A comparison of four receptor models used to quantify the boreal wildfire smoke contribution to surface $PM_{2.5}$ in Halifax, Nova Scotia during the BORTAS-B experiment

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Abstract

This paper presents a quantitative comparison of the four most commonly used receptor models, namely Absolute Principal Component Scores (APCS), Pragmatic Mass Closure (PMC), Chemical Mass Balance (CMB), and Positive Matrix Factorization (PMF). The models were used to predict the contributions of a wide variety of sources to $PM_{2.5}$ mass in Halifax, Nova Scotia during the Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites (BORTAS) experiment. However, particular emphasis was placed on the capacity of the models to predict the boreal wild fire smoke contributions during the BORTAS experiment. The performance of the four receptor models was assessed on their ability to predict the observed $PM_{2.5}$ with an R^2 close to 1.0, an intercept close to zero, a low bias and low RSME. Using PMF, a new woodsmoke enrichment factor of 52 was estimated for use in the PMC receptor model. The results indicate that the APCS and PMC receptor models were not able to accurately resolve total $PM_{2.5}$ mass concentrations below 2.0 μg m^{-3}. CMB was better able to resolve these low $PM_{2.5}$ concentrations, but it could not be run on 9 of the 45 days of $PM_{2.5}$ samples. PMF was found to be the most robust of the four models since it was able to resolve $PM_{2.5}$ mass below 2.0 μg m^{-3}, predict $PM_{2.5}$ mass on all 45 days, and utilized an unambiguous woodsmoke chemical tracer. The median woodsmoke relative contribution to $PM_{2.5}$ estimated using PMC, APCS, CMB and PMF were found to be 0.08, 0.09, 3.59 and 0.14 μg m^{-3}, respectively. The contribution predicted by the CMB model seems to be clearly too high based on other observations. The use of levoglucosan as a tracer for woodsmoke was found to be vital for identifying this source.

1 Introduction

It has been estimated that between 1990 and 2011 wildfires have consumed a median 1.7 million hectares yr^{-1} of Canadian boreal forest (data from Natural Resources Canada). The burning of these forests is a significant source of gases and airborne particulate matter (PM) of different size fractions (Drysdale, 2008).

The tropospheric trace gases and PM generated by wildfires are transported long distances with the potential to harm health and the environment 1000 km from their source (Palmer et al., 2013;Naeher et al., 2007;Franklin et al., 2014). During July 2011, the BORTAS (Quantifying the impact of BOReal forest fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites) experiment was conducted out of Halifax, Nova Scotia, Canada to investigate the impact of North American wildfires on the atmospheric chemistry of the troposphere (Palmer et al., 2013). Central to BORTAS-B was the operation of the UK BAe-146-301 Atmospheric Research Aircraft over Eastern Canada, which was used to characterize size-resolved particulate matter and trace gases in wildfire plumes advecting within the outflow from North America (Palmer et al., 2013). Column profile flights were also made above Halifax. In addition to the aircraft measurements there were a number of continuous and integrated surface and column observations of trace gases and size-resolved particulate matter composition made at Dalhousie University in Halifax. A description of the instrumentations and measurements made at the Dalhousie University Ground Station (DGS) are provide in Palmer et al., (2013), Gibson et al., (2013b) and Franklin et al., (2014).

This paper explores the source attribution of boreal wildfire smoke (and other sources) to surface fine particulate matter ≤ 2.5 μm ($PM_{2.5}$) during the BORTAS-B experiment using four commonly used receptor models.

A number of different receptor modelling approaches are utilized for the source apportionment of $PM_{2.5}$, e.g. multivariate least squares factor analysis approaches such as Positive Matrix Factorization (PMF), Pragmatic Mass Closure (PMC) methods and Chemical Mass Balance (CMB) source profile techniques (Gibson et al., 2013b;Gibson et al., 2009;Ward et al., 2004;Gugamsetty et al., 2012;Harrison et al., 2011). The US Environmental Protection Agency's (USEPA) CMB receptor model has been used in many $PM_{2.5}$ source apportionment studies (Subramanian et al., 2007). The CMB receptor model uses a solution to linear equations that expresses each receptor chemical concentration as a linear sum of products of source fingerprint abundances and contributions (Ward et al., 2006b;Watson et al., 1994). The advantage of CMB is that it can be applied to individual 24 h PM mass and chemical composition. The disadvantage is that the technique relies heavily on available source profiles being representative of regional sources impacting the receptor, which is not always the case (Hellén et al., 2008;Ward et al., 2006b). One assumption of the CMB model is that chemical species emitted from a source are conserved during sampling, and that chemical species do not react with each other (Ward et al., 2006b). CMB is well suited for apportioning local or upwind sources of primary aerosols (those emitted directly as particles). To account for secondary aerosol contributions to $PM_{2.5}$ mass, ammonium sulfate and ammonium nitrate are normally expressed as "pure" secondary source profiles, and represented by their chemical form (Ward et al., 2006b). The USEPA CMB model has been applied to numerous urban and rural $PM_{2.5}$ source apportionment studies in environments impacted by woodsmoke (Ward et al., 2012;Bergauff et al., 2009;Gibson et al., 2010;Ward et al., 2006b).

Pragmatic Mass Closure is a very simple method and works well for the mass closure of the major $PM_{2.5}$ components, e.g. sea salt, secondary ions, surficial fugitive dust, organic and elemental carbon (Gibson et al., 2009). A number of studies have used PMC to apportion the major chemical species to PM mass (Yin and Harrison, 2008;Harrison et al., 2003;Gibson et al., 2009;Dabek-Zlotorzynska et al., 2011).

Another receptor model that has been used extensively in $PM_{2.5}$ source apportionment studies is Absolute Principal Component Scores (APCS) (Song et al., 2006). APCS is a multivariate factorization based model developed by Thurston and Spengler (1985) that is still widely used for the source apportionment of particulate matter.

However, APCS can occasionally return negative mass contributions (Paatero and Tapper, 1994). In order to overcome the negative source mass contribution problem, Paatero and Hopke (2003) introduced a Positive Matrix Factorization (PMF) source apportionment method in the late 1990's (Paatero and Tapper, 1994). PMF has since been applied widely to indoor, outdoor, urban, rural and regional $PM_{2.5}$ source apportionment studies (Gibson et al., 2013b;Harrison et al., 2011;Larson et al., 2004).

Chemical tracers can also be important when conducting source apportionment. Both APCS and PMF rely on expert, *a priori* knowledge of chemical tracers found within the $PM_{2.5}$ chemical composition to identify the source of each $PM_{2.5}$ component factor, e.g. high factor loadings of Al, Si, Ca and Fe are indicative of crustal re-entrained material (Song et al., 2006;Hopke, 1991;Gibson et al., 2013b). Many studies use levoglucosan (1,6-anhydro-β-D-glucopyranose) as an unambiguous chemical tracer of wildfire and residential woodsmoke (Gibson et al., 2010;Ward et al., 2012;Simoneit et al., 1999). Levoglucosan is derived from cellulose burning at temperatures greater than 300°C (Simoneit et al., 1999;Ward et al., 2006a). Potassium (K) is also a good tracer for woodsmoke and often used in conjunction with levoglucosan (Bergauff et al., 2010;Jeong et al., 2008;Urban et al., 2012). Other commonly used $PM_{2.5}$ source chemical markers are described in Gibson et al., (2013b), Harrison et al., (2011) and Jeong et al., (2011). In addition, the source chemical profiles contained within SPECIATE 4.0 are another resource to aid in the identification of $PM_{2.5}$ sources within a speciated $PM_{2.5}$ sample (Ward et al., 2012;Jaeckels et al., 2007;Gibson et al., 2013b).

This paper presents a quantitative comparison of the four most commonly used receptor models: APCS, PMC, CMB and PMF. The objective is to determine the ability of these models to predict overall $PM_{2.5}$ mass and the contributions of minor components. The models are compared based on their ability to apportion boreal wildfire woodsmoke (and other sources) applied to a 45-day contiguous $PM_{2.5}$ data set sampled at the DGS in Halifax during the BORTAS-B experiment. This dataset should provide sufficient variability and contributions of minor sources to permit a comprehensive comparison of the four receptor models.

2 Measurements

A full description of the $PM_{2.5}$ speciated sampling methods employed for this paper are described in Gibson et al., (2013b). Additional supporting instrumentation used at the DGS during BORTAS-B are described in Palmer et al., (2013) and Franklin et al., (Franklin et al., 2014), but we will describe the most relevant sampling and analysis methods for this study here. In summary, 45, 24 h $PM_{2.5}$ filter samples were collected at the DGS from 19:00 UTC on 11 July 2011 to 19:00 UTC on 26 August 2011.

The $PM_{2.5}$ chemical species used in the four receptor models included aluminum (Al), black carbon (BC), bromine (Br), calcium (Ca), chloride (Cl), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), ammonium (NH_4^+), nickel (Ni), nitrate (NO_3^-), organic matter (OM), selenium (Se), sulfur (S), silicone (Si), sulfate (SO_4^{2-}), vanadium (V) and zinc (Zn). The post sample chemical analysis, detection limits, data completeness, precision and bias for the $PM_{2.5}$ chemical species listed above are described in detail in Gibson et al., (2013b). The $PM_{2.5}$ mass filter weighing MDL was 20 µg $filter^{-1}$ (X. Feng, personal communication, 2014). For this paper, the woodsmoke marker levoglucosan was added to the above chemical species in order to unambiguously apportion the boreal forest wildfire woodsmoke contribution to $PM_{2.5}$ at the DGS (Simoneit et al., 1999).

The levoglucosan-$PM_{2.5}$ samples were collected using 47 mm diameter, pre-fired quartz filters. The quartz filters were obtained from Concord Analytical (8540 Keele Street, Unit 38, Concord, Ontario). The quartz filters were housed in a Thermo ChemComb sampler that operated at a flow rate of 10 L min^{-1} over a 24 h period, synchronous with the other $PM_{2.5}$ chemical speciation filter based sampling described in Gibson et al., (Gibson et al., 2013b). Each quartz filter was spiked with deuterated levoglucosan as an internal standard, placed in a covered vial, and allowed to stand for 30 minutes. The filter was then extracted by ultrasonication using ethylacetate containing 3.6 mM triethylamine. The extract was filtered, evaporated to dryness and derivatized with

N-O bis(trimethylsilyl)trifluoroacetamide, trimethylchlorosilane, and trimethylsilylimidazole to convert the levoglucosan to its trimethylsilyl derivative. The extract was analysed by gas chromatography/mass spectrometry on a Hewlett-Packard GC/MSD (GC model 6890, MSD model 5973, Hewlett-Packard Company, Palo Alto, CA, USA) using an HP-5 MS capillary column. Splitless injection was employed. The levoglucosan and internal standard were detected by extracted ion signals at 217 and 220 m/z, respectively. Levoglucosan analysis recoveries for 100 to 2000 ng averaged 96 ±12 % (n = 18, ± 1 sigma). Six laboratory blanks were used to calculate an average levoglucosan blank concentration and the standard deviation and 95% confidence interval for the blank. The limit levoglucosan of detection (LOD) is reported as the average laboratory blank and was found to be 7.7 ng m^{-3} (Bergauff et al., 2008) level plus one 95% confidence interval for the blank. Local meteorological data at the DGS was collected using a Davis Vantage Pro II weather station (Davis Instruments Corp. Hayward, California 94545 USA). Further information on the meteorological sensors onboard the Davis Vantage Pro II and results are provided in Gibson et al., (2013b). In addition, a daily climatology review of synoptic meteorology in the greater Halifax Regional Municipality observed during the $PM_{2.5}$ sampling is also provided in Gibson et al., (2013b).

HYSPLIT 10 day, 5 day and 2 day air mass back trajectories were used to identify the likely upwind source regions of $PM_{2.5}$ (Gibson et al., 2013b). A plot of ensemble HYSPLIT back trajectories by source region during the sampling campaign is provided in Gibson et al., (2013). From Gibson et al., (2013b) it was observed that 40% of the air masses entering Halifax during BORTAS-B originated from the marine sector, 16% from the SW (NE US), 27% from the WNW (Windsor-Québec source region) and 16% from the N. The SW cluster and WNW cluster appear to be mainly associated with boundary layer flow from known upwind source regions of $PM_{2.5}$ that was mainly composed of ammonium sulfate ($(NH_4)_2SO_4$), ammonium nitrate (NH_4NO_3) and organic matter (up to 70% of the total $PM_{2.5}$ mass).

Fire hotspot maps were used to identify active burning regions of Canada. MODIS hotspot locations from NASA (see http://earthdata.nasa.gov/data/near-real-time-data/firms) and AVHRR hotspots from NOAA FIMMA (see http://www.ssd.noaa.gov/PS/FIRE/Layers/FIMMA/fimma.html) were used to generate the fire hot spot maps (Giglio et al., 2003;de Groot et al., 2013).

A Raman Lidar was collocated with the DGS $PM_{2.5}$ sampling (Palmer et al., 2013). The Lidar employs a high-energy Nd:YAG laser that emits pulses of 532 nm wavelength light at a repetition rate of 20 Hz. Two telescopes allow backscattered light to be collected separately from both the near (0–5 km) and far (>1 km) ranges. This allows the simultaneous measurement of aerosols in the boundary layer and free troposphere. Further details of the Raman Lidar are contained in Bitar et al., (2010). The Lidar was used to help guide the airborne atmospheric measurements BAe146 research aircraft into boreal forest wildfire smoke plumes passing over Halifax and to also confirm when aerosol impacted the surface during the $PM_{2.5}$ sampling related to this manuscript (Palmer et al., 2013). The Lidar was also used to verify the GEOS-5 carbon monoxide (CO) forecast model output over Halifax (Palmer et al., 2013). The GEOS-5 forecast model also provided additional evidence that upwind wildfire $PM_{2.5}$ impacted the surface in Halifax during the BORTAS-B experiment.

3 Receptor Models

We employed the Absolute Principal Component Scores method developed by Thurston and Spengler (1985) to determine the relative source contributions to the BORTAS-B $PM_{2.5}$ mass. In this manuscript, levoglucosan was added to the previously modelled $PM_{2.5}$ speciated data as a means to unambiguously identify the presence of woodsmoke (Gibson et al., 2013b). Principal Component Analysis (PCA) was performed using IBM SPSS Statistics software on Al, BC, Br, Ca, Cl, Fe, K, Mg, Na, NH_4^+, Ni, NO_3^-, OM, S, Si, SO_4^{2-}, V, Zn and levoglucosan. Eigenvalues greater than 1 were retained in the analysis. Using the varimax rotated coefficients and scaled concentrations it was possible to calculate the APCS values. Following the method of Thurston and Spengler (1985) the relative source contributions were then determined by multiple linear regression on the measured concentrations. The developed linear regression equations could then be used to produce a time series plot and to identify the relative contributions of the various sources.

We also used the USEPA PMF v3.0 receptor model for the source apportionment of the $PM_{2.5}$ at the DGS. In the previous manuscript by Gibson et al., (Gibson et al., 2013b), six major sources were determined and were Long-Range Transport (LRT) Pollution 1.75 µg m^{-3} (47%), LRT Pollution Marine Mixture 1.0 µg m^{-3} (27.9%), Vehicles 0.49 µg m^{-3} (13.2%), Fugitive Dust 0.23 µg m^{-3} (6.3%), Ship Emissions 0.13 µg m^{-3} (3.4%) and Refinery 0.081 µg m^{-3} (2.2%). The PMF model described 87% of the observed variability in total $PM_{2.5}$ mass (bias = 0.17 µg m^{-3} and RSME = 1.5 µg m^{-3})

(Gibson et al., 2013b). The PMF model initialization procedure used in this paper was the same as described in Gibson et al., (2013b).

We also utilized the pragmatic mass closure (PMC) method as another alternative receptor model (Yin and Harrison, 2008). PMC offers a simple approach to estimate the source attribution or the chemical composition of size-resolved airborne particulate matter (PM) (Harrison et al., 2003). The PMC receptor modelling method is limited to major PM species only, e.g. sodium chloride (NaCl), ammonium nitrate (NH_4NO_3), ammonium sulphate ($(NH_4)_2SO_4$), non sea salt-SO_4, sodium nitrate ($NaNO_3$), organic carbon (OC), elemental carbon (EC), crustal matter, trace element oxides and particle bound water (Gibson et al., 2009;Yin and Harrison, 2008;Dabek-Zlotorzynska et al., 2011). In PMC, molar weight correction factors, or enrichment factors, are applied to the individual measured PM chemical components. This then allows an estimate of the probable species that was present in the original sample, e.g. multiplying NO_3^- by 1.29 yields an estimate of the NH_4NO_3 concentration present in the original $PM_{2.5}$ sample (Dabek-Zlotorzynska et al., 2011). PMC has been used to apportion contributions to urban and rural PM_{10}, $PM_{2.5}$ and $PM_{2.5-10}$ in Ireland (Yin et al., 2005), coastal, rural and urban PM_{10} in Scotland (Gibson et al., 2009), urban background and roadside locations in England (Harrison et al., 2003) and to urban, rural and coastal $PM_{2.5}$ in Canada (Dabek-Zlotorzynska et al., 2011). For the BORTAS-B study a new PMC woodsmoke enrichment factor was calculated. The enrichment factor was calculated by taking the median apportioned woodsmoke concentration (determined by PMF) and dividing it by the levoglucosan concentration. The calculated PMC woodsmoke enrichment factor was found to be 52. Therefore, the woodsmoke apportioned to the $PM_{2.5}$ for each day using the PMC approach is equal to the levoglucosan concentration multiplied by 52 (Gibson et al., 2013a). This new method for determining the woodsmoke contribution to $PM_{2.5}$ using the PMC receptor modelling was first described by Gibson et al., (2013b).

The fourth receptor model applied to the BORTAS-B $PM_{2.5}$ data set was the USEPA Chemical Mass Balance (CMB) model described by Ward et al., (2012). For this paper the source profile for marine salt was taken directly from SPECIATE 4.0. The marine salt profile was then combined with SPECIATE profiles used previously by Ward and Smith (2005) and Ward et al., (2006b). The CMB model fit, quality assurance and quality control criteria are described in Watson et al., (1998) and Ward et al., (2012). The performance of the four receptor models was assessed on their ability to predict the observed $PM_{2.5}$ with an R^2 close to 1.0, an intercept close to zero, a low bias and low RSME. In addition, suitability was also based upon the models ability to closely predict the observed $PM_{2.5}$ during low, median and elevated concentrations.

4 Results and discussion

The descriptive statistics and discussion corresponding to the observed Al, BC, Br, Ca, Cl, Fe, K, Mg, Na, NH_4^+, Ni, NO_3^-, OM, $PM_{2.5}$ mass, S, Si, SO_4^{2-}, V and Zn are provided in Gibson et al., (2013b). From Table 1 it can be seen that the median (min : max) levoglucosan concentration was 1.6 (0.2 : 46.0) ng m^{-3}. These concentrations are two orders of magnitude lower than the winter median (min : max) 234 (155 and 274) ng m^{-3} levoglucosan concentrations observed in the nearby Annapolis Valley, Nova Scotia in 2010, a region impacted by wintertime residential woodsmoke (Gibson et al., 2010). Ward et al. (2006b) found an average levoglucosan concentration of 2840 ± 860 ng m^{-3} in

Libby, Montana, a city impacted by wintertime residential woodsmoke. Leithead et al. (2006) reported summertime average levoglucosan concentrations related to biomass burning in the Fraser Valley, BC of 14.4, 14.7 and 26.0 ng m^{-3} respectively, which are similar to the concentrations measured in Halifax during BORTAS-B. The levoglucosan concentrations observed in the Fraser Valley, BC are an order of magnitude greater than seen during the same season in Halifax during BORTAS-B. Jordan et al., (2006) reported 2003 summertime bushfire related levoglucosan concentrations in Launceston, Australia of 150, 440 and 470 ng m^{-3} respectively, ranging between 10 to 29 times the concentrations seen in Halifax during BORTAS-B.

The first step in APCS is Principal Components Analysis (PCA) of the $PM_{2.5}$ speciated data. When PCA was performed, five factors were identified as shown in Table 2. Following conventional PCA analysis protocols (Harrison et al., 1997), factor loadings ± 0.3 were retained as shown in Table 2 (Harrison et al., 1997). High factor loadings of the species in each factor enabled source identification (Viana et al., 2006). Five factors were identified, which explained 85.4% of the variance of the $PM_{2.5}$ mass. APCS was then used to attribute the mass of each factor to the total $PM_{2.5}$ mass. The five sources identified using PCA are shown in Table 3 and included sea salt, LRT $(NH_4)_2SO_4$, surface dust, ship emissions and woodsmoke (identified by the woodsmoke tracer levoglucosan).

Figure 1. provides parity plots of observed vs. predicted $PM_{2.5}$ estimated by the four receptor models (a) Absolute Principal Component Scores (APCS) (b) Pragmatic Mass Closure (PMC) (c) Chemical Mass Balance (CMB) (d) Positive Matrix Factorization (PMF). It can be seen from Fig. 1a that the intercept is located at 1.9 µg m^{-}

^{3}, the slope was 0.85, R^2 of 0.84, n = 45 and with a bias of 1.3 µg m^{-3}. From Fig. 1b it can be seen from the parity plot of observed vs. PMC predicted $PM_{2.5}$ that the intercept is located at 2.1 µg m^{-3}, the slope was found to be 0.57, R^2 of 0.84, n = 45 and bias of 1.4 µg m^{-3}. From Fig. 1a and Fig. 1b it can be seen the intercepts associated with both the APCS and PMC receptor models mean that they have difficulty predicting $PM_{2.5}$ less than 2.0 ± 1.2 µg m^{-3} and 2.0 ± 0.2 µg m^{-3} respectively. From Fig. 1c it can be seen that the CMB intercept was located at -0.53 µg m^{-3} ±0.21 µg m^{-3}, a slope of 1.0, R^2 of 0.88 and a bias of 4.3 µg m^{-3}. The CMB model was only able to predict $PM_{2.5}$ mass on 36 of the 45 $PM_{2.5}$ sample days. From Fig. 1d it can be seen that the PMF model has the lowest intercept (−0.07 ± 1.57 µg m^{-3}) of the four models, a slope of 0.88, R^2 of 0.88, n = 45 and a bias of 2.9 µg m^{-3}. While the PMF bias is better than for CMB, it is not as good as the bias seen for APCS and PMC. However, because PMF predicts the $PM_{2.5}$ mass on all sample days, has a slope of 0.88 and the ability to predict very low $PM_{2.5}$ mass concentrations, often seen in Halifax, in these respects it is the most useful of the four receptor models.

Figure 2 provides the chemical species source factor profiles and associated percentage mass contributions obtained using the Positive Matrix Factorization receptor model. Figure 2 clearly shows that 95% of the levoglucosan sample total mass and 45% of the K sample total mass are associated with the factor profile identified as woodsmoke. The chemical species used to identify the source in the other seven factor profiles are clearly observed, e.g. NO_3^- and Se for LRT coal/industry originating from the NE USA, $PM_{2.5}$, Ca, Mg, Na, NO_3^- for LRT Pollution Marine Mixture originating from the NE USA and crossing the Gulf of Maine en route to Nova Scotia, Ni and V are unambiguous tracers of ship emissions, Br and Zn are tracers of gasoline vehicles/tire wear, and OM, BC, Ba, Fe and Zn are tracers for diesel vehicle/tire wear (Gibson et al. 2013b).

Figure 3 provides a time series from 7 July 2011 to 25 August 2011 of (a) APCS, (b) PMC, (c) CMB and (d) PMF daily $PM_{2.5}$ source apportionment. Time series plots of the individual $PM_{2.5}$ chemical species (not including levoglucosan) associated with Figure 3 is provided in Gibson et al., (2013b).

Table 3 - 6 show that the four receptor models identify different number and type of $PM_{2.5}$ source respectively, e.g. the APCS model identified 6 sources, PMC 10 sources, CMB 13 sources and PMF 9 sources. The reason for the different number of sources identified by each model is due to the different inherent methodology by which each model generates the source identification. In the case of PMC, a molar correction factor is applied to individual $PM_{2.5}$ species. Therefore, if the species is present and there is a corresponding molar correction factor the source will be identified and quantified. In the case of CMB receptor modelling, the sample chemical species are identified by matching with known source chemical profiles. With CMB, the number of statistically significant and logical matches determines the number of sources identified and quantified by the model, whereas APCS and PMF both use factorization and are open to identify as many sources that meet each model's inclusion criteria and would make sense being observed at the receptor. In PMC the source name is assigned from the molar factor associated with the source, in CMB the source name is assigned from the matching source profile, in APCS and PMF the source name is subjective and assigned by the user, reflecting the chemical species observed within each factor profile. It can be seen from Table 3 - 6 that surface dust and woodsmoke were identified in all four models.

With reference to Fig. 3b, the trace metal oxide values are worthy of note. This is because, within the PMC model, Ni and V are included in the calculation of the apportioned trace metal oxides. Where as, in the PMF and APCS models, Ni and V are used as unique chemical tracer elements of ship emissions. Because of the inclusion of Ni and V in the trace metal oxide apportioned source, it is not possible for the PMC model to apportion ship emissions. The descriptive statistics for the four receptor model results over the 45 days of $PM_{2.5}$ sampling are contained in Tables 3 through 6. The median LRT $(NH_4)_2SO_4$ estimated by the four models ranges from 0.57 μg m^{-3} (PMC), 0.67 μg m^{-3} (CMB), 1.15 μg m^{-3} (PMF) and 3.06 μg m^{-3} (APCS). Clearly APCS tends to estimate a larger contribution of $(NH_4)_2SO_4$ to $PM_{2.5}$ compared with the other three models. The close agreement between PMC and CMB stems from the fact that both of these models use the actual molar values of the pure salt in the sample. Conversely, PMF and APCS have other mass contributions that co-vary with the LRT $(NH_4)_2SO_4$, e.g. OM. It can be seen from Tables 4 and 5 that the median LRT NH_4NO_3 estimated by PMC and CMB were 0.09 μg m^{-3} and 0.54 μg m^{-3}, respectively. Table 3 (APCS) and Table 6 (PMF) contain estimates of the LRT Pollution Aged Marine Aerosol $PM_{2.5}$ (0.61 μg/m^3) and LRT Marine Mixed $PM_{2.5}$ (0.44 μg/m^3) respectively. Because of co-varying species associated with the LRT NH_4NO_3 in the APCS and PMF models, NH_4NO_3 could not be factored into a pure apportioned source. Instead, the LRT NH_4NO_3 in both APCS and PMF is also associated with other LRT species, e.g. OM, BC, Na and is referred to as LRT Marine Mixed $PM_{2.5}$ as the NH_4NO_3 was likely mixed with aged marine aerosol as the air mass crossed the Gulf of Maine and the Bay of Fundy en route to Halifax. This assumption was back by the HYSPLIT air mass back trajectories shown in Gibson et al., (2013b).

The trends in the apportioned woodsmoke estimated from the four receptor models is provided in the time series plot shown in Fig. 4. One obvious feature of Fig. 4 is the large woodsmoke estimate, especially between 17 July and 25 July, from the CMB model. Clearly the CMB estimate is a large departure from the woodsmoke predicted by the remaining three receptor models which are in closer agreement. The reason for this is not known at this time, but it does suggest that the CMB SPECIATE source profiles may not be appropriate for predicting woodsmoke in this region. It can be seen from Fig. 4 that generally the woodsmoke contribution to $PM_{2.5}$ is low or absent with the exception of elevated concentrations of woodsmoke on 17 July, 24 July, 1 August, 6 August and 13 August 2011. The low or absent woodsmoke days are either associated with air flow from the ocean or from Northern Canada when boreal wild fire activity was absent. These days are also associated with low $PM_{2.5}$ mass as described in Gibson et al., (2013b). To help identify upwind forest fire source regions, we used a combination of visible MODIS satellite images, MODIS fire hot spot maps, 5 day HYSPLIT air mass back trajectories (Gibson et al., 2013b), FLEXPART air mass trajectories (Stohl et al., 2005) chemical transport models (Palmer et al., 2013), Raman Lidar (Bitar et al., 2010) and aircraft measurements (Palmer et al., 2013). Together, these approaches helped corroborate the woodsmoke event impacting Halifax on 21 July. Figure 5 provides an example match up of Lidar aerosol backscatter measurements at the DGS (a), GEOS-5 forecast of CO mixing ratio associated with boreal biomass burning above the DGS (b), FLEXPART vertical profile of $PM_{2.5}$ at the DGS (c), a plot of the aircraft profile measurements of CO, acetonitrile and aerosol backscatter obtained at midnight (d). Acetonitrile was used as it is an effective tracer for biomass fire plumes in the atmosphere (Karl et al., 2007). Figure 5a shows elevated aerosol backscatter below 2 km between 00:00 UTC 20 July and 24:00 UTC 21 July 2011. Also there is then a “V-shaped notch” of clear air located above 2 km and below 5 km, followed by further aerosol backscatter between 6 km and 8 km. The elevated surface aerosol backscatter measurements seen in Figure 5a are accompanied by elevated surface $PM_{2.5}$ concentrations as seen in Figure 3. Since the PMF model appears to be the most useful at predicting $PM_{2.5}$ mass, and is anticipated to be the most robust at predicting woodsmoke, it was used to compare with the features contained in Figure 5. From the PMF source apportionment timeseries plot in Figure 3d, it can be seen that the $PM_{2.5}$ was chiefly composed of LRT $(NH_4)_2SO_4$ and LRT Pollution Marine Mixture (NO_3^-, Na, NH_4NO_3), with a small spike in woodsmoke seen on 20 July 2011. Scrutiny of HYSPLIT air mass back trajectories in Gibson et al., (2013b) and HYSPLIT dispersion models in Franklin et al., (2014) show that the air flow crossed a region experiencing extensive boreal forest wildfire in Northern Ontario prior to reaching Nova Scotia. On July 20 that air flow from the NE USA mixed with the air flow from Northern Ontario en route to Halifax, providing a mixture of boreal wildfire smoke from Northern Ontario together with anthropogenic LRT aerosol from the NE USA. It can be seen from Figure 5b that GEOS-5 predicts the exact same feature for CO as the aerosol backscatter observed by the Lidar in Figure 5a. The CO is related to both the LRT from the NE USA mixed with wildfire woodsmoke from Ontario. Evidence for the woodsmoke entrainment on 20 July 2011 in the PMF source apportionment timeseries (Fig. 4) was further corroborated by FLEXPART forward trajectory modelling from the large forest fires in Ontario that were burning on 17 July 2011 (Franklin et al., 2014). It can be seen from Fig. 5c that FLEXPART predicted the impact of woodsmoke particles at the surface in

Halifax, which helps explain the small spike in levoglucosan on 20 July 2011. Finally, further proof of woodsmoke impacts at the DGS come from the aircraft spiral profiles shown in Fig. 5d. Figure 5d shows aircraft column profiles for CO, acetonitrile and aerosol backscatter, which provide further forensic evidence of woodsmoke impacting the DGS in Halifax. Figure 6 provides a NASA AQUA MODIS true colour satellite image that clearly shows boreal forest fire smoke from Northern Ontario advecting over Halifax, Nova Scotia on July 18. These fires continued to impact the DGS on 20 July 2011 as shown in Figs. 4 and 5. In a similar way the largest woodsmoke spike shown in Fig. 4 on 31 July 2011 was due to boreal forest fires in Northern Quebec. This can be seen in Fig. 7 where a NOAA HYSPLIT 5 day air mass trajectory passes over the forest fires in Northern Québec 3 days prior to arriving at the DGS. Using the same approach, it was seen that HYSPLIT 5 day air mass back trajectories together with the fire hot spot maps for 6 August showed that the elevated woodsmoke was related to wild fires in Labrador, while the woodsmoke spike on the 12 August was related to another large fire in Ontario on 8 August 2011.

Table 7 presents the woodsmoke source apportionment descriptive statistics for each receptor model. Details of the performance parameters related to the four receptor models are provided in Fig. 1. It can be seen that the estimated mean woodsmoke contribution to $PM_{2.5}$ by APCS and PMC are almost identical, 0.32 and 0.35 μg m^{-3}. The close agreement between the woodsmoke contribution estimated by APCS validates the new enrichment factor in this paper generated from previous PMF and PMC analyses (Gibson et al., 2013a). It can be seen that CMB estimated the mean woodsmoke contribution to be 3.23 μg m^{-3}, which is an order of magnitude greater than APCS and

PMC. In addition, it can be observed that PMF estimated the mean woodsmoke contribution to be 0.61 μg m^{-3}, which is approximately double that estimated by APCS and PMC. However, because of the PMF model's better $PM_{2.5}$ predictive capability (especially below 2.0 μg m^{-3}) and clear woodsmoke tracer source identification, its known statistical robustness over APCS, its results are likely the most accurate of the four models. However, boreal forest wood combustion product emissions source profiling followed by source apportionment using these four models would be needed to completely validate PMF's superiority over APCS, PMC and CMB receptor model methodologies.

5. Conclusion

Four receptor models were used to improve our understanding of the source contribution of woodsmoke, and other major sources, to $PM_{2.5}$ total mass during the BORTAS-B experiment. During the process, PMF was used to generate a new woodsmoke enrichment factor of 52. The new enrichment factor was used in the PMC model to convert levoglucosan into a woodsmoke concentration (levoglucosan multiplied by 52). Cross-referencing the woodsmoke contribution estimated by APCS helped to validated the utility of this new enrichment factor. It was found that APCS and PMC receptor models mean that they have difficulty predicting $PM_{2.5}$ less than 2.0 ± 1.2 μg m^{-3} and 2.0 ± 0.2 μg m^{-3} respectively. Further, although CMB had an improved intercept and a slope of 1, it could not be run on 9 of the 45 days of $PM_{2.5}$ samples. PMF is considered to be the most robust of the four models since it is able to predict $PM_{2.5}$ mass below 2.0 μg m^{-3}, predict $PM_{2.5}$ mass on all 45 days, has a slope close to 1, has a low bias, and utilizes an unambiguous woodsmoke chemical marker within the model. The median (min : max) woodsmoke contribution to $PM_{2.5}$ estimated using PMF was found to be 0.14 (0.0 : 4.14) μg m^{-3}. The use of a woodsmoke tracer such as levoglucosan is critical when carrying out $PM_{2.5}$ source apportionment studies of boreal forest wild fire smoke. Controlled wood combustion product sampling followed by source apportionment modeling with these four models would greatly improve our understanding of their performance for predicting woodsmoke contributions to $PM_{2.5}$ in future studies of this nature.

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Tables

Table 1. Descriptive statistics for levoglucosan

	n	Mean	Std	Min	25th Pctl	Median	75th Pctl	Max
Levoglucosan *[ng m^{-3}]*	45	6.1	10.0	0.2	0.9	1.6	6.2	46.0

Table 2. Principal component analysis (PCA) of the $PM_{2.5}$ chemical species

	Sea Salt	LRT $(NH_4)_2SO_4$	Surface Dust	Woodsmoke	Ship Emissions
BC		0.52		0.426	
Al			0.91		
Br	0.78				
Ca			0.90		
Fe			0.70		
K				0.74	
Mg	0.96				
Na	0.97				
Ni					0.95
Si			0.98		
V					0.94
Zn				0.86	
Cl	0.81				
S		0.94			
NO3	0.82				
SO4		0.97			
NH4		0.96			
OM		0.74		0.56	
Levoglucosan				0.91	
Eigenvalue	5.72	3.65	3.11	2.03	1.72
Cumulative % var	30.1	49.3	65.6	76.3	85.4

Table 3. Absolute Principal Component Scores (APCS) $PM_{2.5}$ source apportionment descriptive statistics

Metric ***[μg m^-3]***	**n**	**Mean**	**Median**	**Min**	**Max**	**Std Dev**	**C.I.**
Observed $PM_{2.5}$	45	4.36	3.96	0.08	12.50	3.13	0.91
LRT Pollution Aged Marine Aerosol	45	0.75	0.61	0.16	3.42	0.61	0.18
LRT Pollution $(NH_4)_2SO_4$	45	3.76	3.06	0.28	13.95	2.65	0.78
Surface Dust	45	0.73	0.63	0.13	3.32	0.54	0.16
Woodsmoke	45	0.35	0.09	0.01	2.71	0.62	0.18
Ship Emissions	43	0.14	0.09	0.00	0.76	0.15	0.04

Table 4. Pragmatic Mass Closure (PMC) PMC $PM_{2.5}$ source apportionment descriptive statistics

Metric ***[μg m^-3]***	**n**	**Mean**	**Median**	**Min**	**Max**	**Std Dev**	**C.I.**
Observed $PM_{2.5}$	45	4.36	3.96	0.08	12.50	3.13	0.91
LRT Pollution NH_4NO_3	45	0.12	0.09	0.01	0.83	0.13	0.04
LRT Pollution $(NH_4)_2SO_4$	45	0.87	0.57	0.14	4.15	0.84	0.25
Organic Matter	45	1.03	0.77	0.18	2.66	0.68	0.20
Black Carbon	45	0.41	0.39	0.12	1.03	0.21	0.06
Surface Dust	45	0.27	0.22	0.02	1.53	0.24	0.07
Trace Element Oxides	45	1.48	1.48	1.47	1.49	0.00	0.00
Sea Salt	45	0.16	0.11	0.01	1.06	0.18	0.05
Particle Bound Water	45	0.29	0.20	0.05	1.33	0.27	0.08
Woodsmoke	45	0.32	0.08	0.01	2.38	0.55	0.16

Table 5. Chemical Mass Balance (CMB) $PM_{2.5}$ source apportionment descriptive statistics

Metric ***[μg m]***	**n**	**Mean**	**Median**	**Min**	**Max**	**Std Dev**	**C.I.**
Observed $PM_{2.5}$	45	4.57	4.04	0.08	13.73	3.39	0.98
Surface Dust	2	0.81	0.81	0.39	1.24	0.6	0.83
LRT Pollution (Coal/Industrial)	5	0.83	0.85	0.57	1.09	0.2	0.17
Woodsmoke	14	3.23	3.59	1.38	4.72	1.04	0.54
Marine Aerosol	34	0.3	0.24	0.04	1.64	0.3	0.1
Ship Auxiliary Engines	17	1.43	1.2	0.3	3.2	0.84	0.4
LRT Pollution $(NH_4)_2SO_4$	21	1.45	0.67	0.24	6.77	1.58	0.68
Tire Wear	1	0.82	0.82	0.82	0.82	NA	NA
Diesel Trucks	2	1.11	1.11	1.1	1.12	0.02	0.02
Vegetative Burning	2	2.25	2.25	1.42	3.08	1.18	1.63
Small Gasoline Vehicles	5	2.35	2.51	0.58	5.08	1.87	1.63
LRT Pollution NH_4NO_3	2	0.54	0.54	0.14	0.94	0.57	0.79
SO_4	35	1.31	0.95	0.35	5.4	1.08	0.36

Table 6. Positive Matrix Factorization (PMF) $PM_{2.5}$ source apportionment descriptive statistics

Metric *[μg m⁻³]*	n	Mean	Median	Min	Max	Std Dev	C.I.
Observed $PM_{2.5}$	45	4.57	4.04	0.08	13.73	3.39	0.98
Diesel Vehicles/Tire Wear	39	0.05	0.03	0.00	0.17	0.04	0.01
Gasoline/Tire Wear	30	0.14	0.02	0.00	3.43	0.62	0.22
LRT Pollution $(NH_4)_2SO_4$	33	2.05	1.15	0.09	12.12	2.45	0.84
Ship Emissions	34	0.55	0.49	0.04	1.15	0.31	0.11
LRT Pollution Marine Mixture	38	0.88	0.44	0.02	7.00	1.31	0.42
Woodsmoke	29	0.61	0.14	0.00	4.14	1.00	0.36
LRT Pollution (Coal/Industry)	34	0.74	0.48	0.00	2.97	0.69	0.23
Surface Dust	38	0.33	0.19	0.00	2.55	0.44	0.14

Table 7. Boreal wildfire woodsmoke source apportionment ($\mu g\ m^{-3}$) descriptive statistics by receptor model

Receptor Model	n	Mean	Median	Min	Max	Std.Dev.	C.I.
PMC	45	0.32	0.08	0.01	2.38	0.55	0.16
APCS	45	0.35	0.09	0.01	2.71	0.62	0.18
CMB	14	3.23	3.59	1.38	4.72	1.04	0.54
PMF	29	0.61	0.14	0.00	4.14	1.00	0.36

Figures

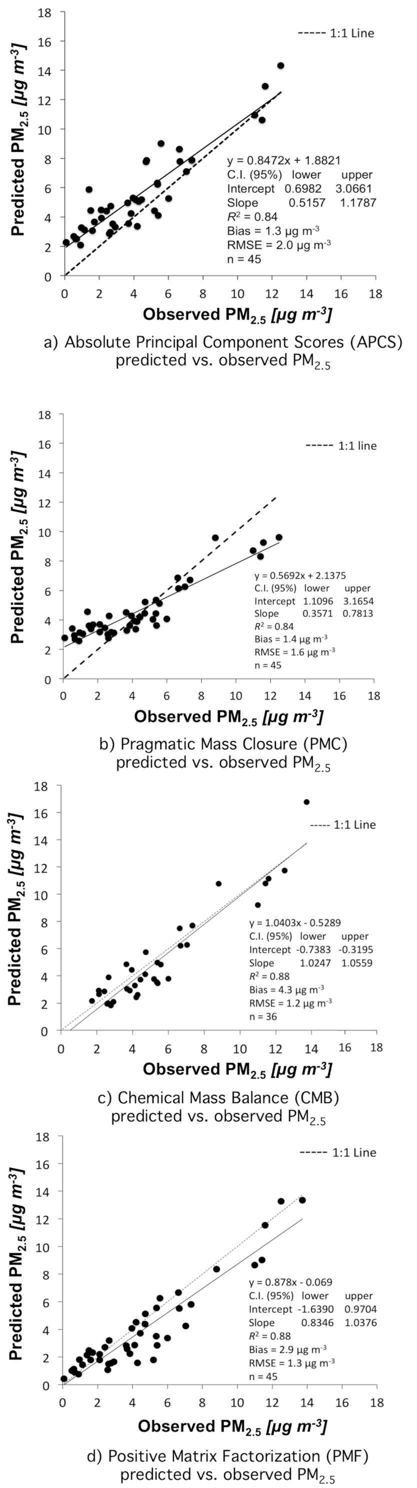


Figure 1. Parity plots of observed vs. predicted $PM_{2.5}$ estimated by the four receptor models (a) Absolute Principal Component Scores (APCS) (b) Pragmatic Mass Closure (PMC) (c) Chemical Mass Balance (CMB) (d) Positive Matrix Factorization (PMF)

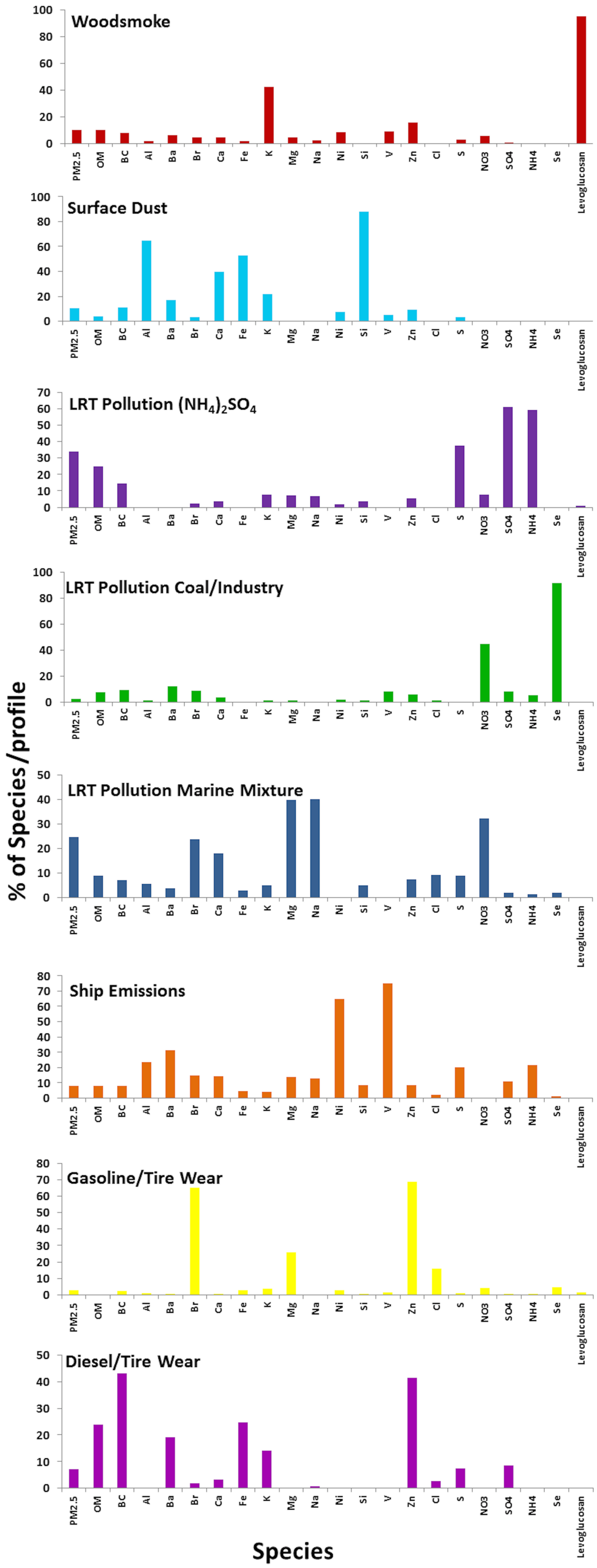
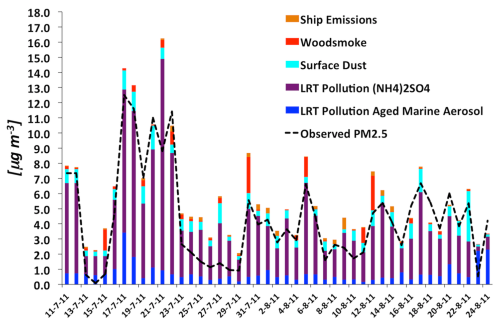
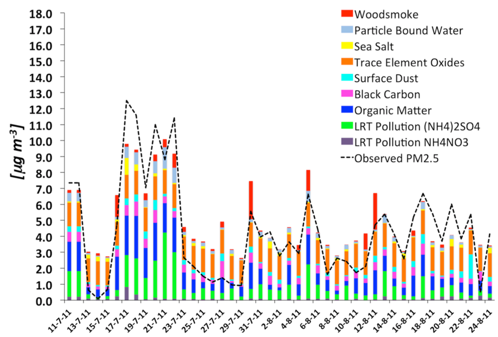


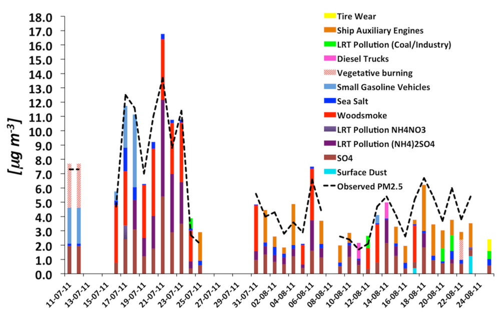
Figure 2. Positive Matrix Factorization chemical species source factor profiles and associated percentage mass contributions



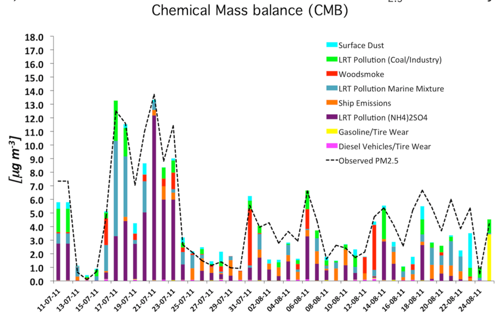
a) Time series of the relevant source contributions to $PM_{2.5}$ estimated by Absolute Principal Component Scores (APCS)



b) Time series of the relevant source contributions to $PM_{2.5}$ estimated by Pragmatic Mass Closure (PMC) receptor model time series



c) Time series of the relevant source contributions to $PM_{2.5}$ estimated by Chemical Mass balance (CMB)



d) Time series of the relevant source contributions to $PM_{2.5}$ estimated by Positive Matrix Factorization (PMF)

Figure 3. A comparison of the four receptor model $PM_{2.5}$ source apportionment timeseries in Halifax during BORTAS-B (a) Absolute Principal Component Scores (APCS) (b) Pragmatic Mass Closure (PMC) (c) Chemical Mass balance (CMB) (d) Positive Matrix Factorization (PMF)

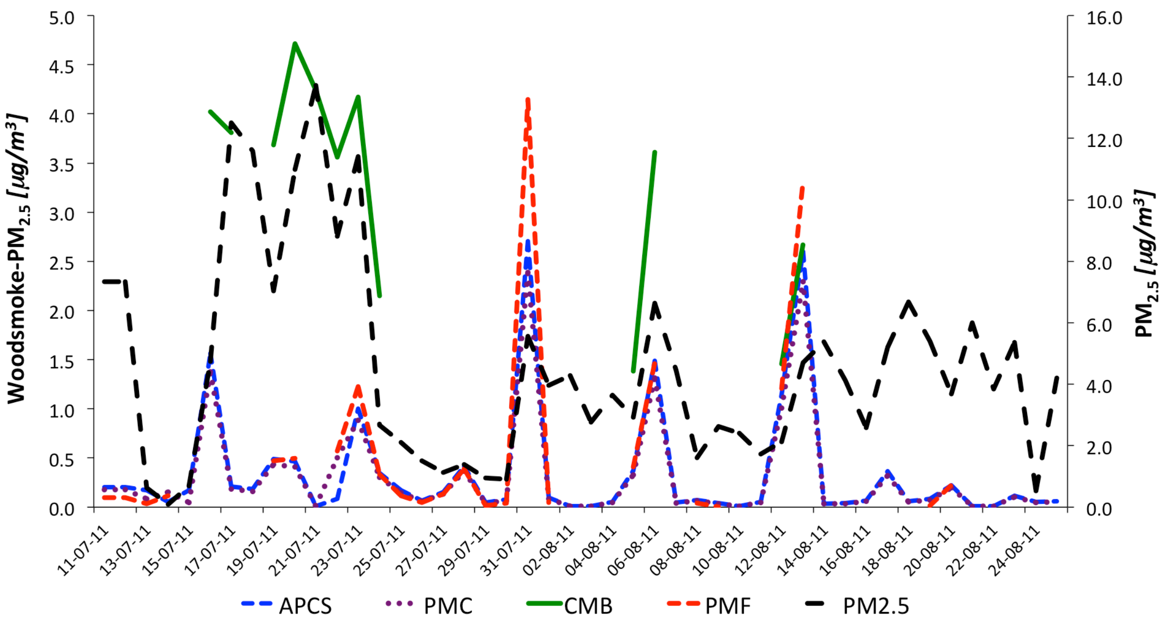


Figure 4. Time series of the woodsmoke contribution to the total $PM_{2.5}$ mass estimated from the four receptor models during BORTAS-B

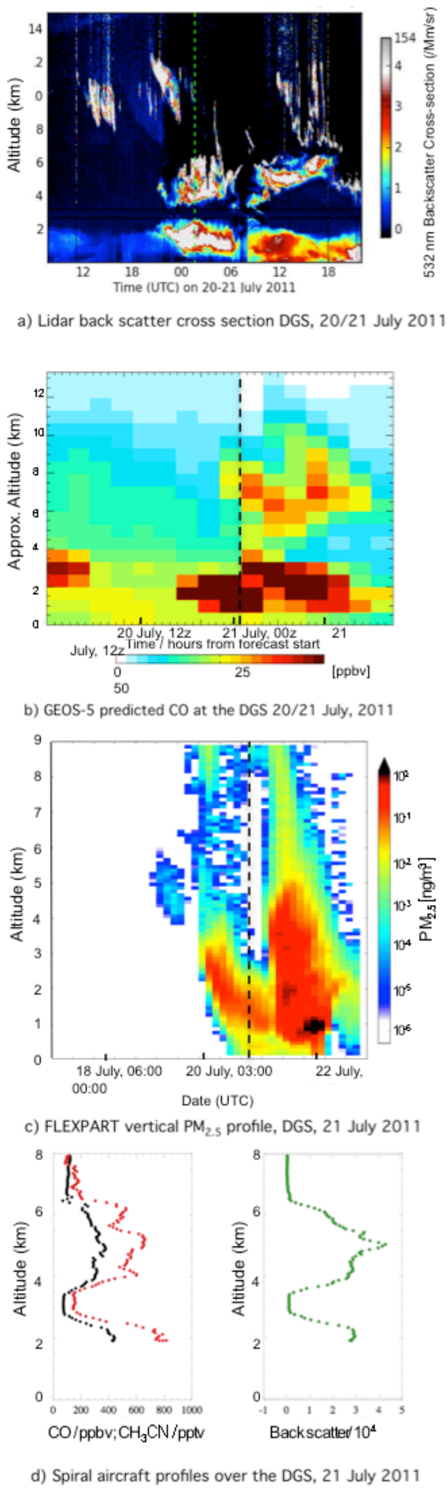


Figure 5. Comparison of simultaneous observations (a) Lidar backscatter cross section DGS, 20/21 July 2011 (b) GEOS-5 CO forecast at the DGS 20/21 July, 2011 (c) FLEXPART vertical $PM_{2.5}$ profile, DGS, 21 July 2011 (d) Spiral aircraft profiles over the DGS, 21 July 2011. Vertical dashed lines in (a), (b) and (c) indicate the time of the spiral aircraft profiles in (d).

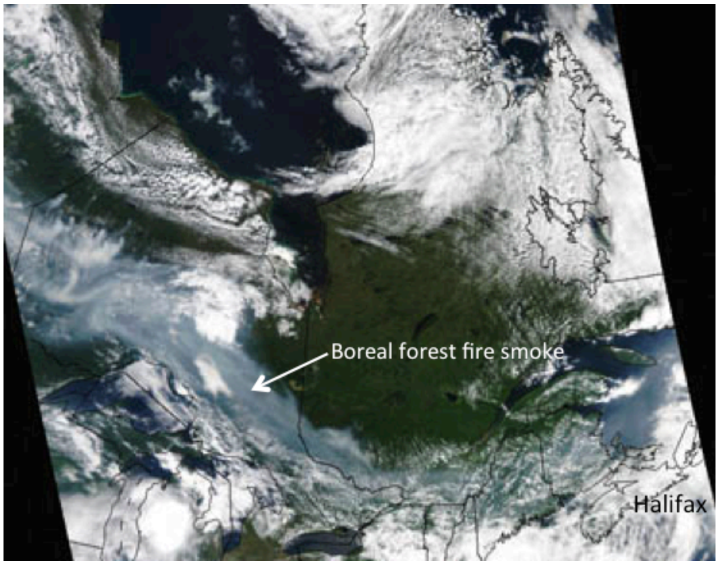


Figure 6. NASA AQUA MODIS true colour satellite image at 18:00 UTC on 18 July 2011 clearly showing boreal forest fire smoke from Northern Ontario advecting over Halifax, Nova Scotia.

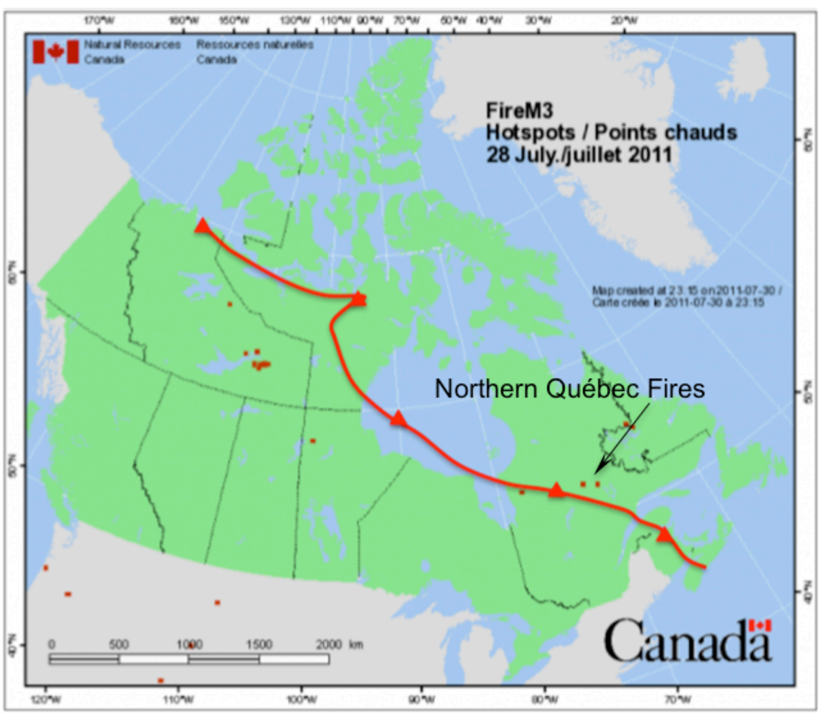


Figure 7. 5 day HYSPLIT air mass back trajectory arriving at 12:00 UTC overlaying the fire hot spot map for 28 July 2011.

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