

# Identifying the sources driving observed PM<sub>2.5</sub> temporal variability over Halifax, Nova Scotia, during BORTAS-B

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## Abstract

The source attribution of observed variability of total PM<sub>2.5</sub> concentrations over Halifax, Nova Scotia was investigated between 11 July – 26 August 2011 using  
30 measurements of PM<sub>2.5</sub> mass and PM<sub>2.5</sub> chemical composition (black carbon, organic matter, anions, cations and 33 elements). This was part of the BORTAS-B (Quantifying the impact of BOREal forest fires on Tropospheric oxidants using Aircraft and Satellites) experiment, which investigated the atmospheric chemistry and transport of seasonal boreal wild fire emissions over eastern Canada in 2011. The US EPA Positive Matrix  
35 Factorization (PMF) receptor model was used to determine the average mass (percentage) source contribution over the 45 days, which was estimated to be: Long-Range Transport (LRT) Pollution 1.75 µg/m<sup>3</sup> (47%), LRT Pollution Marine Mixture 1.0 µg/m<sup>3</sup> (27.9%), Vehicles 0.49 µg/m<sup>3</sup> (13.2%), Fugitive Dust 0.23 µg/m<sup>3</sup> (6.3%), Ship Emissions 0.13 µg/m<sup>3</sup> (3.4%) and Refinery 0.081 µg/m<sup>3</sup> (2.2%). The PMF model describes 87% of the  
40 observed variability in total PM<sub>2.5</sub> mass (bias = 0.17 and RSME = 1.5 µg/m<sup>3</sup>). The factor identifications are based on chemical markers, and they are supported by air mass back trajectory analysis and local wind direction. Biomass burning plumes, found by other surface and aircraft measurements, were not significant enough to be identified in this analysis. This paper presents the results of the PMF receptor modelling, providing  
45 valuable insight into the local and upwind sources impacting surface PM<sub>2.5</sub> in Halifax and a vital comparative data set for the other collocated ground based observations of atmospheric composition made during BORTAS-B.

## 1 Introduction

50 Because of the importance of understanding the impact of North American boreal forest wildfires on northern hemisphere tropospheric chemistry, a multi-national project, led by the University of Edinburgh, was conducted out of Halifax, Nova Scotia, Canada during the summer of 2011. The study aim was to quantify the impact of “BOReal forest

fires on Tropospheric oxidants over the Atlantic using Aircraft and Satellites”. Central to  
55 BORTAS-B was a measurement campaign with the UK Facility for Airborne  
Atmospheric Measurements (FAAM) BAe146 research aircraft (Parrington et al.,  
2012;Palmer et al., 2013). In addition, numerous satellite observations of trace pyrogenic  
gases were made (Tereszchuk et al., 2013).

A vital component of the BORTAS-B project was the Dalhousie University Ground  
60 Station (DGS) in Halifax. The DGS was established to determine the temporal variability  
of size-resolved particulate composition and gas species concentrations both in-situ and  
through the atmospheric column. These measurements were used to help validate air  
quality forecast models used to guide the BAe146 aircraft toward wild fire plume  
outflows from within and exiting Eastern Canada, to validate satellite surface and column  
65 composition observations over Halifax, to validate Lidar surface and column observations  
over Halifax, for identifying wild fire smoke plumes as they passed over or impacted the  
surface in Halifax and used for additional insight into the atmospheric chemistry  
prevalent during the BORTAS-B campaign. This paper presents the chemical speciation  
and mass concentration of atmospheric fine particulate matter composition less than, or  
70 or equal to, a median aerodynamic diameter of 2.5 microns ( $PM_{2.5}$ ). Receptor modelling of  
the  $PM_{2.5}$  mass and chemical species was used in this paper to identify the local and  
upwind sources responsible for driving the observed temporal variability of  $PM_{2.5}$  in  
Halifax sampled during the BORTAS-B mission.

## 2. Measurements

Figure 1 shows the geographical location of the Dalhousie Ground Station (DGS). The  
DGS is 65 m above sea level with the sampling inlets 15 m above ground level on the  
roof of the Sir James Dunn building, Dalhousie University in the south end of Halifax  
80 ( $44^{\circ}38'17.46''$  N,  $63^{\circ}35'37.52''$  W). The building is located in a residential area of  
Halifax away from strong local sources of  $PM_{2.5}$ . However, during the BORTAS-B study  
there was visible fugitive dust emissions caused by street landscaping and building  
renovations taking place in the vicinity of the DGS. This fugitive dust did not cause any  
operational issues with the instruments related to the receptor modelling of  $PM_{2.5}$ .

85 A 24-hour filter sample was collected at the BORTAS-B DGS from 20:00 UTC on 11  
July 2011 to 20:00 UTC on the 12 July 2011. Uninterrupted 24-hr filter samples were  
then taken from 20:00 UTC on 13 July 2011 to 20:00 UTC on 26 August 2011 resulting  
in a further 44 consecutive days of PM<sub>2.5</sub> samples, providing a total of 45 filter samples.  
The DGS sampling was scheduled for 20:00 UTC (16:00 Atlantic Standard Time) as this  
90 was the most practical time of day for the DGS research staff to synchronize multiple  
instrument 24-hr sampling. Continuous measurements of PM<sub>2.5</sub> mass concentration, black  
carbon (BC), organic matter (OM) and meteorology were also collected over the same  
sampling period. The other collocated measurements at the DGS that are not featured in  
this paper are described in Palmer et al. (2013).

95 A Thermo 3500 ChemComb (Thermo Fisher Scientific Inc. Waltham, MA, US 02454)  
sampler operating at 10 L/min was loaded with a 47 mm diameter nylon filter for the  
collection of PM<sub>2.5</sub> anions (Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>), cations (Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup> and  
Mg<sup>2+</sup>) and water soluble elements (As, Cr, Mn, P, Pb, Se and Sr). A sodium carbonate  
denuder was used in the ChemComb to scrub SO<sub>2</sub> from the sample air stream to prevent  
100 the formation of SO<sub>4</sub><sup>2-</sup> artifacts on the nylon filter (Maykut et al., 2003; Dabek-  
Zlotorzynska et al., 2011). The flow rate of the ChemComb sampler was checked at the  
start and end of sampling with a NIST traceable Dry Cal Defender flow meter (accuracy  
of ± 2% of flow reading). A flow rate of ± 20% was deemed acceptable. In addition PM<sub>2.5</sub>  
were collected onto a 47 mm diameter, 2 µm Teflon filter (Whatman part #7592-104) for  
105 the analysis of mass and 33 elements using a Partisol 2025 dicotomous sampler (Dabek-  
Zlotorzynska et al., 2011). The Partisol flow rate was checked weekly with a Dry Cal  
Defender flow meter. The Partisol stopped sampling if the flow rate deviated by more  
than ± 10% of the set flow. Weekly internal and external leak checks were performed on  
the Partisol as per the manufactures instructions with no failures reported during the  
110 study.

No duplicate filter samples were taken during the study. 10% of the nylon and Teflon  
filters were field blanks with an addition 5% acting as laboratory blanks. Blank  
subtraction was conducted on all filter samples where required.

Assembly and disassembly of the ChemComb sampler and Partisol filter cassettes was  
115 conducted in a high efficiency particle air (HEPA) cleaner hood.

The total PM<sub>2.5</sub> mass concentration was determined by gravimetric analysis of the Teflon filter sample at Alberta Innovates (Highway 16A and 75th Street, Vegreville, Alberta, Canada, T9C 1T4) in accordance with USEPA protocol for the determination of ambient PM<sub>2.5</sub> mass concentration using filter based sampling systems (USEPA, 1998).

120 The analysis of 33 elements (Ag, Al, As, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Fe, In, K, Mg, Mn, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Ti, V, Zn and Zr) on the Teflon filter was conducted using a Thermo Fisher Scientific Quant'X energy dispersive x-ray fluorescence (ED-XRF) at RTI International (3040 Cornwallis Road, Building 7, RTP, NC, USA 27709). Due to low PM<sub>2.5</sub> sample mass, the following 14 elements measured by  
125 ED-XRF were not detected in any of the samples: Ag, Cd, Ce, Cs, In, P, Pb, Rb, Sb, Se, Sn, Sr, Ti and Zr.

The anions, cations and water soluble elements were extracted from the nylon filters using 100 µL of HPLC grade isopropanol and 8 mL Type-1, 18 MΩ cm water followed by 30 min sonication. The anion and cation analysis was conducted using a Thermo  
130 Fisher Scientific, Dionex ICS-1000 ion chromatograph (Dionex Canada Ltd, RPO Maple Grove Village, Oakville, Ontario, L6J 7P5). Details of the Dionex instrument configuration and analysis protocol for the anion analysis is reported in Gibson et al. (2013). Cations were analyzed using the Dionex ICS-1000 fitted with an IonPac CS-12 analytical column and guard column, 20 mM methanesulfonic acid eluent with an inject  
135 loop of 25 µl. The method used to determine the detection limit of the anions and cations is described in Gibson et al. (2013). Anions and cations not detected by ion chromatography in any of the samples included Br<sup>-</sup>, F<sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, Mg<sup>2+</sup> and NO<sub>2</sub><sup>-</sup>. The water soluble elements (As, Cr, Mn, P, Pb, Se, and Sr) extracted from the nylon filter were analyzed using a Thermo X-Series II single quadrupole inductively coupled plasma-  
140 mass spectrometer (ICP-MS). A five-point standard curve of the isotope masses <sup>75</sup>As, <sup>52</sup>Cr, <sup>55</sup>Mn, <sup>31</sup>P, <sup>208</sup>Pb, <sup>82</sup>Se and <sup>88</sup>Sr were used for qualification and quantification. These elements were found to be above the detection limits in all samples.

Black carbon was estimated from continuous 1-minute averages of light absorption at 880 nm using a Magee Scientific Corporation, AE42 aethalometer (1916A M. L. King Jr.  
145 Way Berkeley CA 94704, USA)(Lawless et al., 2004;Babu and Moorthy, 2002). The mass absorption conversion factor used was 16.6 (Hansen, 2005). The relative bias for the two

monitors was determined by comparing the mean values over 5759 minutes of collocated readings. All readings of one monitor were multiplied by this factor to bring the means into agreement. The Precision was then determined by calculating the absolute value of the difference between the monitors (after adjustment for the bias) divided by the sum of the readings for each minute as follows:  $\text{abs}[(A-B)/(A+B)]$  (where A is the reading of the first monitor, B is the reading of the second monitor adjusted by the bias). The median value for the 1-minute readings was 0.18. (IQR 0.07-0.40). A precision and bias for 24-hr was not possible as there were only three data points. The 1-minute data points were averaged to match the 24-hour PM<sub>2.5</sub> filter samples.

An Aerodyne Research, Inc., (Billerica, MA, US, 01821-3976) Aerosol Chemical Speciation Monitor (ACSM) (Ng et al., 2011) was operated by Environment Canada for the purposes of measuring continuous  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , OM and  $\text{SO}_4^{2-}$ , and at a temporal resolution of 30 minutes. The ACSM, 30-minute data points were averaged to match the 24-hour PM<sub>2.5</sub> filter samples. Only the OM from the ACSM was used in the receptor modelling of the PM<sub>2.5</sub> as the  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , from the nylon filter are recognized as the standard protocol for PM<sub>2.5</sub> speciation used in receptor modelling (Dabek-Zlotorzynska et al., 2011). Filter based samples of OM were not available in this study, hence the use of the ACSM OM. The upper size cutoff (50% transmittance) for the ACSM is close ~650 nm and the lower cut is 80-100 nm (Liu et al., 2007). While most of the organic (both primary and secondary) aerosol mass is at sizes smaller than 650 nm, it is possible that some of the mass between 650 nm and 2.5  $\mu\text{m}$  was lost (Ng et al., 2011). Mass calibrations were performed before and after the experiment at Environment Canada in Toronto using nearly monodisperse particles of ammonium nitrate. The data completeness for the ACSM during BORTAS-B was 85% (missing data between 2 August and 8 August). Stepwise regression (SR) was used to predict OM during the period of missing data. 21 PM<sub>2.5</sub> species variables and meteorological variables were used in the SR model. The significant OM predictor variables (p-values, coefficient) used in the SR model were K (p=0.001, 10.801), Ni (p=0.007, -204.097), Zn (p=0.003, 121.884) and  $\text{SO}_4^{2-}$  (p<0.001, 0.531). The SR constant was 0.157 with a model  $r^2$  of 0.86. The artificial data generated for the 7 missing days of OM samples were used in the PMF model. It was felt that this was superior to using the median OM concentration for the

missing data period as suggested in the PMF user guide.

Meteorological data at the BORTAS-B DGS was collected every 15 minutes using a Davis Vantage Pro II weather station (Davis Instruments Corp. Hayward, California 94545 USA). The Davis Vantage Pro II weather sensors included wind speed, wind direction, temperature, pressure, solar radiation, UV radiation, relative humidity and precipitation. The meteorological data was integrated to match the 24-hour filter based sampling. The descriptive statistics of the meteorological variables that cover the PM<sub>2.5</sub> sampling period at the BORTAS-B DGS are provided in Table 1. The average wind vector coinciding with each 24-hour PM<sub>2.5</sub> sample was determined using WRPLOT View (Lakes Environmental, Waterloo, Ontario, N2V 2A9, Canada).

In addition, Environment Canada used the meteorological data from Halifax International airport (26.8 km distant at a heading of 012°) to provide an overview of meteorological conditions within the Halifax Regional Municipality during the 45 days of filter sampling at the BORTAS-B DGS. A climatology review of synoptic meteorology patterns over Maritime Canada indicates a general west to east progression of transport flow. The period of the filter-based measurements at the DGS in summer 2011 was influenced by numerous weak low pressure systems during the first half of the sampling period (to 4 August). These systems, along with onshore moist southerly air flows provided extended periods with low level clouds and occasional periods of rain, drizzle and fog. Low cloud tends to inhibit photochemistry and promote aqueous-phase production of SO<sub>4</sub><sup>2-</sup>. Precipitation favors removal of particles from the atmosphere. Of the 45 sampling days, 13 had periods with sunny skies (6+ hours). Ten of these days were in the latter portion of the sampling period, from August 6<sup>th</sup> onward, indicating limited photochemistry in the first portion of the sample period. Maximum 5-min averaged wind speed was significant (8.0 m/sec or more) on 7 days with 20 August being the windiest. Rain with amounts >0.2 mm occurred on 16 days with 3 days (20 July, 2 August, 8 August) when amounts were greater than 20 mm. The 2 August rain event was due to a nearly stationary line of thunderstorms that developed over Halifax in the late afternoon. The line of thunderstorms did not move east of the area until the early hours of 3 August after providing 60+ mm of rain. A daily climatology review prepared by Environment Canada is presented in Table 2. These data were accessed via:

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### 3. Models

The HYbrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model was used to investigate the source regions of PM<sub>2.5</sub> measured at the DGS during BORTAS.

215 The source of the data was the Global Data Assimilation System (GDAS) model accessed through the HYSPLIT web archive (<http://ready.arl.noaa.gov/archives.php>). Ten-day, 5-day and 2-day ensemble air mass back trajectories for the Halifax DGS during BORTAS were generated using the online HYSPLIT archive data (Draxler and Rolph, 2012; Rolph, 2012). Two trajectories were obtained for each 24-hour sampling period (08:00 UTC and 220 20:00 UTC). The HYSPLIT default of 950 hPa (500m) was chosen as the arrival height to avoid trajectories hitting the ground before they arrive at the DGS. The trajectory resolution was 1-hour. It was found that a 2-day air mass trajectory identified the same upwind source region as a 10-day or 5-day trajectory. In addition, the visualization of the ensemble trajectories was improved using 2-day trajectories. Therefore, 2-day ensemble 225 air mass trajectories are presented.

The US EPA Positive Matrix Factorization (PMF) receptor model v3 was used for source apportionment of the PM<sub>2.5</sub> sampled during BORTAS-B in Halifax. The PMF method has an extensive heritage, having been applied to many PM<sub>2.5</sub> source apportionment studies (Paatero, 1997; Paatero and Trapper, 1994; Martello et al., 230 2008; Jeong et al., 2011; Brown et al., 2007; Bari et al., 2009). Details of the PMF model are provided in Hopke (1991). A priori knowledge of sources, meteorology and the chemical markers present in the PMF factor profiles are used to identify the source, e.g. factors containing Ni and V are indicative of ship emissions (Jeong et al., 2011).

For the BORTAS-B PM<sub>2.5</sub> mass and species data set the uncertainty was set to the PMF 235 default of 20%. For all model base runs, twenty random initializations were conducted. Once the base run was completed the scatter plots and times series of the modelled and observed PM<sub>2.5</sub> species were scrutinised with outliers being investigated. The normality of the model scaled residuals for each PM<sub>2.5</sub> species was also scrutinized. Any PM<sub>2.5</sub> species scaled residuals found to be  $\pm 3$  from zero were investigated further for poor

model fit. Two checks on model performance were then made, bootstrapping and the PMF FPeak function. To fine tune the model the FPeak function within PMF was used to robustly minimise the effect of outliers. However, FPeak failed to improve the model and so was set to zero. The G-Space function was used to also check for model performance with no issues found with any of the species bi-plots. Once confidence in the model was achieved the PMF factor profiles were allocated a “source name” based upon the factor loadings of the key chemical markers present.

Chemical markers are used to help identify sources within the PMF source profiles, e.g. biomass burning has a number of characteristic chemical markers, e.g. K, BC and levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) (Bergauff et al., 2010; Ward et al., 2012; Jeong et al., 2008). Potassium is a good marker of long-range wildfire smoke plumes as it is conserved from source to receptor (Ward et al., 2012). Levoglucosan is also a good marker for local biomass burning, but it is readily oxidized to 17% of its original primary mass after 3.5 hours of exposure to hydroxyl radicals (OH) (Hennigan et al., 2011), which may reduce its ability to identify Long Range Transport (LRT) of biomass burning. However, internally mixed levoglucosan may not be oxidized, being protected by the outer layer of the particulate, and so may still be useful as a marker of LRT Boreal wildfire burning (Hennigan et al., 2011). Robust chemical markers of ship emissions include  $\text{SO}_4^{2-}$ , V, Ni and BC (Hobbs et al., 2000; Isakson et al., 2001; Zhao et al., 2013). V/Ni ratios originating from heavy fuel oil (HFO) used in ships range from 1.9 – 6.5 (Zhao et al., 2013). The sulphur content of HFO is currently between 1.0% and 3.5%, and during combustion produces particulate  $\text{SO}_4$  (Lack et al., 2011). Ship emissions also contain large quantities of BC particulate (Lack and Corbett, 2012). Unambiguous markers of fugitive surficial dust include Fe, Al, Ca and Si (Jeong et al., 2011; Martello et al., 2008; Gugamsetty et al., 2012). Primary Sea Salt markers include  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  (Gibson et al., 2009) and  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{NO}_3^-$  for aged marine secondary aerosol (Jeong et al., 2011; Gibson et al., 2009). Nitrate,  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  are markers of long-range secondary inorganic PM produced by photochemical reactions of pre-cursor gases ammonia ( $\text{NH}_3$ ),  $\text{NO}_2$  and  $\text{SO}_2$  (Yin and Harrison, 2008; Gibson et al., 2009). Chemical markers for vehicular emissions include BC, Br, Fe, Mn and Sb (Larson et al., 2004; Huang et al., 1994). Barium, Cu and Fe are markers for

vehicle brake wear (Harrison et al., 2011; Bukowiecki et al., 2010; Chen et al., 2007) and Cd and Zn are markers for vehicle tire wear (Bukowiecki et al., 2010; Olajire and Ayodele, 1997; Chen et al., 2007). Diesel emissions have been previously characterized by high PMF loading of PM<sub>2.5</sub> mass and BC (Martello et al., 2008; Chen et al., 2007).

Selenium is often used as a good marker for coal combustion with Pb acting as a good marker for industrial emissions (Chow et al., 2004; Jeong et al., 2011). The source chemical profiles contained in the US EPA Speciate database provide additional evidence to identify source chemical markers in PMF chemical species factor profiles (Ward et al., 2012; Jaeckels et al., 2007).

The sum of the masses associated with apportioned sources obtained from PMF will be compared with the original total PM<sub>2.5</sub> mass. The bias of the PMF model is calculated as  $(A - T)/T$ , where  $A$  is the PMF PM<sub>2.5</sub> mass concentration and  $T$  is observed PM<sub>2.5</sub> mass concentration over the 44 days of sampling. The root-mean-square error (RMSE) (Laupsa et al., 2009) will be used to determine the accuracy of the PMF model, Eq. (3).

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (\hat{y}_i - y_i)^2} \quad (3)$$

where  $\hat{y}$  = PMF model total PM<sub>2.5</sub> mass concentration and  $y$  = observed total PM<sub>2.5</sub> mass concentration with units expressed in  $\mu\text{g}/\text{m}^3$ .

## 4. Results and Discussion

### 4.1 HYSPLIT Cluster Analysis

The HYSPLIT 2-day ensemble air mass back trajectories are provided in Figure 2 with the mean location of the trajectory over the 2-day travel time used to group the trajectories into four clusters: 1) N (315° to 45°), 2) marine (45° to 235°), 3) SW (235° to 265°), and 4) W-NW (265° to 315°). These clusters were chosen to reflect known source regions in Central Canada, Atlantic Canada and the North East United States, e.g.

trajectory clusters coloured cyan are clearly under the influence of marine aerosol, the

SW cluster (red) covers the Ohio valley, the interstate-95 corridor and other source regions in the NE US (Jeong et al., 2011;Dabek-Zlotorzynska et al., 2011). The NW cluster (green) covers the Windsor-Québec corridor, which is the population and industrial core of Central Canada and, as such, a major source region of secondary inorganic species and secondary OM (Jeong et al., 2011;Dabek-Zlotorzynska et al., 2011). The N cluster (blue) is a region of low anthropogenic emissions and should represent fairly clean air parcels impacting Halifax. Figure 2 shows that 40% of the air masses entering Halifax during the BORTAS-B PM<sub>2.5</sub> sampling campaign originated from the marine sector, 16% from the SW (NE US), 27% from the WNW (Windsor-Quebec source region) and 16% from the N. Figure 3 shows that air mass back trajectories from all four clusters have a high likelihood that the trajectory profiles were in the boundary layer during the previous 48 hours. Our analysis also showed that over 80% of the back trajectories were below 1.5 km for the entire 48 hours. The profiles from the N (blue) show the highest probability of air subsiding from the free troposphere; however, it was anticipated that these profiles would be associated with clean air regardless of the altitude of the back trajectories. The Marine cluster mostly originate from the boundary layer, as expected (Holzinger et al., 2007). Of the two potentially polluted clusters shown in Fig. 3, the SW cluster and WNW cluster appear to be mainly associated with boundary layer flow.

## 4.2 Descriptive Statistics

Table 3 shows the descriptive statistics for the PM<sub>2.5</sub> species and associated meteorological variable sampled during BORTAS-B. The median PM<sub>2.5</sub> concentration is 3.9 µg/m<sup>3</sup>, which is considerably lower than historical (2006-2008) summer time value (median 9.0 µg/m<sup>3</sup>) measured at the National Air Pollution Surveillance (NAPS) station in down town Halifax and reported by Jeong et al. (2011). The difference between these two values might be due to greater vehicle density in the downtown core of Halifax compared to the BORTAS-B DGS in the more residential south end of Halifax. Unfortunately, the Federal Government PM<sub>2.5</sub> monitoring in downtown Halifax during BORTAS-B was too sparse to make any direct comparison with our data possible. The

BORTAS-B PM<sub>2.5</sub> median is also considerably lower than summertime median PM<sub>2.5</sub> concentrations found in Toronto (12 µg/m<sup>3</sup>) and Windsor, Canada (15 µg/m<sup>3</sup>) (Jeong et al., 2011), which can be attributed to the significantly lower population, vehicle and industrial density in Halifax in comparison to these other Canadian cities. In addition, with reference to Table 2, precipitation amounts >0.2 mm occurred on 16 days, with two days (2 August and 8 August) when amounts were greater than 20 mm. The significant precipitation occurring during roughly half of the sampling period helps explain the reduced average PM<sub>2.5</sub> concentrations observed during BORTAS-B when compared with previous years. Despite the low PM<sub>2.5</sub> sample mass, the key chemical species needed to conduct PMF modelling were above the limit of detection (LOD).

### 4.3 PM<sub>2.5</sub> Composition

Figures 4—7 shows time series of daily major, macro, minor and trace PM<sub>2.5</sub> components together with the total PM<sub>2.5</sub> mass concentration. The main contributing species seen during the relatively low PM<sub>2.5</sub> concentrations observed between 13 July and 15 July were Na and Cl (indicative of Sea Salt) as well as some OM and BC (local combustion emissions; also, filter absorption can be affected by other absorbers, such as brown carbon, and at 880 nm by scattering due to larger particles of Sea Salt), with greatly reduced, or absent, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Se and Pb (indicative of LRT pollution), compared to other time periods (Chow et al., 2004; Dabek-Zlotorzynska et al., 2011). The air mass back trajectories during this low PM<sub>2.5</sub> mass period were from the north, a region of low primary and secondary PM<sub>2.5</sub> emission, thus providing evidence to explain the low concentrations experienced on 13 July and 15 July. Between 16 July and 24 July there was a PM<sub>2.5</sub> episode as shown by Figure 4. Figures 4 and 5 show that the dominant species during this period were BC, NH<sub>4</sub><sup>+</sup>, S, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and OM with input from Se and Pb, as shown in Figure 7. The presence of Se indicates input from coal fired power stations and Pb being a marker of industry, the likely source region being the NE US airshed (Martello et al., 2008). The elevated Cl and Na provide evidence that the air mass also crossed the ocean before reaching Halifax. This is corroborated by air mass trajectories over this period which show that the airflow was from the SW and Eastern

seaboard of the US, and this will be discussed later with the PMF results. With reference to Table 2, there was a thunderstorm on 19 July that likely explains the sudden reduction in PM<sub>2.5</sub> concentration due to aerosol “wash-out” on this day compared to the preceding and following days.

Figure 6 shows a fugitive dust event on 23 August, which is characterized by elevated concentrations of Al, Ca, Fe, K and Si, which are known crustal elements. The weather on 23 August was dry, warm (23°C), with clear skies and accompanied by high winds (3-4 m/sec) throughout the 24-hour period, conditions favourable to the re-suspension of surficial dust. There was also considerable street landscaping and exterior building restoration taking place on this day, again providing supportive evidence for fugitive dust suspension. Figure 7 shows elevated Ba and Cu on 23 August, which are known markers of brake wear contamination of re-suspended road dust and urban soils (Harrison et al., 2011; Bukowiecki et al., 2010). Therefore, brake wear components are probably an additional component of the elevated fugitive dust seen on 23 August. From Figure 7 it can be seen that there were elevated concentrations of As, Ba, Cu and Zn on 31 July and 13 August which are known markers for vehicles (Harrison et al., 2011; Bukowiecki et al., 2010). The wind direction on these two days was from the NW, which is in-line with the 102 Highway and other major and minor roads upwind of the sampling site (again, this will be shown with the PMF results). In addition, on 31 July and 13 August it was dry, with winds between 4-6 m/sec and 4 m/sec respectively, conditions that favour transport and re-suspension of vehicle emissions, tire debris and brake wear which are the probable sources of these elevated metal concentrations seen on 31 July and 13 August. Figure 7 also shows elevated Ni, V and SO<sub>4</sub><sup>2-</sup> on 10 August. The local wind direction on this day was from the SE and aligned with Halifax harbour. The wind direction coincident with the harbour, together with the presence of elevated Ni, V and SO<sub>4</sub><sup>2-</sup> suggest ship emissions as the probable source contributing to the PM<sub>2.5</sub> mass on this day (Zhao et al., 2013).

#### 4.4 PMF Receptor Modelling

The number of factors (sources) that PMF could apportion were explored in an iterative process from 5 factor profiles through to 15 factor profiles. The number of factors chosen was based on the high factor loadings of key chemical markers, the ensemble HYSPLIT trajectory clusters (Fig. 2), wind roses analysis and *a priori* knowledge of known sources impacting Halifax. The seven factors chosen were LRT Pollution (LRTP), LRT Pollution Marine Mixture (LRTPMM), Refinery, Ship Emissions, Vehicles, Fugitive Dust and Sea Salt which were anticipated by the individual chemical markers related to these sources as discussed in section 4.3. High factor loadings of  $\text{NH}_4^+$ , OM,  $\text{PM}_{2.5}$  and  $\text{SO}_4^{2-}$ , S and were used to identify LRTP. High factor loadings of  $\text{Na}^+$ ,  $\text{NO}_3^-$  and OM were used to identify LRTPMM. The LRTPMM is likely a mixture of aerosol pollution outflow from the NE US and Sea Salt that has undergone  $\text{Cl}^-$  loss via reactions with acidic aerosol (Gibson et al., 2009; Leaitch et al., 1996; Calvert et al., 1985). The presence of  $\text{NO}_3^-$  in the LRTPMM could also be attributed to night-time reactions of  $\text{NO}_2$  with  $\text{O}_3$ , with  $\text{NO}_3^-$  also reacting with Sea Salt to remove  $\text{Cl}^-$  (Finlayson-Pitts and Pitts, 1999; Calvert et al., 1985). The Refinery factor was identified by the presence of Cr, Cu, Pb, V and Zn (Jeong et al., 2011). Ship Emissions were identified by the high factor loadings of BC, Ni,  $\text{SO}_4^{2-}$  and V (Zhao et al., 2013). Vehicles were identified by the high factor loadings of Ba, BC, Br, Cu, OM and Zn (Gietl et al., 2010). It was not possible with this data set to split the vehicle factors into gasoline or diesel emissions, brakes or tire wear sources. Fugitive Dust was identified by high factor loadings for Al, Ca, K, Fe and Si (Jeong et al., 2011). Sea Salt was identified from the high factor loadings for Cl and Na, 88% and 55% respectively, which is the same ratio as found in sea water (Gibson et al., 2009). Figure 8 shows the source profiles for the seven factors identified within the PMF model.

Although Sea Salt was observed in all PMF factor iterations, 5 through 15, the mass contribution was so low that PMF failed to apportion mass to any of the PMF model runs. This is perhaps not surprising given the very low  $\text{PM}_{2.5}$  mass observed during BORTAS-B and the fact that Sea Salt PM are mostly associated with the coarse size fraction. However, there was evidence of a contribution of aged marine aerosol (as indicated by the presence of Na and  $\text{NO}_3^-$  markers) to the LRTPMM source coincident with airflow from the NE US and crossing the ocean en route to Halifax (Leaitch et al., 1996). Therefore, the PMF receptor model apportioned six  $\text{PM}_{2.5}$  sources. Figure 9 presents a

time series of the six contributing sources to  $PM_{2.5}$  mass estimated using PMF during BORTAS-B.

Figure 10 shows the local wind directional dependence of the  $PM_{2.5}$  source contributions estimated by PMF. Ship emission  $PM_{2.5}$  source contribution aligns with the cruise ship terminal, harbour shipping lane and Naval base with little ship emission contribution directly to WNW, which is in the opposite direction to the harbour. Figure 10 confirms that ship emissions were correctly allocated to the PMF factor profile. Figure 9 shows that between 13 July and 16 July the main contributing  $PM_{2.5}$  source were Vehicles, which can be explained by the N and NW wind directions (Table 2) aligned with the highways directly upwind of the DGS. The Fugitive Dust source is most probably associated with immediate local surficial material re-suspension (Harrison et al., 2011). From Fig. 10., it was found that the Fugitive Dust was associated with a westerly wind direction. This wind direction is coincident with the major street landscaping that occurred directly below the western side of the DGS throughout BORTAS-B. It was found that the Refinery Source does not appear to have a strong local wind directional dependence. The refinery is on the other side of Halifax harbour so that the local wind direction is less appropriate than for more immediate local sources such as vehicles and fugitive dust. Air mass back trajectory analysis did not yield any further insight into wind direction dependence for the refinery source. Marine inversions and the complexity of the harbour and city topography that lay between the refinery and the DGS may have perturbed any wind directional dependence for this source.

Figure 11 shows the PMF source contribution for LRTP and LRTPMM associated with the SW and W air mass back trajectories. The back trajectories associated with the days with high loadings of LRTP have all passed over eastern Canada or the NE US (Figure 11). This is a known large upwind source of sulphur to the region (Jeong et al., 2011). The days with high loadings of LRTPMM (Figure 11) have more variability. While the trajectories generally come from the W, several of the back trajectories have primarily been over the ocean for most of the 48-hours. The presence of Na and the loss of Cl associated with the LRTPMM source suggests continental acidic aerosol outflow mixing with marine aerosol en route to Halifax (Holzinger et al., 2007; Leaitch et al., 1996).

Figure 12 shows the average mass and (percentage) contribution from the six sources

estimated by PMF during BORTAS-B. The Refinery contribution of  $0.081 \mu\text{g}/\text{m}^3$  (2.2%)  
 during BORTAS-B is somewhat lower than  $0.3 \mu\text{g}/\text{m}^3$  (3.5 %) obtained by PMF  
 conducted by Jeong et al. (2011) (Jeong-PMF)(Jeong et al., 2011). The comparison for  
 the BORTAS-B PMF vehicles with Jeong-PMF vehicle  $\text{PM}_{2.5}$  mass contribution was  $0.49 \mu\text{g}/\text{m}^3$  (13.2%) and  $1.0 \mu\text{g}/\text{m}^3$  (14.2 %) respectively which is very similar in terms of %  
 contribution but half the  $\text{PM}_{2.5}$  mass seen during BORTAS-B. The comparison between  
 the BORTAS-B PMF and Jeong-PMF for the Ship Emission was  $0.13 \mu\text{g}/\text{m}^3$  (3.4%) and  
 $0.6 \mu\text{g}/\text{m}^3$  (9.1%) respectively, showing a 4.6 times mass reduction and 3 times reduction  
 in % contribution between the previous PMF study conducted on 2006-2008 data and the  
 BORTAS-B study. This could be due to the reduction in the sulphur content (3.5% to 1%)  
 of HFO used in ships in the intervening period between these two studies which,  
 coincidentally, is the same ratio of sulphur reduction in HFO as the  $\text{PM}_{2.5}$  mass reduction  
 seen in the BORTAS-B study. The comparison between BORTAS-B PMF and Jeong-  
 PMF Fugitive Dust is  $0.23 \mu\text{g}/\text{m}^3$  (6.3%) and  $0.3 \mu\text{g}/\text{m}^3$  (3.8%) respectively. Both are  
 similar in magnitude for  $\text{PM}_{2.5}$  mass but with a 39% greater contribution to  $\text{PM}_{2.5}$  during  
 BORTAS-B. The fugitive dust contribution during BORTAS-B can be explained by street  
 landscaping and exterior building restoration work that occurred during BORTAS-B. The  
 comparison between BORTAS-B PMF and Jeong-PMF for the LRTP was  $1.75 \mu\text{g}/\text{m}^3$   
 (47%) and  $2.6 \mu\text{g}/\text{m}^3$  (37.3 %), which are similar in magnitude; providing confidence in  
 the BORTAS-B PMF results. The comparison between BORTAS-B PMF LRTPMM and  
 Jeong-PMF LRTPMM, Jeong et al. (2011) estimated that secondary  $\text{NO}_3$  aerosol in  
 Halifax was  $1.0 \mu\text{g}/\text{m}^3$  (27.9%) and  $0.7 \mu\text{g}/\text{m}^3$  (9.3 %), which is again similar in mass  
 contribution to BORTAS-B but roughly three times the % contribution when compared to  
 the Jeong-PMF results. The factor associated with ‘unaltered’ Sea Salt was identified in  
 the BORTAS-B samples but there was too little mass for PMF to apportion, although  
 aged marine aerosol did contribute to the LRTPMM source. The Jeong-PMF reported a  
 Sea Salt contribution of  $1.3 \mu\text{g}/\text{m}^3$  (18.3 %) contribution to  $\text{PM}_{2.5}$  mass in Halifax,  
 however this was an average over two years and include all seasons (Jeong et al., 2011).

Linear regression of the PMF model versus observed  $\text{PM}_{2.5}$  mass yielded a slope of  
 0.874, intercept of 1.24 and  $R^2 = 0.87$ . The PMF model bias = 0.17 and the RSME = 1.5

$\mu\text{g}/\text{m}^3$ , showing that the PMF model skill was high.

485

## 5. Conclusion

The PMF model was used to determine six major sources contributing to the  $\text{PM}_{2.5}$  mass sampled during the BORTAS-B study. Although other BORTAS-B related  
490 observations (Palmer et al., 2013) showed that transient Boreal wildfire smoke plumes did pass over and impact the surface in Halifax, there was insufficient mass for PMF to apportion. However, this study does provide valuable new insight into the major local and distant sources contributing to surface  $\text{PM}_{2.5}$  mass at the DGS during BORTAS-B.

It was shown that the dominant source contribution to summertime  $\text{PM}_{2.5}$  mass in  
495 Halifax was from LRT Pollution with a contribution from aged marine aerosol (75%) coincident with SW air flow. This is consistent with the conventional wisdom that Nova Scotia is the “tail pipe of North America”. Comparison of the PMF total  $\text{PM}_{2.5}$  mass with the observed total  $\text{PM}_{2.5}$  mass over the sampling period showed good agreement ( $R^2 = 0.87$ , bias = 0.17 and RSME =  $1.5 \mu\text{g}/\text{m}^3$ ), demonstrating the PMF receptor model  
500 performed well. The study highlights the utility of using air mass back trajectories coupled with local wind direction dependence to help identify the source of  $\text{PM}_{2.5}$ . The techniques used in this study show considerable promise for further application to other sites and to identify other source categories of  $\text{PM}_{2.5}$ . In addition, the individual  $\text{PM}_{2.5}$  species and source apportionment data provides valuable comparative data that can be  
505 used to interpret other collocated ground based measurements of atmospheric composition made at the BORTAS-B Dalhousie Ground Station.

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Table 1. Descriptive statistics for the daily averages of the meteorological variables obtained at the DGS during the PM<sub>2.5</sub> sampling period based upon 15-minute average data.

	n	Mean	Std Dev	Min	25th Pctl	Median	75th Pctl	Max
Wind Speed (m/sec)	45	2.6	1.1	0.9	1.5	2.5	3.3	5.4
Temperature (°C)	45	18.9	1.9	15.1	17.5	19.2	20.3	24.2
Relative Humidity (%)	45	84	9	64	78	84	91	97
Pressure (kPa)	45	100.2	0.4	99.1	99.9	100.2	100.6	101.1
Average Wind Vector: 238° ~ SW								

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Table 2. Daily meteorological summary covering the filter sampling period 11 July 2011 to 25 August 2011 from Halifax International Airport

	<b>Meteorological Data Summary Key</b>  <i>Dates in bold italics</i> indicate a date with significant sunshine ( $\geq 6$ hours). <b>Dates in bold</b> indicate a date with precipitation $>0.2$ mm. <b>Descriptive text in bold</b> highlights a significant meteorological feature Wind speed (m/sec) Temperature ( $^{\circ}\text{C}$ ) Time UTC
July 11	Cloudy with mid day and afternoon sunshine. Wind S to SW 3 became SW 6-8 14:00. High 25.
<b>July 12</b>	Overnight fog then rain or showers to 18:00. Wind S 6-7 then light in eve. High 17.
July 13	Fog to 11:00 then mostly cloudy. Wind N at 6-8. High 23.
<b>July 14</b>	Clear to start then cloudy before sunrise with rain by 21:00. Wind N 6-8 and High 13
<b>July 15</b>	Rain ended at sunrise then cloudy then rain from 23:59. Wind N <b>6-11</b> . High 19.
July 16	Mostly cloudy with wind NW <b>8</b> then dropped off by 23:00. High 20.
July 17	Mostly clear to 12:00 then mostly cloudy. Wind SW 6. <b>High 30</b>
July 18	Mostly cloudy with a shower a noon. Clearing in evening. Wind SW 4-6. High 25.
July 19	Fog overnight then mostly cloudy with scattered shower. Wind SW 3. High 26.
<b>July 20</b>	Mainly clear to 21:00 then cloudy. Wind W 3 except SW <b>8</b> at 21:00 then SW 6-7. High 27.
<b>July 21</b>	Cloudy then Rain Fog and a Thundershower in late evening. Wind SW 6-8 <b>except 8</b> late evening. High 28.
July 22	Fog to 14:00 then mostly cloudy. Wind W 3 then light then SE 6 then N 4. High 28.
July 23	Fog to 14:00 then mostly cloudy, 20:00 shower then Fog. Wind light N then S 4-6
July 24	Clear early morning then mostly cloudy then clear in evening. Wind NW-N 4-6 then light in the evening. High 23.
<b>July 25</b>	<b>Clear. Wind light.</b> Then S 4 from mid afternoon. High 24.
<b>July 26</b>	Clear at first then mostly cloudy to cloudy with and fog in the evening. Wind SE 4-6 light in the eve.
<b>July 27</b>	Fog to mid day then cloud with supertime showers. Wind SE 3. High 19.
July 28	Fog early then mostly cloudy. Wind NW-N 4. High 20.
July 29	Clear then mostly cloudy after 09:00. Wind light then SW 6-7 after midday. High 23.
<b>July 30</b>	Fog to morning then mostly rain through day – drizzle in the evening. Wind S-SE 4-6 became N 7 late eve. High 18.
July 31	Mostly cloudy except clear midday and then in evening. Wind NW 4-6. High 25.
Aug 01	Clear to sunrise then mostly cloudy to sundown. Wind light then SE 4 after noontime. High 24.
<b>Aug 02</b>	Fog then cloudy. Thunderstorms from mid afternoon through evening. Wind SE 6-8. High 22.
<b>Aug 03</b>	Thunderstorms and rain until 07:00 then cloudy, showers in the morning. Wind ESE 6-8. High 17.
<b>Aug 04</b>	Cloudy, showers to midday. Wind NE 4-6. High 18.
Aug 05	Mostly cloudy to late evening. Wind N 4-7. High 19.
<b>Aug 06</b>	Fog overnight then mainly clear after 12:00. Wind NW 3 then light in evening. High 24.
<b>Aug 07</b>	Cloudy to late morning then some sun. Rain late evening. Wind S-SE 3. High 25.
<b>Aug 08</b>	Fog, Drizzle and showers then rain by midday ended in the evening. Wind S-SE 4-6. High 19.
<b>Aug 09</b>	Fog overnight then cloudy with evening drizzle. Wind N 6-8 then light in evening. High 20.
<b>Aug 10</b>	Fog and Drizzle to midmorning then cloudy. Showers in the evening. Wind SE 6 occasionally <b>8. High 16</b>
Aug 11	Fog then morning drizzle then cloudy with some late day sun. Wind SE 4-6. High 19.
<b>Aug 12</b>	Some early morning fog otherwise clear. Wind W 1-3 then SE 4 later afternoon. High 24.
<b>Aug 13</b>	<b>Clear.</b> Light except NW 4 midday hours. High 25.
<b>Aug 14</b>	Clear then mostly cloudy in the afternoon. Wind SW 4-6. High 26.
<b>Aug 15</b>	Fog then mostly cloudy with eve showers and rain. Wind SE 3-4. High 23.
<b>Aug 16</b>	Rain and drizzle. Clear to supper. Then Cloudy with late drizzle. Wind SE 6 then to <b>8 in the afternoon.</b>
<b>Aug 17</b>	Showers and drizzle end overnight. Then clear by 13:00. Wind NW 6. High 24.
<b>Aug 18</b>	<b>Clear.</b> Wind light SW then S-SW 6-8. High 25.
<b>Aug 19</b>	Fog patches to sunrise then cloudy but Clear by noon. Wind SW 3-4 the S 6 from mid afternoon. High 25.
Aug 20	Fog patches overnight then mostly cloudy with sunny periods. Clear late eve. Wind SW-S 4-7. High 26.
Aug 21	Fog overnight. Then clear in the am then mostly cloudy. Wind S-SW 10 becoming 6-7 at 16:00.
<b>Aug 22</b>	Cloudy with overnight fog. Rain showers from mid afternoon onward. Wind S 6-8 <b>with G 11</b> . High 22.
<b>Aug 23</b>	Mainly clear. Wind NW 4-6 becoming W 3-4 late in the day. High 23.
<b>Aug 24</b>	Clear then mostly cloudy from 15:00 onwards. Wind W 3 but SSW 6-8 in afternoon evening. High 24.
<b>Aug 25</b>	Few sunrise fog patches. Otherwise Clear to early afternoon then cloudy. Wind S 3-4 then <b>SSW 8-11</b> dropping to SSW 6 in evening. High 25. Remnants of TS. Irene forecast for Sunday the 28 <sup>th</sup> .
Precipitation Summary: 17 days with more than 0.2 mm. Heavy precipitation days $> 20$ mm: July 20 <sup>th</sup> , August 2 <sup>nd</sup> and August 8 <sup>th</sup> .	

Table 3. Descriptive statistics of PM<sub>2.5</sub> mass (µg/m<sup>3</sup>) and species mass (µg/m<sup>3</sup>) used in the PMF analysis

	n	Mean	Std	Min	25th Pctl	Median	75th Pctl	Max	Data Completeness %	LOD
Total PM <sub>2.5</sub>	45	4.5	3.4	0.08	2.1	3.9	5.6	13.7	100	0.04
Black Carbon	45	0.41	0.21	0.12	0.26	0.39	0.52	1.03	100	0.01
Organic Matter	45	1.05	0.72	0.18	0.48	0.77	1.50	2.77	85	0.10
Al	45	0.020	0.016	0.0091	0.0091	0.011	0.028	0.086	100	0.0070
As	45	0.0010	0.00076	0.00015	0.00054	0.00087	0.00114	0.0040	100	0.00010
Ba	45	0.0063	0.0020	0.0031	0.0056	0.0056	0.0063	0.0163	100	0.0026
Br	45	0.0015	0.00079	0.00095	0.0010	0.0013	0.0017	0.0047	100	0.00086
Ca	45	0.017	0.019	0.0021	0.0089	0.014	0.016	0.13	100	0.0015
Cl	45	0.046	0.070	0.0019	0.0042	0.011	0.045	0.32	100	0.0015
Cr	45	0.0022	0.00079	0.00035	0.0017	0.0020	0.0027	0.0040	100	0.00030
Cu	45	0.0013	0.00050	0.00062	0.00095	0.0013	0.0015	0.0028	100	0.00060
Fe	45	0.0240	0.0200	0.00110	0.0110	0.0180	0.0280	0.0970	100	0.00065
K	45	0.023	0.019	0.0017	0.011	0.018	0.027	0.11	100	0.0010
Mg	45	0.017	0.018	0.0039	0.0060	0.014	0.020	0.11	100	0.0035
Mn	45	0.00031	0.00029	0.00010	0.00010	0.00025	0.00036	0.0017	100	0.00005
Na	45	0.11	0.12	0.0089	0.037	0.090	0.13	0.73	100	0.00081
NH <sub>4</sub> <sup>+</sup>	45	0.23	0.27	0.0030	0.066	0.15	0.27	1.45	100	0.0010
Ni	45	0.0011	0.00078	0.00044	0.00046	0.00070	0.0015	0.0037	100	0.00016
NO <sub>3</sub> <sup>-</sup>	45	0.093	0.10	0.0074	0.042	0.067	0.10	0.64	100	0.0030
P	45	0.0020	0.0017	0.000040	0.00079	0.0015	0.0023	0.0081	100	0.000010
Pb	45	0.00037	0.00035	0.000060	0.00014	0.00027	0.00050	0.0017	100	0.000032
S	45	0.39	0.34	0.0022	0.18	0.29	0.42	1.81	100	0.0009
Se	45	0.00019	0.00027	0.000080	0.000080	0.000080	0.000080	0.0015	100	0.00008
Si	45	0.042	0.048	0.0044	0.014	0.030	0.056	0.29	100	0.0036
SO <sub>4</sub> <sup>2-</sup>	45	0.78	0.97	0.14	0.26	0.47	0.70	5.59	100	0.070
Sr	45	0.00055	0.00034	0.000010	0.00041	0.00049	0.00060	0.0021	100	0.000010
V	45	0.0033	0.0027	0.0016	0.0016	0.0026	0.0038	0.017	100	0.00092
Zn	45	0.0023	0.0017	0.00070	0.0012	0.0019	0.0030	0.0089	100	0.00051