies clearly demonstrated that biomass burning for residence space heating is a significant contributing factor to air pollution, especially within constrained valleys. These studies, however, did not take into account the impact of forest fire events and as such little is currently known how forest fires contribute to PM<sub>2.5</sub>.

A forest fire is defined as “a large scale natural combustion process consuming various types, sizes and ages of botanical specimen growing outdoors in a defined geographical area” (Miranda et al, 2009). Most natural ignited forest fire occur due to lightning (Flannigan et al, 2000). Lightning ignited forest fire are usually occur in remote area where it is difficult to reach. As a result, it is difficult to detect lightning ignited forest fire events and the response time can be significantly longer than human-caused forest fire events. In Canada, although most of fire can be attributed to human activities, it is estimated that 85% of area burned was caused by lightning (Wotawa and Trainer, 2000). In United States, Strauss et al (1989) shows that 1% of wildland fires in western United States are responsible for 98% of area burned. Therefore, although human start most fires, either accidentally or deliberately, lightning-ignited wildfire is the most serious (Flannigan et al,

2000; Wotawa and Trainer, 2000). From air quality perspective, however, there is no distinction or differences in PM and gases emitted from forest fire whether its cause is natural or anthropogenic. As a result, this paper will refer to forest fire regardless of causality.

Globally, forest fires are significant contributing sources of carbon dioxide (CO<sub>2</sub>) and other greenhouse gases and produce precursors of greenhouse gases such as O<sub>3</sub> to the atmosphere (Miranda et al, 2009). There are estimates that fires account for about one fifth of the total global emission of CO<sub>2</sub> (Miranda et al, 2009). Forest fires emit significant amount of carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>), nitrogen oxides (NO<sub>x</sub>), ammonia (NH<sub>3</sub>), PM<sub>2.5</sub> and PM<sub>10</sub>, non-methane hydrocarbons (NMHC), volatile organic compounds (VOCs) and other chemical compounds (Miranda et al, 2009). These compounds can significantly degrade air quality on both local and regional scale by reducing visibility, contributing to smog and increasing the level of harmful particulates in the air (Wiedinmyer et al, 2006; Miranda et al, 2009). Moreover, gaseous and aerosol emissions can react to create atmospheric oxidant such as O<sub>3</sub>, a major constituent of photochemical smog, and hydroxyl radicals (Wiedinmyer et al, 2006; Miranda et al, 2009).

Climate change can add to the complexity of forest fire because forest fire event depend heavily on weather condition. Intergovernmental Panel on Climate Change (IPCC, 2001) reported that the occurrence frequency of forest fire may be increasing as global temperature increasing. IPCC report (2001) showed that the fire frequency in Canada has been increase after 5 decades of decreasing. Additionally, the burned area in Western North America has been double, from 0.28% in the 1970s to 0.57% in the 1990s, within 20 years (IPCC report, 2001). Flannigan et al (2000) estimates an increase of 10-50% in

seasonal severity rating (SSR) in United States in 2060. SSR is a seasonal mean of daily estimate of the control difficulty of a potential fire, which derives from an estimate of the potential intensity of a fire (Natural Resources Canada, 2011). As a result, it is estimated that forest fire will be more frequent in near future. In Canada, the number of forest fire has increase from 6000 annually during 1930-1960 to 1000 annually in 1980 (Wotawa and Trainer, 2000).

Air pollution from forest fire smoke can extend beyond countries' political borders. There has been evidence that wildfires in Canada and Mexico accounted for 40-70% of annual mean particulate elemental carbon and 20-30% of annual mean natural particulate organic carbon in the United States for 1998 (Park et al, 2003). Debell et al (2004) shows that emission from wildfire in Quebec, Canada, on July 2002 caused an air pollution episode throughout region of northeastern United States. Wotawa and Trainer (2000), showed that Canadian forest fire in Northwest Territories account for as much as 74% of episodes of high CO concentration in Giles County, Tennessee over 2 weeks periods between June 25 and July 10 of 1995. In that study, it is shown that forest fire plumes were transport as far as 3500 kilometres from the Northwest Territories, Canada, to Tennessee, United States.

### **Project significance**

The studies above clearly demonstrate that a better understanding about the impact of forest fires on air quality both locally and regionally is crucial to government and health authorities. They can use such information to make informed decision on policies regarding air quality and health and for public advisories during forest fire events. Moreover, understanding the impact forest fires have on air quality, especially about the significant

contribution of gaseous and aerosol particles, can help further improve our understanding of forest fires and their contributions to climate change (Parrington et al, 2011).

## **Materials and method**

### *Site location:*

The sampling location was situated on the top of the Sir James Dunn Building located at Studley campus of Dalhousie University in Halifax, Nova Scotia. This location was accessible with the agreement from Dr. Tom Duck, Associate Professor, Department of Physics and Atmospheric Science. The utility of the monitoring site on the Dunn roof is that it is secure, has electrical power and is tall enough to collect air representative of mixed urban air.

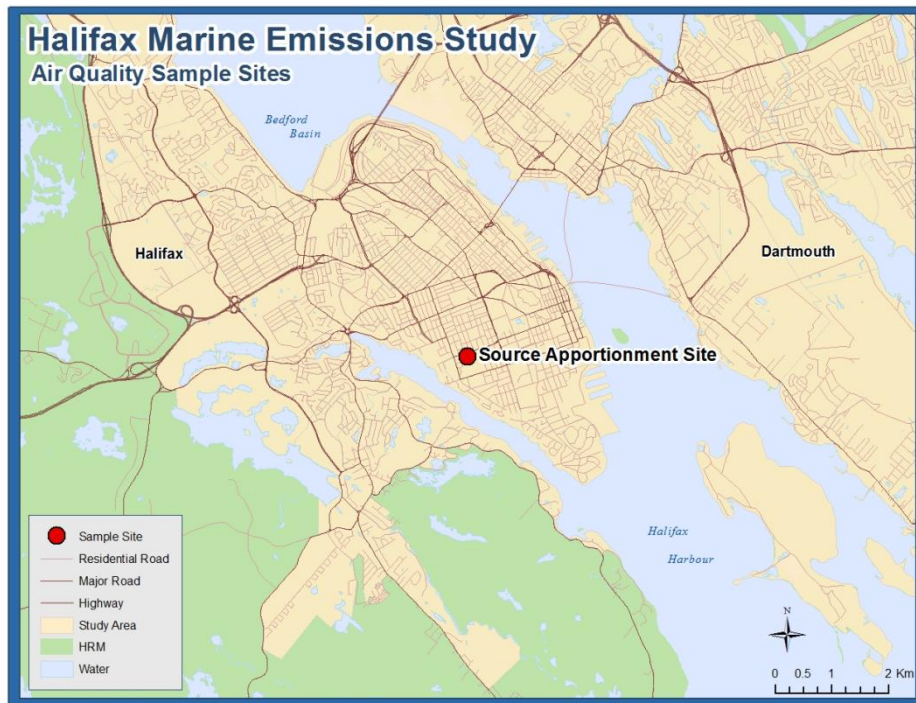


Figure 1: Map of sampling site in Halifax provide by Rainham. D, 2011

*Data collection period:*

Data collecting period started on July 11, 2011 and ended on August 26, 2011. Thus, the total days of sampling period was 47 days.

*Instrumentation:*

For sample collecting instrumentation, four active air samplers were used. Each sampler contained different filters in order to capture different PM<sub>2.5</sub> component including elemental carbon, organic carbon, chloride, nitrate, sulfate, O<sub>3</sub>, metals and persistent organic pollutants such as polynuclear aromatic hydrocarbons.

Four 24-hour ChemComb speciation samplers were used, each with a different filter. The first and second ChemCombs contained 47 mm diameter, pre-fired quartz filters operating at a flow rate of 16.7 l min<sup>-1</sup>. The third ChemComb contained a 47 mm diameter, pre-fired quartz filter operating at 10 l min<sup>-1</sup> and the fourth ChemComb contained a 47 mm diameter nylon filter operating at the same flow rate. The ChemComb flow rates were set at the start of sampling using a TSI Inc. model 400 digital flow meter (TSI Incorporated, Shoreview, MN, 55126-3996 USA). The 2300 automatically shut off if the flow rate deviated by more than ± 10% of the set flow. The uncertainty of the Partisol 2300's flow rate was found to be 1%. Monthly leak checks were performed on the Thermo Partisol 2300 PM<sub>2.5</sub> chemical speciation sampler as per the manufactures instructions. Samplers were run over a 24-hour period, which started at 4PM and ended at 4PM the next day, and were changed daily.

In addition to the active samplers that were running, a field blank sampler was also used simultaneously. One field blank was used for each sampling day. Therefore, there are total of 47 field blank filters. A field blank sampler is a ChemComb sampler with a 47 mm



diameter nylon filter. However, the sampler was not actively sampling air. Thus, the field blank went through the same assembly steps, transport process as well as disassembly steps. Since a field blank filter is essentially a “clean” filter, analyzing field blank filter helps to identify any contaminations coming from the nylon filter itself.

In order to identify significant PM<sub>2.5</sub> episodes, concentration of PM<sub>2.5</sub>, EC and O<sub>3</sub> were continuously measured at the sampling site. Continuous measurements of EC were collected using a Magee Aethalometer. Continuous PM<sub>2.5</sub> was measured using a DustTrak nephelometer. DustTrak operated with a 2.5 μm size selective inlet and as such only aerosol PM that have median aerodynamic diameter equal or less than 2.5 μm can pass through. Since all PM<sub>2.5</sub> can pass through DustTrak nephelometer without being captured by any filter, DustTrak nephelometer does not give information about PM<sub>2.5</sub> speciation. Rather it gives the total mass of PM<sub>2.5</sub>. All of the DustTrak's operated at a flow rate of 1.7 l/min. DustTrak cleaning, zeroing, flow rate checking and data downloading was conducted weekly. The data from these continuous measurements allowed for identification of any significant PM<sub>2.5</sub> episodes.

Ion Chromatography (IC) was used to analyze anions speciation. Analysis for anions was conducted using DIONEX ICS-1000 with an auto sampler AS 40 and the following column specifications:

- The anion column was a IonPac® AS 9 – HC, Analytical (4x 250 mm) with flow rate 1.0 mL/min, using ambient temperature.
- The column detection used suppressed conductivity with a suppressor: Anion Self-Regenerating Suppressor (ASRS® 300 4mm), AutoSuppressor® recycle Mode.

- The IonPac® column had an injection volume of 25µL and applied current of 45mA. The column guard is DIONEX RFIC™ IonPac® AG9 – HC.
- The software that was used to analyze the data was Chromeleon Client Version 6.80 SRIO build 2818.

*Sample processing:*

Assembly and disassembly of the ChemComb was conducted in a Clean-Ceil, high efficiency particle air (HEPA) flow hood to avoid dust contaminating the filters prior to chemical analysis. The filters have been packaged and sent to different laboratories for chemical analysis. More specifically, the Teflon filters were sent to Environment Canada for metal analysis. The Teflon filters were weighted before and after sampling under controlled humidity and temperature to obtain mass of PM. After being weighed, the Teflon filters were, then, analyzed for 22 elements metal by energy dispersive X-ray fluorescence (ED-XRF) followed by inductively coupled plasma-mass spectrometry (ICP-MS) of 20 elements. The XRF lower detection limits were in the range of 1-15 ng m<sup>-3</sup> with typical analytical uncertainties were estimated to be in the range of 5-15% for Si, Fe Ca, K, Ti, S, and 5-25% for the remaining elements analyzed. The ICP-MS analytical lower detection limits were in the range of 0.02 - 4.0 ng m<sup>-3</sup>, and the analytical uncertainties for determined trace metals were estimated to be in the range of 10-25%. It is important to use XRF method before ICP-MS because XRF is a non-destructive method whereas IPC-MS is a destructive method. XRF shoots X-ray onto the filters and the speciation was given based on the unique reflective characteristic of each metal. Therefore, the filters are still in their original condition. ICP-MS, on the other hand, requires dissolving the filters in a stock

solution. Thus, IPC-MS is considered as a destructive method because the samples are not in the original condition

One of the Quartz filters will be sent to Concordia University for analysis of Organic Carbon (OC) and Elemental Carbon (EC). The nylon filter will be analyzed for anions in the Department of Process Engineering and Applied Science under the supervision of Dr, Mark Gibson. All extraction procedures for nylon filters were carried out under HEPA flow hood in order to eliminate dust contamination. Each filter was taken out of the package and laid flat in a plastic jar with sealable lid and soaked with a mixture of a stock solution made up of 100  $\mu$ l of Isopropyl alcohol (IPA) and 7.9 ml of type one H<sub>2</sub>O (17.9 – 18.0  $\Omega$  resistance). The jar was, then, sealed and sonicated for 30 minutes. After sonication, the solution in the jar was filtered through a 0.45 micron filter which was attached to a pre-cleaned syringe into a 14 ml sample storage container. All the jars, syringes and containers were washed by rinsing multiple times with isopropyl alcohol and type one H<sub>2</sub>O to avoid contamination. The stock solution was also used as lab blank while running IC. By using stock solution as lab sample blank, it is possible to identify contaminations of the stock solution. It is important to acknowledge that lab blanks are different from field blank. Field blanks are “clean filters” while lab blanks are “clean stock solution”

#### *Sample analysis:*

Samples were analyzed for anions using ion chromatography (IC). Standard solution was purchased from DIONEX. The product used was Seven Anions Standard I, 50 mL, product number: 056933, lot number: 43-123AS. Table 1 summarizes the components and their concentration in the standard solution.

Table 1: Summary table of components and concentration of the seven standard solutions I, 50 mL (<http://www.dionex.com/en-us/webdocs/86212-DS-IC-Accessories-04May2010-LPN2497-01.pdf>)

Components	Concentration
Fluoride	20 mg/L
Chloride	30 mg/L
Bromide	100 mg/L
Nitrite	100 mg/L
Nitrate	100 mg/L
Phosphate	150 mg/L
Sulfate	150 mg/L

*Receptor modelling analysis:*

Receptor modelling was used as a method to estimate relative contribution of different sources based on measurement at receptor site. The model used was Positive Matrix Factorization (PMF). PMF model is one of four modelling approaches to conduct sources apportionment receptor modeling (Gibsons, 2010, US EPA, 2011). PMF functions by examining the correlation structure in PM speciation temporal variability using a weighted multivariate statistical approach. Once association between components are found, composition of potential factors can be estimated (Jeong et al, 2011). The advantage of PMF method to other methods is that PMF does not require prior information on pollutant sources. In other words, PMF can use the provided data set to make estimation about contributing factor. As a result, using PMF eliminate the need to have a source profile database which can be difficult to obtain for airborne particle. Another source apportionment method is Chemical Mass Balance (CMB). Unlike PMF, CMB requires a source profile of PM. Airborne PM sources profiles, however, are often unknown or too similar to each other (Jeong et al, 2011). As a result, there are potential errors in modelling

results. Some studies suggest that the error can be as much as 85% in some case when estimation was made for biomass burning (Munchak et al, 2011; Bullock et al, 2007; Sheesley et al, 2008). Therefore, PMF modelling is preferred over other methods in this study

**Results:**

Table 2 shows the mean concentration of PM<sub>2.5</sub> and PM<sub>10</sub> over the measurement period. Three different methods were done to ensure data consistency. XRF was conducted by Analysis and Air Quality Section (Environment Canada, Ottawa, Ontario, Canada, K1V 1C7). The mean concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> obtained by XRF were 4.504 µg/L and 9.881 µg/L respectively. Ions Chromatography (IC) was conducted in the Department of Process Engineering and Applied Science under the supervision of Dr, Mark Gibson. Mean concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> obtained by IC were 4.286 µg/L and 9.586 µg/L respectively. Total concentration PM<sub>2.5</sub> and PM<sub>10</sub> was collected by DustTrak nephelometer while active samplers were running during the samples collecting period. The mean concentrations of PM<sub>2.5</sub> and PM<sub>10</sub> obtained by DustTrak were 4.536 µg/L and 10.263 µg/L respectively. Standard deviation values are 3.362 and 5.708 for PM<sub>2.5</sub> and PM<sub>10</sub> respectively for XRF measurement. Similar values were obtained with IC and DustTrak measurements.

Table 2: Summary table of mean concentration of PM<sub>2.5</sub> and PM<sub>10</sub> obtained by three different methods: XRF, IC-Chromatography, and Nephelometer.

	X-Ray Florescence (XRF)		IC- Chromatography		Nephelometer	
	<i>PM<sub>2.5</sub></i> µg/L	<i>PM<sub>10</sub></i> µg/L	<i>PM<sub>2.5</sub></i> µg/L	<i>PM<sub>10</sub></i> µg/L	<i>PM<sub>2.5</sub></i> µg/L	<i>PM<sub>10</sub></i> µg/L
<b>Average</b>	4.504	9.881	4.286	9.586	4.536	10.263
<b>Standard Deviation</b>	3.362	5.708	3.253	5.758	3.358	5.587
<b>Confident interval</b>	0.031	0.053	0.888	1.572	0.031	0.052

Table 3 shows the percent difference when comparing mean values between the three analysis methods. When compared XRF with IC, the differences for mean value of PM<sub>2.5</sub> and PM<sub>10</sub> are 4.832% and 2.986% respectively. Similarly, the differences between

XRF and DusTrak mean concentrations were 0.717% and 3.870% for PM<sub>2.5</sub> and PM<sub>10</sub> respectively. The differences between IC and DusTrak mean concentrations were 5.830% and 7.067% for PM<sub>2.5</sub> and PM<sub>10</sub> respectively.

Table 3: Summary table of percent differences between mean values of PM<sub>2.5</sub> and PM<sub>10</sub> by three different methods.

	<b>XRF vs IC</b>		<b>XRF vs Dustrak</b>		<b>IC vs Dustrak</b>	
	<i>PM<sub>2.5</sub></i>	<i>PM<sub>10</sub></i>	<i>PM<sub>2.5</sub></i>	<i>PM<sub>10</sub></i>	<i>PM<sub>2.5</sub></i>	<i>PM<sub>10</sub></i>
<b>% Difference</b>	4.832	2.986	0.717	3.870	5.830	7.067

Figure 2 shows the concentration change over the experiment period of metals of interest. Figure 3 shows the rest of the metal that were not included in figure 2 because their concentrations were too low to show in Figure 2. Figure 4 demonstrates the change in concentration of PM<sub>10</sub>, PM<sub>2.5</sub>, and anions over that period. By observing the change in concentration of element metals, anions, and PM, it is possible to identify a period where there were significant changes which are identified with orange circles on the graphs.

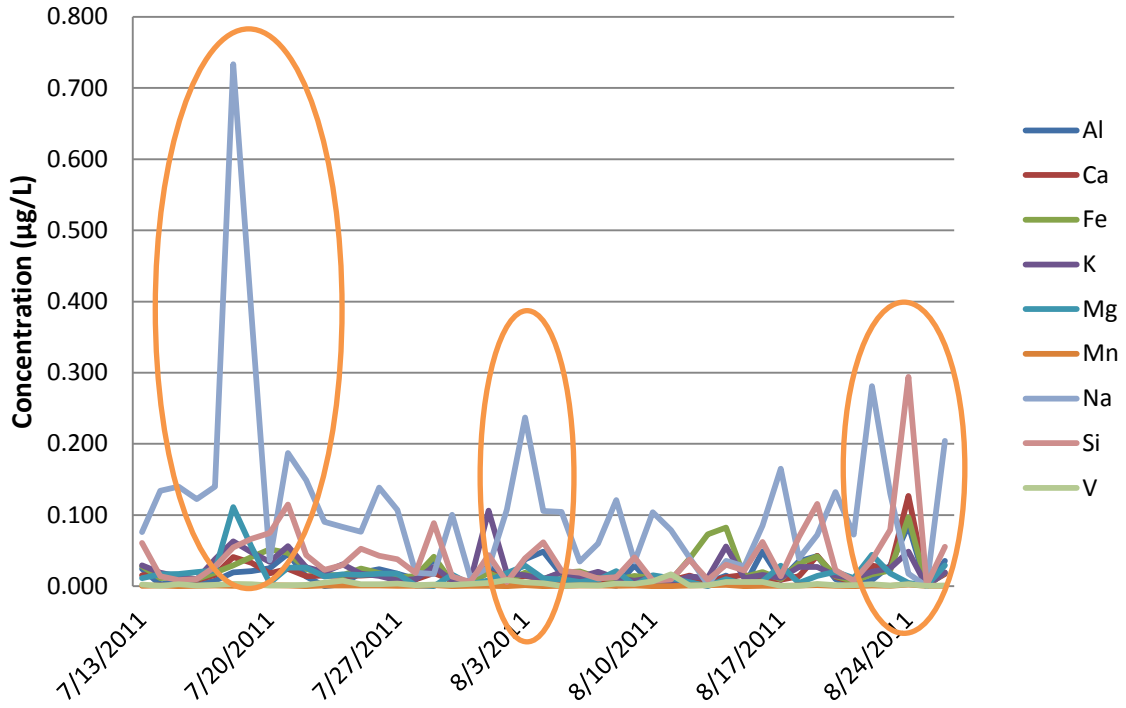


Figure 2: Concentration change of high concentration metal elements over sampling period

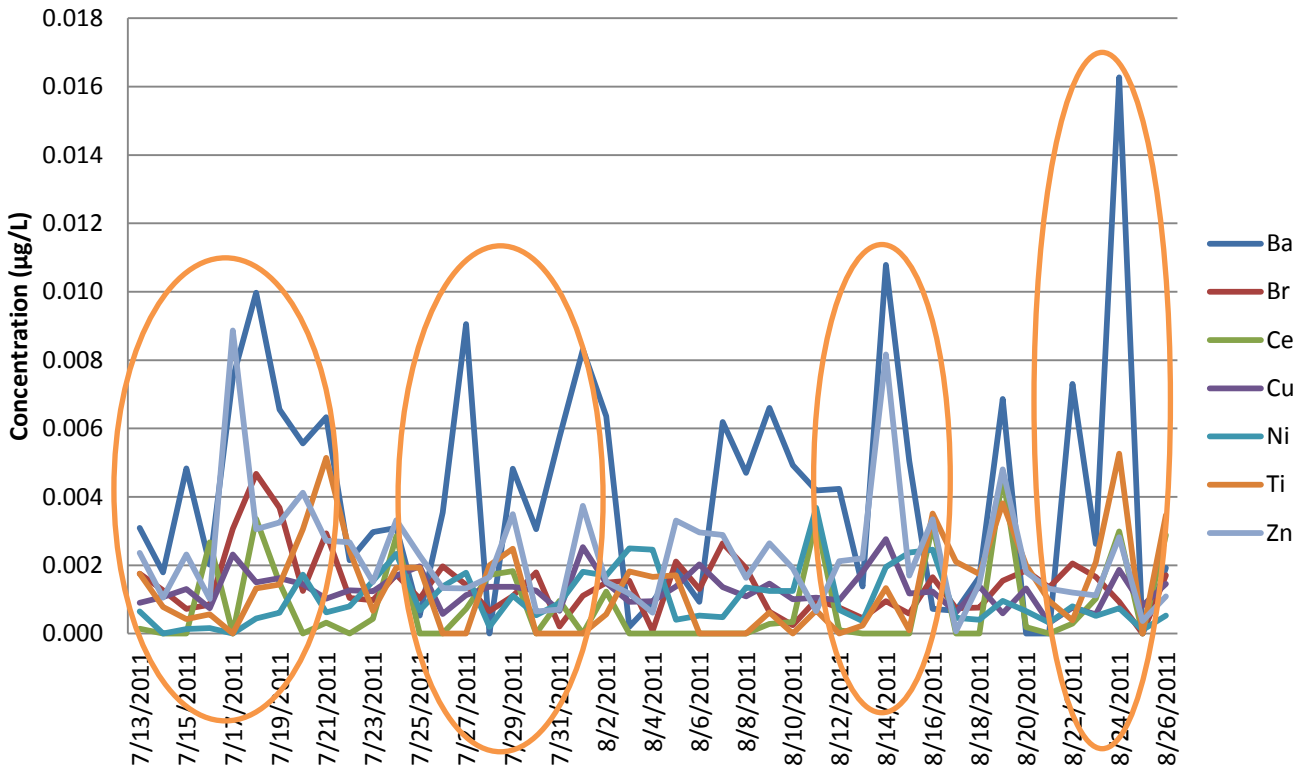


Figure 3: Concentration change of low concentration metal elements over sampling period



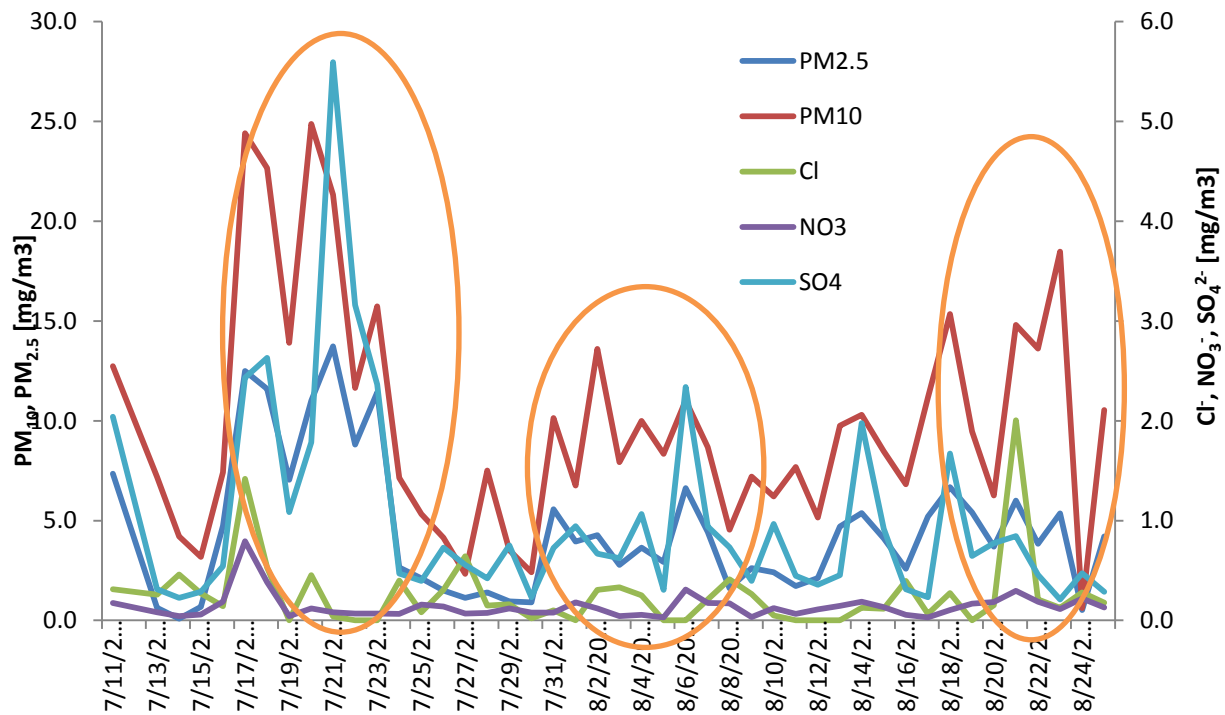


Figure 4: Concentration change of PMs and anions over sampling period.

As shown in figure 5 and 6, sodium (Na) and sulfate ( $\text{SO}_4^{2-}$ ) contributed the most to the total concentration of metal species and anions. Figure 5 shows the composition of element metals species from XRF results. The main metal element is sodium (Na) which accounted for 42% of total metals concentration. Other main element metals are silicon (Si), potassium (K), iron (Fe), aluminum (Al), calcium (Ca) which accounted for 16%, 9%, 9%, 7%, 6% of the total metal concentration respectively. Figure 6 represents the composition of total anions concentration. Three anions collected were sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), and chloride ( $\text{Cl}^-$ ). Sulfate contributes 64% to the total anion concentration while nitrate and chloride contribute 9% and 22% respectively.

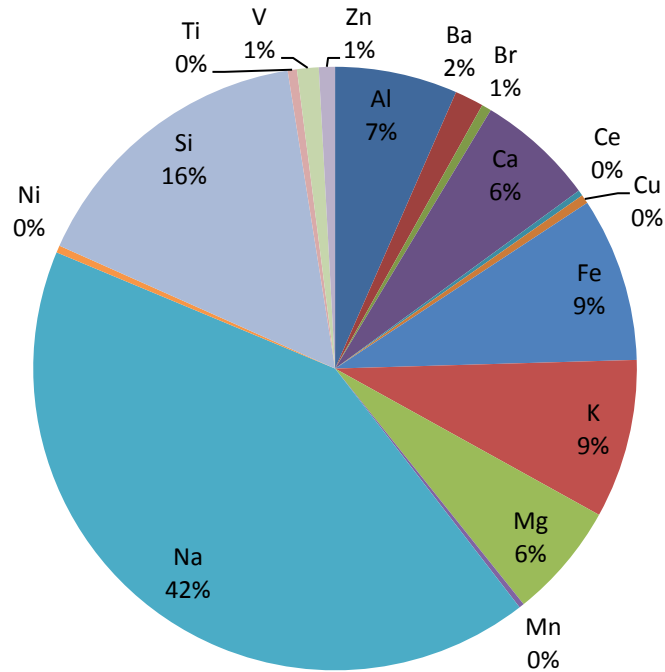


Figure 5: Contribution of each metal to the total metal concentration

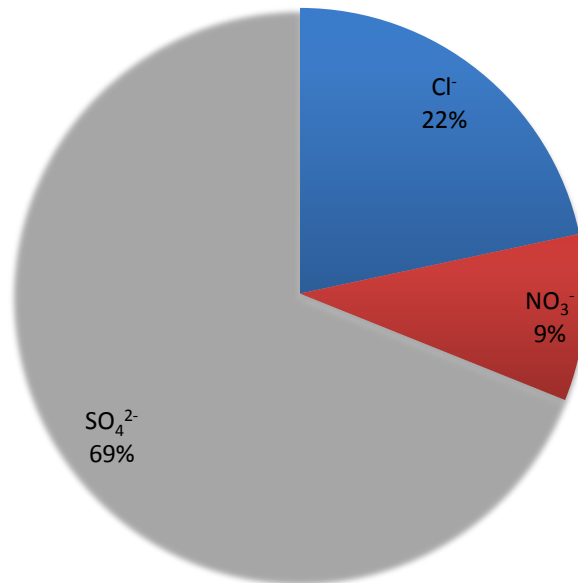


Figure 6: Contribution of each anion to the total anions concentration

Figure 7 shows the PMF result of contributing sources to aerosol PM<sub>2.5</sub> in Halifax over the sampling period. There were five factors that were considered which are biomass burning (Factor 1), surface material (Factor 2), sea salt (Factor 3), long-range transportation (Factor 4), and shipping emission (Factor 5). These factors will be discussed in more detail in the next section. As shown in figure 6, biomass burning is the biggest contributing factor to the PM<sub>2.5</sub> concentration. Biomass burning accounted for 56.2% of PM<sub>2.5</sub> in Halifax over the sampling period. The second biggest contributor was shipping emission which accounted for 20.3% of PM<sub>2.5</sub>. Long range transportation factor and surface materials accounted for 11.3% and 12.2% of PM<sub>2.5</sub> respectively. Sea salt factor were not a contributing factor to the total PM<sub>2.5</sub> during sampling period.

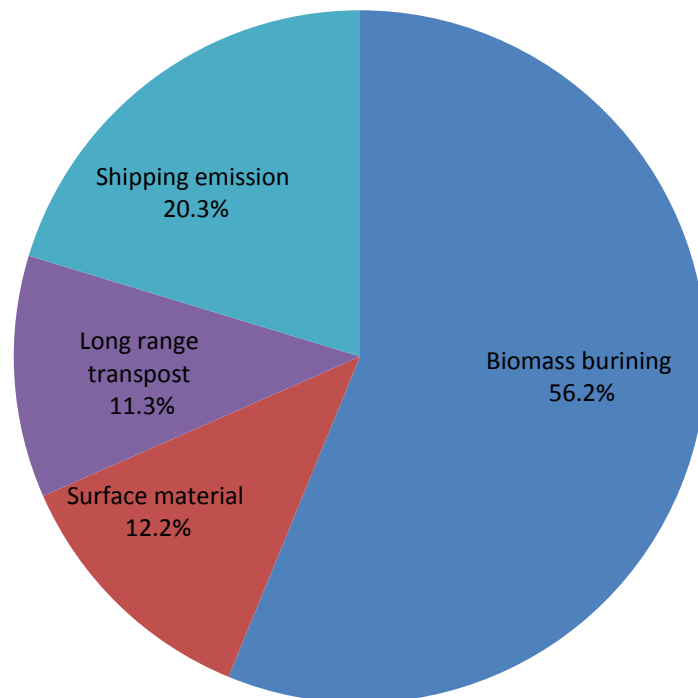


Figure 7: Source apportionment result

## **Discussion:**

### *Mean values*

The mean values for PM<sub>2.5</sub> and PM<sub>10</sub> were about 4.5 µg/L and 10 µg/L respectively. These values have high standard deviation of 3.3 and 5.7. In other words, there were significant variations within the sample. This is expected because the data were not completely random and are not independent from each other. The high variations indicate that there were significant changes in the chemistry composition of air over sampling period. The significant changes occurred episodically, as shown in figure 2, 3 and 4. There were episodes of significant increase in concentration of element metals, anions, PM<sub>2.5</sub>, PM<sub>10</sub>, and black carbon, which are marked on figure 2, 3 and 4. Those episodes occurred in the beginning, middle, and at the end of the sampling period. Those episodes are expected to have linked with forest fire occurrence episode. However, more data such as forest fire occurrence inventory and air mass back tracking trajectory are needed in order to draw conclusion. Unfortunately, within the limit time frame of the project, the link between forest fire occurrence and those episodes was not considered. Nonetheless, as discussed in the section of PMF result, some connection can be made because the sampling period was in the summer.

Comparing the means obtained by three different methods, XRF, IC, and DusTrak can insure data consistency. The difference amongst the means of PM<sub>2.5</sub> and PM<sub>10</sub> were well below 10% difference. This means that the data is consistent because three different methods yielded statistically non-different data. The mean values for PM<sub>2.5</sub> and PM<sub>10</sub> are about 4.5 µg/L and 10 µg/L which are well below the recommend guideline of the Environmental Protection Agency (EPA) and the Canada Wide Standard (CWS). The EPA

guidelines for PM<sub>2.5</sub> and PM<sub>10</sub> are 35 µg/L and 150 µg/L respectively (EPA, 2012). The CWS limit is lower than EPA standard. CWS guideline concentration is 30 µg/L for PM<sub>2.5</sub> and 60 µg/L for PM<sub>10</sub> (CCME, 2012). The maximum value of PM<sub>2.5</sub> was 15.265 µg/L and PM<sub>10</sub> was 27.623 µg/L. As a result, the concentration of PM, both PM<sub>2.5</sub> and PM<sub>10</sub>, did not exceed the guideline during the sampling period.

#### *PMF result*

There were five factor profiles that were considered for the PMF analysis. They were coded from F1 to F5, each with a characterized factor profile. Each factor profile is characterized by a unique combination of concentration of metal elements, black carbon, and anions.

Figure 8 shows the PMF factor profile for biomass burning (F1). Biomass burning factor, in this profile, is characterized by high concentration of potassium (K), black carbon (BC), and PM<sub>2.5</sub>. There are other chemical markers for biomass burning such as levoglucosan which is a product of burning cellulose in biomass (Shafizadeh, 1982). Sullivan et al (2008) suggest that levoglucosan and soluble potassium, aside from many other molecular markers, are specifically relevant chemical markers for wildland fire. Therefore, soluble potassium is more relevant as biomass tracer than element potassium. The reason is that insoluble potassium can be present in aerosol minerals, which can increase probability of error of source apportionment (Munchak et al, 2011). As a result, cations data, which has concentration of soluble potassium or potassium cation (K<sup>+</sup>), is preferred in order to get accurate result. Due to the time constrain in this project, however, only elemental metal data was obtained in time for analysis. Therefore, the PMF result can contain error and should be carefully considered. Moreover, future analysis is needed in

order to draw accurate conclusion about contribution of biomass burning factor to total  $PM_{2.5}$  concentration. Additionally, more comparisons should be done when more data of cations and other organic compounds are obtained. Nonetheless, elemental metal data can still give a reasonable estimate of source apportionment.

The PMF result, as shown in figure 7, suggests that 56.2% of concentration of  $PM_{2.5}$  came from burning of biomass. Biomass burning sources can come from local and regional sources. The local sources include small scale wood burning and do not travel far such as wood burning appliances for cooking or heating purposes, burning wood from camping sites, local small forest fire, or local prescribed forest burning. Regional biomass burning sources are large scale forest fire whose plumes got carried long distance by wind. Unfortunately, identifying the origin of forest fire sources is not in the scope of this project due to the limited time. However, it is clear that biomass burning is the main contributing source of  $PM_{2.5}$  and it is likely that biomass burning sources came from forest fire. Given the time of sampling period was in the summer, wood burning for heating purposes is not a relevant contributing factor. Moreover, HRM has a strict policy about open area wood burning, especially inside the city of Halifax. Thus, the immediate local biomass burning sources can be reasonably disregarded. As a result, it is likely that the biomass burning factors is due to forest fire events.

Figure 9 shows the PMF factor profile for surface materials (F2) such as road dusts and soil dust. It is characterized by high concentration of silicon (Si), aluminum (Al), calcium (Ca), and iron (Fe). This is consistent with study done by Jeong et al (2011). It is suggested that road dust profile is associated with high Ca, Mg, and Fe while soil dust profile is associated with high Al, and Si (Jeong et al, 2011). Surface materials accounted for

12.2% of PM<sub>2.5</sub> concentration. Road dust factor has a weekday high pattern and strong correlation with vehicular emission. As a result, traffic volume will affect the result. The sampling location is located in the main campus of Dalhousie University. The traffic is very high during the school semester in the fall and winter, especially at rush hour, on Robie street and Oxford street. These are the main streets to highway 102 and 101 which most commuters use to get into Halifax for work. The volume of traffic is significantly increase during the school time due to the high school and hospital traffic which are located very close to the sampling site. However, the sampling period took place over the summer when traffic is not at peak season. The number of student around campus significantly dropped comparing to the fall and winter. Thus the volume of traffic also dropped significantly. As a result, the contribution of re-suspended surface materials to the total PM<sub>2.5</sub> concentration could be underestimated due to the lack of traffic.

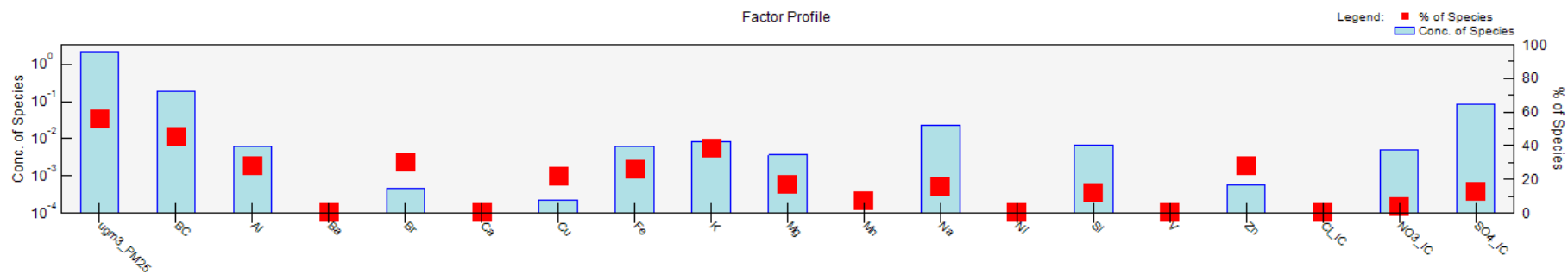


Figure 8: Factor profile 1 - Biomass burning

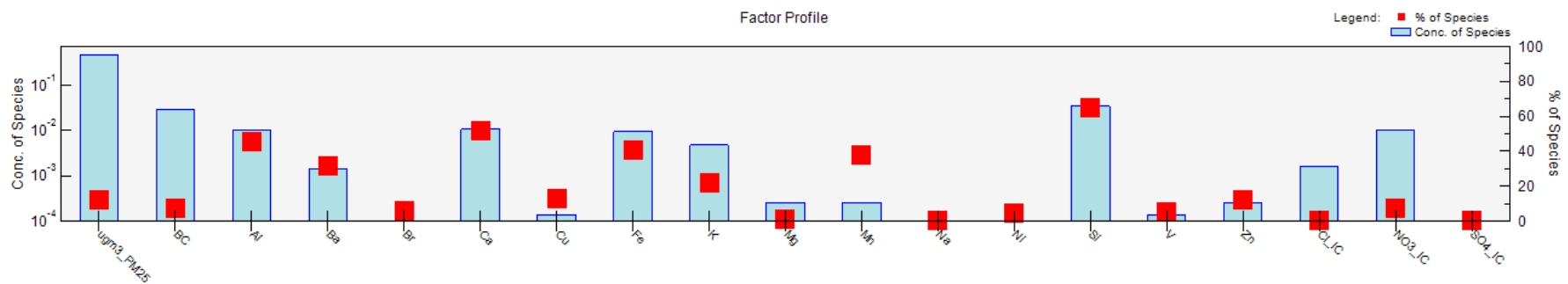


Figure 9: Factor profile 2 - Surface material



Figure 10 shows the factor profile of sea salt (F3). Sea salt profile is characterized mostly by high concentration of chloride ( $\text{Cl}^-$ ). Interestingly, the PMF result suggests that sea salt factor did not contribute to the total concentration of  $\text{PM}_{2.5}$  over the sampling period. This result is not consistent with the result of Jeong et al (2011). Jeong et al (2011) suggest that sea salt and road salt are the highest contributing factor to the  $\text{PM}_{2.5}$  concentration due to the influence of fresh sea salt. Sea salt is the most relevant contributing factor in the winter and spring because sea salt and road salt factor have a winter and spring high pattern (Jeong et al, 2011). The reason can be because HRM uses road salt during winter and spring. Therefore, the inconsistent results may be due to the difference in sampling period. Jeong et al (2011) sampling period were from April 14, 2006 to January 19, 2008. The sampling period for this project lasted from July 11, 2011 to August 26, 2011. The sampling time for this project was in the summer season. As a result, sampling during summer season may not give the true contribution to  $\text{PM}_{2.5}$  of sea salt factor to the yearly atmospheric inputs.

Figure 11 shows the profile of long range transported aerosol materials and smog factor (F4). F4 has the characteristics of high in nitrate ( $\text{NO}_3^-$ ), sodium (Na), and magnesium (Mg). F4 factor is the long distance pollution such as vehicle emission and industrial pollution that got carried down wind into the sampling site. PMF result, as shown in figure 6 suggests that F4 accounted for 11.3% of total  $\text{PM}_{2.5}$ . This factor does not account for long range transport of forest fire plumes. Therefore, there is a difference between this result and Jeong et al (2011). Jeong et al (2011) estimated that, in Halifax, only 35% to 44% of  $\text{PM}_{2.5}$  mass came from local source. This means that long range transport accounted for the majority of  $\text{PM}_{2.5}$  in Halifax which conflicts with the results of this study. One reason

can be because of the difference sampling periods between two studies. Another reason can be because Jeong et al's study included forest fire as long range transport. This inclusion can significantly increase the contribution of long range transport factor to the total PM<sub>2.5</sub>.

Figure 12 shows the PMF factor profile for shipping emission (F5). This is the emission comes from ship vessels such as container transport vessels as well cruise ship vessels. F5 is characterized by high concentration of nickel (Ni), vanadium (V), and sulfate (SO<sub>4</sub><sup>-</sup>). Jeong et al (2011) suggest that ship engine burned low cost residual oil which contain high concentration of sulfate, Ni, and V. The PMF result suggests that shipping emission factor contribute as much as 20.1% to the total concentration of PM<sub>2.5</sub>. Jeong et al (2011), however, suggest that only 9% of total PM<sub>2.5</sub> came from shipping emission. Again, this difference can be explained by the difference in sampling period. Halifax is a coast city with busy marine traffic, especially in the summer with many cruise ships dock in the port. Therefore, the result can overestimate the contribution of shipping emission factor because the sampling period was over the busy tourism time.

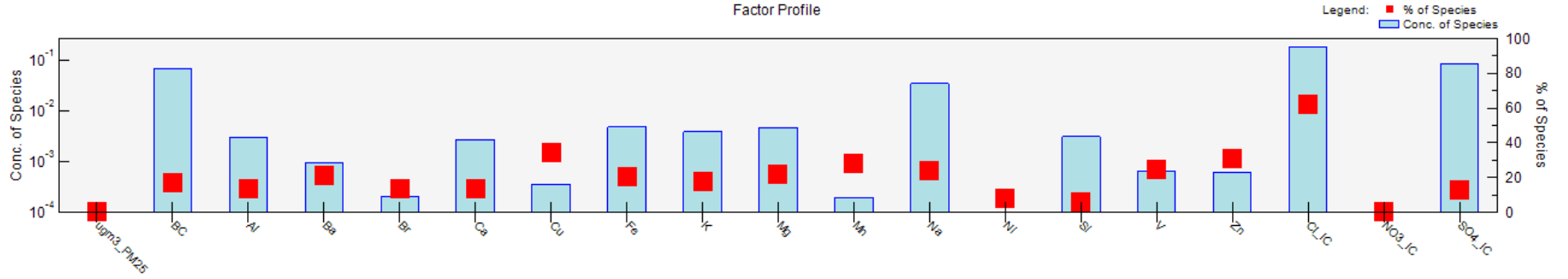


Figure 10: Factor profile 3 - Sea salt

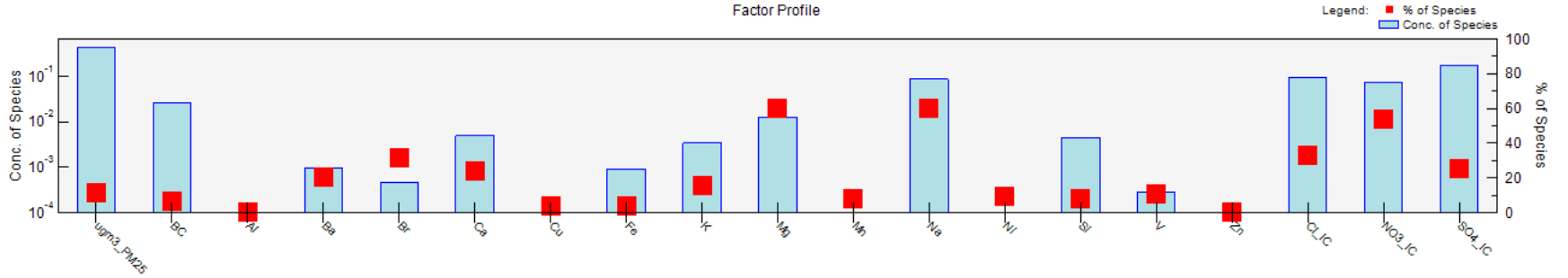


Figure 11: Factor profile 4 - Long range transport

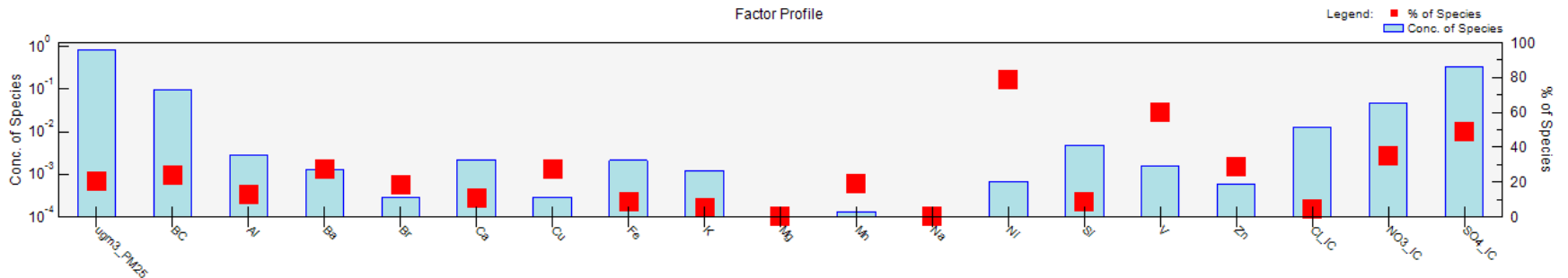


Figure 12: Factor profile 5 - Shipping emission

### *Blank methodology*

As mentioned in the material and methods section, field blank filters were collected simultaneously with sample filters. Field blank filters went through the same assembly process as sample filters i.e. nylon filters were assembled into ChemComb active samplers. Field blank ChemCombs, however, did not draw air through the sampler. The blank filters were collected, stored, and analyzed in the same way as sample filters. As a result, comparing data from field blank filters and sample filters can account for contamination because the field blank filter should be free of any ions or cations. Therefore, positive readings from the field blank filters can be considered as contamination. There was not sufficient evidence to identify any systematic contamination of field blank filters in this study. As mentioned elsewhere above, it is important to distinguish the difference between field blanks and lab blanks. Field blanks are used as a control group for sample filters in order to detect contamination. Lab blanks are used as a control for running samples in order to detect contamination from sample extraction steps. In other words, lab blanks are the stock solution, which is a mixture of type-1 H<sub>2</sub>O and isopropyl alcohol (IPA) which undergoes the exact same treatment as the samples to control for any contamination.

Figure 14 shows a representative graph of ions in a lab blank sample. As predicted, the lab blank graph shows a significant water peak at about 3.5 mins. Other ions did not produce significant readings. Therefore, neither the stock solution nor the analytic steps used to process the samples did not introduce contamination in the sample. Figure 15 is a graph of ions in standard solution. All of the ions produced significant peaks as expected. Figure 13, however, indicates that the field blank filter produced a significant chlorine peak at 6.9 min. Although the graph represents one sample (labeled BB BLK 001), the pattern of

high chlorine peak was consistent for all other field blanks. This indicates that the nylon filters were systematically contaminated with chlorine. As a result, the chlorine data for sample filters were adjusted by subtracting the mean chlorine from 6 blank filters thus leaving the sample chloride on the filters. The standard deviation of the blank chloride filter was low which gives confidence in this adjustment. Continued research is being conducted to identify the cause of this contamination, and the use of nylon filters has been discontinued until the contamination source is located

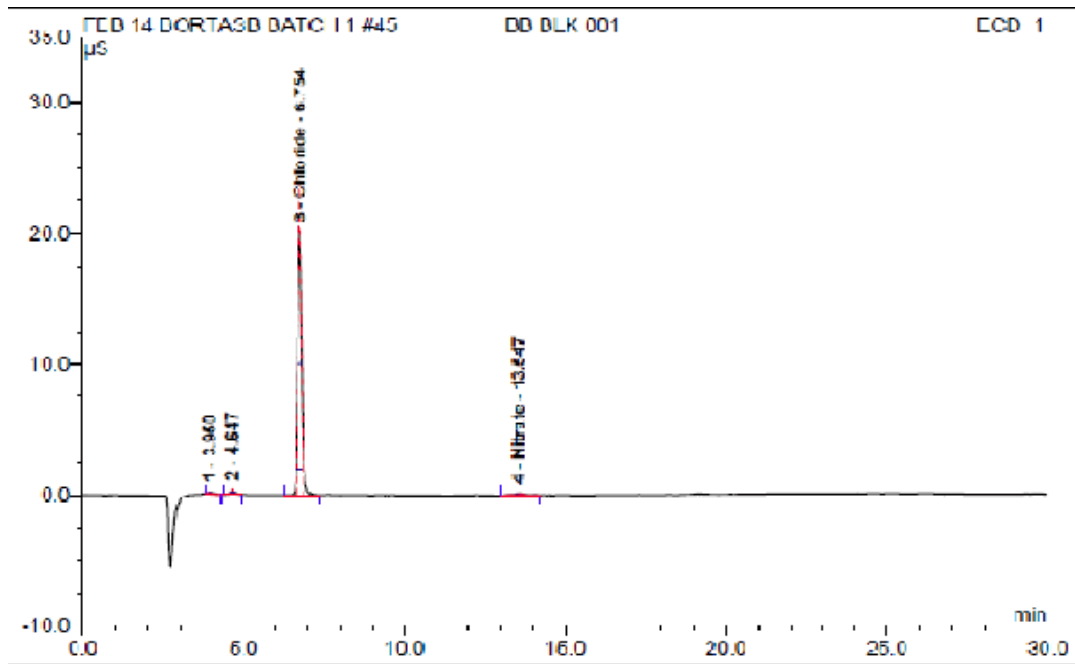


Figure 13: Ions chromatogram graph of field blank.

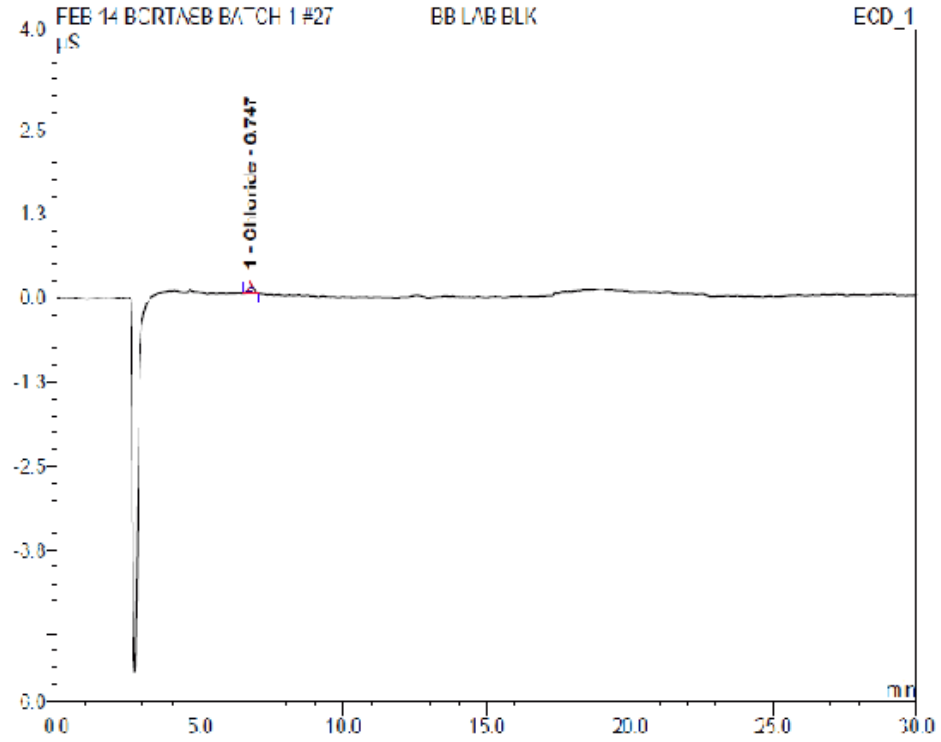


Figure 14: Ions chromatogram graph of lab blank.

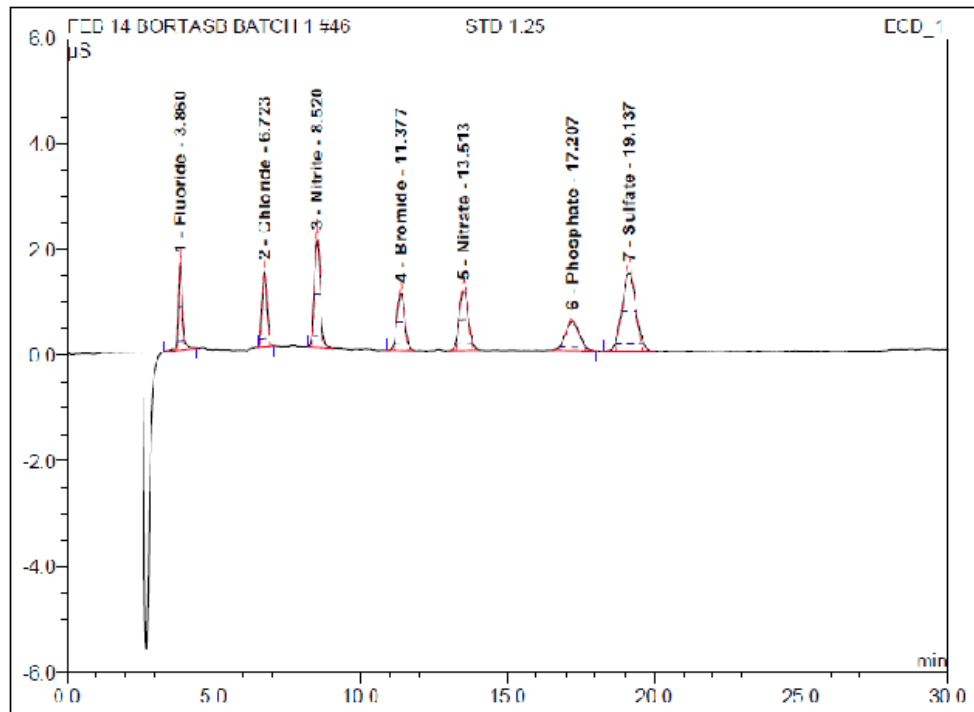


Figure 15: Ions chromatogram graph of 1.25 standard solutions.

*Correlation:*

Figure 2, 3 and 4 show the changes in concentration of metals, anions, PM<sub>2.5</sub>, PM<sub>10</sub> and black carbon during the sampling period. From observing the graphs, it is suspected that some of elements tend to change together. In other words, there can be correlation among those elements. As a result, Student t-test was performed with 95% confidence. The equation used to calculate  $\rho$ -value in t-test is:

$$t\text{-value} = r * \sqrt{\frac{n-2}{1-r^2}} \quad \text{with: } n \text{ is the sample size, } r \text{ is the correlation, and } r^2 \text{ is the calculated } R^2$$

R<sup>2</sup> was calculated using Microsoft<sup>®</sup> Excel and n values were 45 for all of the columns except chloride and black carbon columns which have n=36 and n=43 respectively. This is because there were some days the chloride level was below the detectable limit of IC. Black carbon was missing data for 2 days because of instrument difficulty. Specifically, the machine was accidentally disconnected with the power cord.

After calculated, t-values were compared with t-critical value. t-critical value at 95% confidence for n=45 is 1.681, n=43 is 1.683, and n=36 is 1.691. The t-critical values were calculated using statistical software R. If the correlation is statistically significant, the calculated t-values will be equal or bigger than the t-critical values.

Table 4 summarizes the correlation result. It is important to note that this result does not show the true correlation relationship. It is because the concentrations are collected over time period. Thus the data of one day depends on the days before that. Therefore, the data sets are not truly random and independent. As a result, table 4 should

be used with careful consideration. It should serves as a general idea in order to narrow down any specific correlation between elements of interest.



Table 4: Student t-test correlation among metals element, black carbon and anions. (\*) indicates that the correlation is statistically significant ( $\rho > 0.05$ )

	Al	Ba	Br	Ca	Ce	Cu	Fe	K	Mg	Mn	Na	Ni	Si	Ti	V	Zn	Cl-	NO3	SO4	BC
Al	X	*		*	*		*	*		*			*	*						*
Ba		X	*	*	*	*	*	*		*			*			*		*		
Br			X					*	*		*					*	*	*	*	*
Ca				X	*		*	*		*			*	*						
Ce					X				*				*	*	*					
Cu						X	*	*		*						*				
Fe							X	*		*			*	*		*				*
K								X	*	*	*		*	*		*		*		*
Mg									X		*						*	*	*	
Mn										X			*	*		*				*
Na											X						*	*	*	
Ni												X			*					
Si													X	*						*
Ti														X						*
V															X					
Zn																X				*
Cl-																	X	*		
NO3																		X	*	
SO4																			X	*
BC																				X

## Conclusion

PMF result shows that biomass burning was a significant contributing source of PM<sub>2.5</sub> of Halifax over the summer period of 2011. Due to the time limit, there was not sufficient data to conclude about the link between forest fire and biomass burning. However, based on the time of sampling period and previous research, it is likely that the majority of biomass burning are linked to forest fire episodes. This assumption is further supported by the trend of the chemistry composition change. The trend of episodic changes over the sampling period suggests they are likely linked to forest fire episodes driven by wind from long distance into Halifax. However, more data are needed to support the correlation. Many element metals, anions, PM<sub>2.5</sub>, PM<sub>10</sub> and black carbon are likely to be statistically correlated. However, the correlation should be re-examined with further statistic testing because the data sets are not completely independent and randomized.

Interestingly, PMF result suggests that sea salt factor did not contribute to the PM<sub>2.5</sub> concentration because Halifax is a port city with very close proximity with the ocean. Other factors also had potential for being over-estimated is shipping factor and surface material factor had potential for under-estimated due to the sampling period. More specifically, the surface materials factor can be under-estimated due to the lack of traffic in the summer. The shipping emission factor can be over-estimated because summer is the peak season of cruise ship tourism in Halifax.

In this experiment, the nylon filters were contaminated with chloride. Therefore, the result for chloride had to be adjusted for contaminant factor. Including field blank filters in the sampling process helped discover the contamination problem. As a result, it is important to include field blanks in the methodology in quality control project such as this

one. It is unclear about the contamination source. In order to ensure quality for future project, nylon filters will not be used in any future project; at least until the contamination sources have been identified.

The seasonal variation among PM<sub>2.5</sub> contributors is clear when compared with other studies. This variation demonstrates the complexity of the interaction among the contributing factors. As a result, further long term research should be conducted in order to gain better understanding of these complex interactions. Forest fire event are likely to be the cause of episodic changes in concentration of PM<sub>2.5</sub>, and black carbon. This project provides future research with the estimate time when those episodic changes happened. As a result, the future task of connecting the time with the time of forest fire event would be much easier. Another benefit provided by this project is the correlation among metals, anions and black carbon. This will help narrow down the focus of selection process for correlated elements for future studies. Last but not least, this project found a systematic contamination of nylon filters. As a result, this study can be beneficial to future studies because nylon filters will not be used until the contaminating source is identified.

## References:

- Bell, M., Davis, D., L., (2001). Reassessment of the lethal London fog of 1952: novel indicators of acute and chronic consequences of acute exposure to air pollutants. *Environ Health Perspect*, 190: 389-394
- Burnett, R., T. et al. (1995). Associations between ambient particulate sulphate and admission to Ontario hospitals for cardiac and respiratory disease. *Am J Epidemiol*. 142: 15-22
- Canadian Council of Minister of Environment (CCME). (2012). Retrieved from [http://www.ccme.ca/ourwork/air.html?category\\_id=99](http://www.ccme.ca/ourwork/air.html?category_id=99) on March 30, 2012
- Dabek-Zlotorzynska, E. et al. (2011). Canadian National Air Pollution Surveillance (NAPS) PM<sub>2.5</sub> speciation program: Methodology and PM<sub>2.5</sub> chemical composition for the year 2003-2008. *Atmospheric Environment*, 45: 673-686.
- Davis, D., L. et al. (2002). A look back at the London smog of 1952 and the half century since. *Environ Health Perspect*, 110, A: 734-735
- Dockery, D. W. and others 1993. An Association between Air Pollution and Mortality in Six U.S. Cities. *N Engl J Med* 329: 1753-1759.
- Dockery, D. W., and P. H. Stone. 2007. Cardiovascular Risks from Fine Particulate Air Pollution. *The New England Journal of Medicine* 356: 511-513.
- Englert, N. (2004). Fine particles and human health – a review of epidemiological studies. *Toxicology Letters*, 149: 235-242.
- Flannigan, M., D. et al. (2000). Climate change and forest fire. *The Science of the Total Environment*, 262: 221-229.
- Gibson, M. D. et al., (2009). Using Mass Reconstruction along a Four-Site Transect as a Method to Interpret PM<sub>10</sub> in West-Central Scotland, United Kingdom. *Journal of the Air & Waste Management Association*. 59 (12), 1429-1436.
- Gibson, M. D.; et al (2010). Woodsmoke source apportionment in the Rural Annapolis Valley, Nova Scotia, Canada. *Conference Proceedings of the 103rd Annual Conference of the Air and Waste Management Association, Calgary* (June 22-25).
- Héroux, M.-E.; et al (2011). The daily and seasonal variability in residential concentrations of aldehydes in two Canadian cities. . *Proceedings of the 12th International conference on Indoor Air and Climate, Austin*,
- Intergovernmental Panel on Climate Change. (IPCC). Report. (2001). Retrieved from <http://www.ipcc.ch/ipccreports/tar/wg2/index.php?idp=246> on April 5, 2012.
- Jeong, H., C. et al. (2011). Receptor model based identification of PM<sub>2.5</sub> sources in Canadian cities. *Atmospheric Pollution Research*, 2: 158-171.
- Maykut et al. (2003). Source apportionment of PM<sub>2.5</sub> at an urban IMPROVE site in Seattle, Washington. *ENVIRONMENTAL SCIENCE & TECHNOLOGY*. 37 (22): 5135 - 5142
- Miranda, A., I. et al. (2009). Forest Fire Emission and Air Pollution in Southern Europe. *Development in Environmental Science*, 8: 209-231
- Munchak et al. (2011). Development of wildland fire particulate smoke marker to organic carbon emission ratios for the conterminous United States. *Atmospheric Environment*, 45: 395-403.
- Naeher, L., P. et al. (2007). Woodsmoke Health Effects: A Review. *Inhalation Toxicology*, 19: 67-106

- Natural Resources Canada website. (2011). Retrieved from:  
[http://cwffis.cfs.nrcan.gc.ca/en\\_CA/background/summary/ffws](http://cwffis.cfs.nrcan.gc.ca/en_CA/background/summary/ffws) on Friday November 11, 2011
- Nemmar. A. et al. (2002). Passage of inhaled particles into blood circulation in human. *Circulation*: 411-414
- Overpeck. J., T. et al. (1990). Climate-induced changes in forest disturbance and vegetation. *Nature*. 343: 51-53
- Park. R, J. et al. (2003). Sources of carbonaceous aerosols over the United States and implications for natural visibility. *Journal of Geophysical Research*. 108, D12: 4355
- Parrington, M. et al. (2011). The influence of boreal biomass burning emissions on the distribution of tropospheric ozone over North America and the North Atlantic during 2010. *Atmos. Chem. Phys. Discuss.* 11: 25099-25153.
- Reid, J.S.; et al (2009). Global Monitoring and Forecasting of Biomass-Burning Smoke: Description of and Lessons From the Fire Locating and Modeling of Burning Emissions (FLAMBE) Program. *Selected Topics in Applied Earth Observations and Remote Sensing, IEEE Journal of*, vol.2, no.3, pp.144-162
- Sandler. D., V. et al. (2002). Wildland Fire in Ecosystems: Effects of Fire on Air. *USDA Forest Service General Technical Report*. RMRS-GTR-42, 5.
- Schwartz. J. (2001). Is there harvesting association of airborne particles with daily deaths and hospital admissions? *Epidemiology*, 12: 55-61
- Shafizadeh. F. (1982). Introduction to Pyrolysis of Biomass. *Journal of Analytical and Applied Pyrolysis*, 3: 283-305
- Sheesley. R. J. et al. (2007). Sensitivity of molecular marker-based CMB models to biomass burning source profiles. *Atmospheric Environment*. 41: 9050-9063
- Simkhovich. B, Z. et al. (2008). Air Pollution and Cardiovascular Injury: Epidemiology, Toxicology, and Mechanisms. *Journal of the American College of Cardiology*. 52, 9, 719-726
- Sullivan. A.P et al. (2008). A method for smoke marker measurement and its potential application for determining the contribution of biomass burning from wildfire and prescribed fire to ambient PM<sub>2.5</sub> organic carbon. *Journal of Geophysical Research*. 11, D22302
- US EPA website (2011). Retrieved from: <http://www.epa.gov/scram001/receptorindex.htm> on November 13, 2011
- US EPA website (2012). Retrieved from  
<http://www.epa.gov/oar/particlepollution/naaqsrrev2006.html> on March 30, 2012
- Ward. J., T. et al. (2006). The 2003/2004 Libby, Montana PM<sub>2.5</sub> Source Apportionment Research Study. *Aerosol Science and Technology*, 40: 166-177.
- Waugh. D. et al. (2010). Forecast Support to BORTAS-A (2010): Predicting Forest Fire Smoke Plumes over Nova Scotia. *The Canadian Smoke Newsletter*, Fall/Winter: 7-11
- Wheeler, A. J. et al (2011). Optimization of a Passive Sampling Method for Determination of Airborne Naphthalene for Residential Indoor Air Monitoring. *Indoor Air 2011. Conference Paper* (Austin, Texas)
- World Health Organization (WHO). (2003). Health Aspects of Air Pollution with Particulate Matter, Ozone and Nitrogen Dioxide. Report on a WHO Working Group, Bonn, Germany. WHO Regional Office for Europe, Copenhagen

- Wiedinmyer. C. et al. (2006). Estimating emissions from fires in North America for air quality modeling. *Atmospheric Environment*. 40: 3419-3432.
- Wotawa. G, Trainer. M., (2000). The influence of Canadian forest fires on pollutant concentrations in the United State. *Science*. 288, 5464: 324-328
- Zanobetty. A. et al. (2000). Airborne particles are a risk factor for hospital admission for heart and lung disease. *Environ Health Perspect*, 108: 1071-107