Source Apportionment of PM$_{2.5}$ in Montréal, Canada and Health Risk Assessment for Potentially Toxic Elements

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Abstract. Source apportionment of PM$_{2.5}$ was performed using positive matrix factorization (PMF) based on detailed chemical composition data from 24-h filters collected over 3-months period (August-November 2020) at an urban site in Montréal, a Canadian city with a population of approximately 4 million people. This source apportionment study, which examined the main contributing sources to PM$_{2.5}$ using a large suit of organic molecular markers, is the first of its sort in Canada. A focus of this study was on quantifying previously unresolved sources of PM$_{2.5}$ through the inclusion in the PMF analysis of additional organic molecular markers beyond those measured typically by the Canadian government's National Air Pollution Surveillance Program (NAPS). The organic species included in the PMF model were namely, n-alkanes, hopane, fatty acids, dicarboxylic acids, and biogenic secondary organic aerosols (SOA) tracers. Secondary inorganic aerosols (SIA) and SOA were the dominant components and constituted 39% of the measured PM$_{2.5}$ mass while the local primary anthropogenic sources, namely traffic exhaust, road dust, industrial, and cooking emissions contributed 23%. The chemical transport model GEOS-Chem revealed that ammonium sulfate concentrations in Montréal are strongly influenced by both local sources in Québec and transboundary input from the United States, with the transboundary input exceeding the local emissions for SOA. Co and Cr(VI) presented an elevated cancer risk, highlighting that more attention should be given to these trace metals, which were associated with industrial emissions by the PMF analysis. Furthermore, the results showed that industrial emissions were minor contributors to the total PM$_{2.5}$ mass, but the largest contributors to Co and Cr(VI) concentrations. Thus, the health hazards associated with this source cannot be entirely established by the PM$_{2.5}$ mass concentration alone. This study highlights that, when evaluating air quality in Montréal and other urban regions, the prioritization of sources for mitigations strategies will diverge if one considers total PM$_{2.5}$ mass concentration or the concentration of individual particulate-bound contaminants. Furthermore, the large transboundary contribution from the United States to total PM$_{2.5}$ levels suggests that future municipal, provincial and federal monitoring and regulations would be more effective if they focus on specific high-risk contaminants (e.g., Co and Cr(VI) rather than total PM$_{2.5}$.

1 Introduction

Outdoor air pollution is a serious threat to human health and is responsible for over 4 million premature deaths worldwide annually (Nansai et al., 2021). Among the various air pollutants, particulate matter (PM) is one of the most problematic and has been classified within Group 1 "carcinogenic to humans" by the International Agency for Research on Cancer (IARC).

40 Particle size is a critical parameter for assessing health impacts, and PM with an aerodynamic diameter less than 2.5 µm ($PM_{2.5}$) represents a greater threat to health than coarser particles as these fine particles can penetrate deeply into the respiratory tract and induce adverse health effects such as respiratory and cardiovascular diseases (Lelieveld et al., 2019). Outdoor air pollution continues to have serious health consequences in Canada (EAR, 2019; Jeong et al., 2011; Bari & Kindzierski, 2016). The government of Canada estimates that approximately 15,300 premature deaths per year are linked to

45 air pollution (Health Canada, 2021). Montréal, a Canadian city in the province of Québec, is the largest city in the province and the second largest in Canada with a population of approximately 4 million people. The city maintains a network of 14 monitoring stations that continuously measure the concentrations of major pollutants (e.g., PM, ozone, sulfur dioxide (SO_2), nitrogen oxides (NO_X), ozone etc.). These municipal monitoring stations also belongs to Environment and Climate Change Canada's National Air Pollution Surveillance (NAPS) program which is the principal source of ambient air quality data in

50 Canada (EAR, 2020) and provides also speciated PM composition measurements via off-line analyses at a limited number of sites. The resulting data enable a portrait to be drawn of the evolution of pollutant concentrations in Montréal over the years. The concentrations of $PM_{2.5}$ in Montréal's ambient air have been decreasing since 2011. The 3-year average concentration of $PM_{2.5}$ decreased from 9.7 µg/m^3 (2011-2013) to 7.3 µg/m^3 (2018-2020) (EAR, 2017; 2018; 2019; 2020). However, in September 2021, WHO released revised global air quality guidelines with a recommended $PM_{2.5}$ concentration of 5 µg/m^3,

55 meaning that the $PM_{2.5}$ concentrations in Montréal exceed WHO recommendations (WHO, 2021). Thus, it is important to continue to improve air quality in the city.

To effectively reduce PM emissions in the metropolitan area and design effective local PM control strategies, it is necessary to have a better understanding of the dominant emission sources and associated health risk. Over the years several efforts have been made to improve the knowledge about the sources of atmospheric particles in Canada using the receptor-based

60 source apportionment model positive matrix factorization (PMF) and NAPS $PM_{2.5}$ chemical speciation datasets as inputs (Bari & Kindzierski, 2016; Dabek-Zlotorzynska et al., 2011; Jeong et al., 2011; Celo et al., 2021). In Québec, there are six NAPS sites that provide speciated $PM_{2.5}$ measurements, three of which are in the Montréal area namely Chateauneuf (NAPS ID: S50124), Molson (NAPS ID: S50134) and Riviere des Prairies (NAPS ID: S50129). However, samples are collected once every 3 or 6 days, and operating on this sampling frequency does not allow reliable quantification of the concentration

65 distribution's extremes because this sampling schedule may exclude days of very high or low concentrations from a given source. Another limitation is the lack of data on organic compounds, which can be valuable tracers for certain $PM_{2.5}$ sources (Fadel et al., 2021, Fakhri et al., 2023). To date, investigations of PM concentrations and chemical composition from NAPS

sites in Canada have generally focused on determining the elemental (EC) and organic carbon (OC) concentrations as well as the elemental and ionic content of PM.

70 In this work, $PM_{2.5}$ chemical composition and emission sources as well as potential human health risk associated with trace elements in the $PM_{2.5}$ are investigated for an urban site in Montréal over a 3-month period (August-November). In addition to water-soluble ions, elements, EC, and OC, the measurements of $PM_{2.5}$ composition included a large suite of organic molecular markers. This study uses these measurements to explore qualitatively potential sources (e.g., via correlations of elements) before proceeding to a more quantitative approach to source apportionment using PMF. Source apportionment of

75 $PM_{2.5}$ was performed using simultaneously organic and inorganic species in the PMF model. The aim of this work is to investigate previously unresolved PM sources in Montréal, such as primary and secondary biogenic and anthropogenic sources by using some selected organic markers, namely n-alkanes, hopane, fatty acids, dicarboxylic acids, and biogenic secondary organic aerosol tracers in the PMF model. To our knowledge, this study represents the first time that such extensive composition measurements were included in a source apportionment study in Montréal. Furthermore, the GEOS-

80 Chem chemical transport model was used to evaluate local and long-range contributions to the most significant PM components, providing more information on the origin of PM. Lastly, a health risk assessment model was used to determine the associated risk of the elemental components from the sources identified using the PMF model.

2 Method

2.1 PM₂.₅ Sampling

85 Sampling was conducted at an urban site in Montréal from 13 August to 11 November 2020. The sampling site, labeled as MTL, was located on the rooftop of Campus MIL (12 m above ground level) at the University of Montréal (45°31′23" N, 73°37′10" W) in the neighborhood of Outremont. The site is characterized by a high density of residential and commercial premises.

A total of 80 $PM_{2.5}$ filters (150 mm quartz-fiber filters, PALL) were collected with a 24 h resolution using a high-volume

90 sampler (CAV-A/MSb, MCV S.A., Spain) operating at 30 m^3/h. Filters were baked at 550 °C for 12 h before sampling to eliminate the organic impurities and kept at -20 °C until sampling. Collected filters were also stored at -20 °C until analysis. Field blank samples were collected by loading filters into the sampler but without operating the sampler's pump. A total number of 8 field blank samples were also analyzed with the same techniques as the sample filters. The concentrations of the species in the $PM_{2.5}$ samples were corrected by subtracting the average field blank values. Additional QA/QC procedures

95 were applied on the different analysis techniques/protocols used (e.g., determination of detection limits and recovery, as well as validation using certified reference material) (Fakhri et al., 2023). $PM_{2.5}$ mass concentration was determined by weighing the filters before and after sampling using a VWR microbalance with a 1 µg readability (Abdallah et al., 2018, Fadel et al., 2022b).

2.2 Chemical analysis

100 The chemical analyses are detailed in Fakhri et al. (2023) and will only be briefly presented here. Elemental carbon (EC) and organic carbon (OC) were analyzed using the thermo-optical transmission method on a Sunset Laboratory analyzer following the EUSAAR2 (European Supersites for Atmospheric Aerosol Research) protocol (Cavalli et al., 2010).

Major (Al, Fe, K, Mg, Na) and trace (Zn, Ni, Sr, Cu, Ti, Co, Cr, V, Mn, Cd, Mo, Sb, Pb) metals and metalloids were analyzed using an inductively coupled plasma mass spectrometer (PerkinElmer, NexION, 300x). In brief, a punch (18 mm^2)

105 was taken from the quartz filters and digested in a mixture of ultrapure HNO_3 (4 mL of 67-70% (w/w), Baker ARISTAR ULTRA supplied by VWR International) and HCl (1 mL of 35-38% (w/w), Trace Metal Grade, Fischer Chemical) in a Microwave Reaction System (CEM, Mars-Xpress, MARS 230/60). The oven program was set to an initial temperature ramp reaching 180 °C in 5.5 min with a subsequent holding period of 9.5 min. Matrix-matched ICP-MS calibration standards were prepared using IV-ICPMS-71a (Inorganic Ventures) and quality control standards were prepared using QCS-27 (High-Purity

110 Standards). Two external calibration methods were used for sample analysis: one for trace metals and metalloids where the calibration range was between 0.05 and 10 µg/L, and the other for the analysis of major metals where the calibration range was between 3 and 500 µg/L. The calibration curves showed good linearity with R^2 greater than 0.999. An internal standard solution comprised of Sc, Y, In, and Bi was analyzed along with the samples, with recovery ranging from 90 – 130%. The analytical procedure was validated by considering a certified reference material NIST-SRM 1648a (Urban particulate matter,

115 National Institute of Standards and Technology, United States of America). Data for a given metal were accepted as quantitative if NIST SRM 1648 recovery was 80 – 110%.

Soluble anions and cations were analyzed by ionic chromatography after extracting a punch (20 mm) of each quartz filter by ultrasonic agitation in 6 mL of MilliQ water (Elga Veolia Purelab Chorus 1, 18.2 MΩ at 25 °C) for 45 min, by means of a Dionex ICS 5000$^+$ instrument. For anion analysis, a Dionex IonPac AS11-HC anion column (2×250 mm), a Dionex IonPac

120 AG11-HC (2×50 mm) pre-column and a Dionex AERS 500 suppressor were used. Thermo Scientific Dionex KOH with a gradient of 1-45 mM was used as the eluent in the anion analysis with a flowrate of 0.5 mL/min. For cation analysis, a Dionex IonPac CS12 cation column (2×250 mm), a Dionex IonPac CG12 (2×50 mm) pre-column and a Dionex CSRS 300 4 mm suppressor were used during the cation analysis. Thermo Scientific Dionex 12 mM methanesulfonic acid with a flowrate of 0.3 mL/min was used as eluent in the cation analysis.

125 Sugar alcohols were analyzed by ion chromatography with pulsed amperometric detection (IC-PAD) by means of a Dionex ICS 5000$^+$ instrument using a Dionex CarboPac MA1 column (4×250 mm) and a Dionex CarboPac MA1 (4×50 mm) pre-column. Thermo Scientific Dionex 0.35 M NaOH with a flowrate of 0.6 mL/min was used as eluent in the sugar analysis.

The method used for the organic compounds analysis was described elsewhere (Fadel et al., 2021; Fakhri et al., 2023; El Haddad et al., 2011). Briefly, a punch of the sample filter (73 cm^2) was spiked with two internal standards (D50-tetracosane

130 and D6-cholesterol obtained from Sigma Aldrich) followed by an extraction using an accelerated pressurized solvent extraction device at 100 °C and 100 bars (ASE, Dionex 350) and an acetone/dichloromethane mixture (1/1, v/v). After

extraction, samples were concentrated to a volume of 200 µL using a constant gentle flow of nitrogen gas. 50 µL of the extracts was then derivatized with the addition of 50 µL of N,O-bis(trimethylsilyl)- trifluoroacetamide (BSTFA) (99%, Sigma Aldrich) with 10 µL of pyridine (catalyst) (99%, Sigma Aldrich) at 70 °C for 2 h. Aliquots of 2 µL of the derivatized
135 extracts were immediately analyzed using a GC-MS in split mode. In addition, aliquots of 2 µL of the non-derivatized fraction were also analyzed using the GC-MS in split mode. The gas chromatograph (Agilent 6890N) was equipped with a HP-5MS UI fused silica capillary column (5%-phenyl, 95%-methylpolysiloxane, 0.25 µm film thickness, and 30 m × 0.25 mm) and interfaced to an ion trap MS with an external electron ionization (EI) source (200 °C, 70 eV). Full scan mode was used in the mass range of 50-550 m/z.

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2.3 Enrichment factor

The enrichment factor (EF) was calculated to determine whether a certain element in $PM_{2.5}$ may have a significant anthropogenic source. EF (Eq. 1) is defined as the ratio of the considered element concentration (C_X) to the reference element concentration Al (C_{Al}) in $PM_{2.5}$ divided by the same ratio for crustal material retrieved from the upper crust (Mason
145 & Moore, 1982). An EF value close to 1 indicates an element originates from crustal materials while an EF higher than 10 indicates a strong anthropogenic source (Esmaeilirad et al., 2020).

$$EF= \left(\frac{C_X}{C_{Al}}\right)_{air} / \left(\frac{C_X}{C_{Al}}\right)_{crust} \qquad (Eq. 1)$$

2.4 Health risk assessment

The United States Environmental Protection Agency (USEPA) recommends using a health risk assessment model to
150 determine the health risks from airborne elements. For each of the three exposure pathways, namely inhalation, ingestion, and dermal contact, the carcinogenic and non-carcinogenic health risks were evaluated for children and adults using the measurements taken at the MTL site. This study analyzes the non-carcinogenic risks of Al, Fe, Cu, Zn, Sb, Co, Cr(VI), Ni, V, Cd, Pb and Mn as well as the carcinogenic risk of Cr(VI), Co, Ni, V, Cd and Pb. The average daily dose (ADD in mg/kg per day) for children (0-17 years) and adults (18-70 years) for the three exposure pathways and the exposure concentration
155 through inhalation ($EC_{inhalation}$ in mg/m³) were calculated following Eqs 2-5 (Fadel et al., 2022a, 2022b; Roy et al., 2019). Each of the parameters used in the various formulas are listed in **Table 1** and were retrieved from USEPA reports (USEPA 2004, 2011). Moreover, since chromium toxicity is attributed to its hexavalent state, Cr(VI) concentration was determined as one-seventh of total Cr (Dahmardeh Behrooz et al., 2021; Hao et al., 2020, Fadel et al., 2022b).

160 $$ADD_{ingestion} = \frac{C \times IngR \times EXP \times ED \times CF}{BW \times AT} \qquad (Eq. 2)$$

$$ADD_{dermal} = \frac{C \times SA \times AF \times ABS \times EXP \times ED \times CF}{BW \times AT} \qquad (Eq. 3)$$

$$ADD_{inhalation} = \frac{C \times InhR \times EXP \times ED \times CF}{BW \times AT} \qquad (Eq. 4)$$

$$EC_{inhalation} = \frac{C \times EXP \times ED \times ET \times CF}{AT \times 24} \qquad (Eq. 5)$$

165 **Table 1:** Exposure parameters for children and adults.

Exposure parameters		Unit	Adults	Children
Concentration of metal in PM$_{2.5}$	C	ng/m^3 (inhalation) and mg/kg (ingestion and dermal)		
Ingestion rate	IngR	mg/day	50	100
Inhalation rate	InhR	m^3 per day	15.6	12.3
Exposure frequency	EXP	days/year	350	350
Exposure duration	ED	years	52	17
Conversion factor	CF	kg/mg	10^{-6}	10^{-6}
Body weight	BW	kg	70	37
Exposed skin area	SA	cm^2	5700	2800
Adherence factor	AF	mg/cm^2	0.07	0.2
Exposure time	ET	h/day	8	8
Dermal adsorption factor	ABS	-	0.001 for Cd 0.01 for other metals	
Averaging time	AT	days	Non-carcinogens: AT=ED × 365 (days) Carcinogens: AT=70 years × 365	

The hazard quotient (HQ), which is determined by dividing the ADD from each exposure pathway by a specified reference dose (R_fD) (mg/kg per day) for the same exposure route, can be used to measure the non-carcinogenic health risk effects
170 from metals as presented in Eq. 6 (Fadel et al., 2022a, 2022b; Hao et al., 2020). The non-cancer risk refers to the likelihood of developing health issues other than cancer as a result of exposure to chemical pollutants such as asthma, nervous system disorders, cardiovascular and respiratory disorders (Fadel et al., 2022a).

To assess the overall potential for non-carcinogenic consequences produced by multi-element exposure for one exposure pathway, the hazard index (HI_i) was calculated as the sum of the HQ_{ij} (i is the exposure pathway which is either inhalation, ingestion, or dermal contact, and j is the targeted compound) (Eq. 7). HI_{total} represents the total hazard index (HI_{total} = $HI_{inhalation}$ + $HI_{ingestion}$ + HI_{dermal}). An HI value higher than one implies that the non-cancer risk merits attention and indicates that adverse health effects are likely to occur (Dahmardeh Behrooz et al., 2021).

$$HQ_i = \frac{ADD_i}{R_f D_i} \qquad (Eq. 6)$$

$$HI_i = \sum HQ_{ij} \qquad (Eq. 7)$$

The carcinogenic risks (CR) are estimated using Eq. 8-10, which refers to the probability that a person might develop a cancer over a lifetime because of exposure to a carcinogen chemical (Dahmardeh Behrooz et al., 2021; Fadel et al., 2022a, 2022b). According to the USEPA, a cancer risk value between 10^{-6} (one additional case per one million people) and 10^{-4} (one in a ten thousand) indicates that the carcinogenic risk is considered as tolerable while a value higher than 10^{-4} indicates that a serious risk of cancer exists (Bari and Kindzierski, 2016; Dahmardeh Behrooz et al., 2021). CR_{total} represents the total carcinogenic risk (CR_{total} = $CR_{ingestion}$ + $CR_{inhalation}$ + CR_{dermal}).

$$CR_{ingestion} = ADD_{ingestion} \times CSF \qquad (Eq. 8)$$

$$CR_{inhalation} = EC_{inhalation} \times IUR \qquad (Eq. 9)$$

$$CR_{dermal} = ADD_{dermal} \times CSF \qquad (Eq. 10)$$

In the equations above CSF is the cancer slope factor for a chemical in a specific exposure pathway (mg/kg per day) and IUR is the inhalation unit risk (m^3/mg) (**Table S1**).

2.5 Source apportionment

The USEPA PMF v5.0 software was used to identify and quantify the major emission sources in Montréal. PMF is a multivariate factor analysis tool that decomposes a data matrix X (n x m) into two matrices: source contributions G (n x p) and sources profiles F (p x m), where n is the number of samples, m is the number of species and p is the number of factors or sources. The PMF model requires the concentration data set of the samples and associated uncertainty as inputs. The goal is to solve the chemical mass balance (Eq. 11) between the measured species concentrations and source profiles:

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$$x_{ij} = \sum_{k=1}^{p} g_{ik} \, f_{kj} + e_{ij} \qquad \text{(Eq. 11)}$$

where x_{ij} is the concentration of the species j in the ith samples, g_{ik} is the contribution of the kth source in the ith samples, f_{kj} is the relative concentration of species j from the source k, and e_{ij} is the residual of species j in the ith sample. The values of g_{ik} and f_{kj} are adjusted until a minimum value of Q (Eq. 12) for a given number of factors p is found:

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$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left(\frac{e_{ij}}{u_{ij}}\right)^2 \qquad \text{(Eq. 12)}$$

where e is the residual value and u is the uncertainty in a measurement. The residual value is the difference between the measured value and the PMF-modeled concentration of each compound. In the present work, samples below the detection

215 limit (DL) were replaced by half of the DL and were given an uncertainty of 5/6 times the detection limit (Polissar et al., 1998). Missing samples were replaced by the median value of that species and were given an uncertainty of 4 times the median value (Polissar et al., 1998).

After screening the integrity of the input data, 27 species were included in the PMF model. The overall number of samples (80 samples) and the number of species complies with the ratio of at least 3:1, as proposed by Belis et al., (2019). The

220 species included were OC and EC, major water-soluble ions (Na^+, Cl^-, NH_4^+, NO_3^- and SO_4^{2-}) and a selection of elements (Al, Fe, Ti, Cu, Sb, Cd and Co). Levoglucosan was included as a tracer for biomass burning, 17α[H]-21β[H]-Hopane as a tracer for vehicular emissions, fatty acids (hexadecanoic acid and octadecanoic acid) for cooking activities, a set of n-alkanes for biogenic (C27, C29) and anthropogenic emissions (C20, C21, C24, C25), and finally a dicarboxylic acid (oxalic acid) and α-pinene oxidation products (pinic acid and cis-pinonic acid) as tracers for SOA.

225 All the included species were defined from weak to strong in the PMF model based on their signal-to-noise ratio (S/N). When the S/N ratio was less than 0.2, the PM species were classified as "bad," "weak" when the S/N ratio was between 0.2 and 2, and "strong" when the S/N ratio was greater than 2 (Esmaeilirad et al., 2020). The bad species are excluded from the analysis while the uncertainty for the weak species is tripled. PM$_{2.5}$ was designated as a "total variable" and was automatically classified as "weak". All the included species were successfully modeled by PMF with their concentrations

230 reconstructed accurately and were qualified as "strong" except for nitrate which presented a S/N ratio of 0.9 and was defined as "weak".

The final solution was selected based on several criteria such as (1) comparison of the resulting source profiles against the literature, (2) lack of correlation between the resolved factors, (3) correlation between the predicted vs measured PM$_{2.5}$ concentrations (4) correlation between the modeled and measured species concentrations (R^2 higher than 0.8), (5) maximum

235 individual mean (IM) and maximum individual standard deviation (IS) (**Fig. S1**). The R^2 between the reconstructed and

measured PM$_{2.5}$ mass was 0.87 (**Fig. S2**). The robustness of the PMF solution was tested by the two-error estimation method (bootstrap and displacement) as instructed in the PMF manual to ensure the solution was stable (**Table S2**) (USEPA, 2014).

2.6 GEOS-Chem Simulations

240 We performed simulations using the GEOS-Chem chemical transport model (version 14.0.1, doi:10.5281/zenodo.7271960) (Bey et al., 2001, Park et al., 2004). GEOS-Chem is driven by assimilated meteorology from the Modern-Era Retrospective analysis for Research and Applications, Version 2 (MERRA-2), at the NASA Global Modeling and Assimilation Office (GMAO). The atmosphere was resolved using 47 vertical layers from the surface to 0.01 hPa. The vertical resolution of the model is about 100 m near the surface, but it becomes coarser at higher altitudes. We generate boundary conditions using a

245 global simulation at 2° latitude x 2.5° longitude resolution. We then used a nested grid with 0.5° latitude x 0.625° longitude resolution, spanning 35° N to 65° N, 90° W to 50° W (**Fig. S3**) in order to include the full province of Quebec as well as the strong source regions of the Great Lakes region and the northeastern US. We use the recently developed treatment of wet scavenging described by Luo et al. (2020, 2019), which has been previously shown to yield better agreement for nitrate and ammonium concentrations over eastern North America.

250 Biomass-burning emissions were simulated from the Copernicus Atmosphere Monitoring Service Global Fire Assimilation System (GFAS, Kaiser et al., 2012). We used global emissions from the Community Emissions Data System version 2 (CEDS v2, O'Rourke et al., 2021, Hoesly et al., 2018), except where overwritten by regional emissions inventories, as described in Keller et al. (2014). These regional emissions inventories included anthropogenic emissions from the US and most of Canada up to 54° N, provided by the National Emissions Inventory for 2016 (EPA, 2021a), with annual scaling

255 factors to account for changes in emissions since 2016 (EPA, 2021b). Shipping emissions were provided by CEDS v2, and aircraft emissions were provided by the Aviation Emissions Inventory Code (AEIC, Stettler et al., 2011, Simone et al., 2013). Anthropogenic emissions of fine dust aerosols were from the Anthropogenic Fugitive, Combustion, and Industrial Dust (AFCID) inventory (Philip et al., 2017), while natural dust emissions were calculated according to the Mineral Dust Entrainment and Deposition (DEAD) parameterization (Zender, 2003). Formation of SOA was parameterized using the

260 "simple" SOA scheme that treats all organic aerosol as non-volatile, as described in Pai et al. (2020). It has been shown to reproduce observed organic aerosol concentrations with similar skill to a more complex scheme. GEOS-Chem resolves mineral dust in four size bins spanning radii of 0.1-1.0, 1.0-1.8, 1.8-3.0, and 3.0-6.0 µm. In this study, we will approximate the concentration of dust in particles smaller than 2.5 µm in diameter by adding 38 % of the concentration of dust in the 1.0-1.8 µm size bin to the concentration of dust in the 0.1-1.0 µm size bin (Fairlie et al., 2010, Zhang et al., 2013).

265 GEOS-Chem has previously been evaluated against NO$_2$ concentrations from the USEPA Air Quality System sites (Silvern et al., 2019), satellite observations of aerosol optical depth, speciated aerosol concentrations from aircraft measurements over the United States (US) and speciated surface observations from the USEPA Chemical Speciation Network (CSN), Interagency Monitoring of Protected Visual Environments (IMPROVE), and the Southeastern Aerosol Research and

Characterization (SEARCH) Network (Kim et al., 2015), and ozone concentrations from the Clean Air Status and Trends

270 Network (CASTNet, Reidmiller et al. 2009). In all cases, GEOS-Chem has been shown to adequately resolve emissions, atmospheric processes, and large-scale transport. The model performance was evaluated against the observations presented in this study and good correlation with the observed values was obtained (R=0.24-0.76) (**Table S3**). Some of the indicators are not within the acceptable limits (Abdallah et al., 2018) and this is likely because of the vertical and horizontal resolution of the model. Thus, the PMF results and the model outputs will be compared qualitatively. Furthermore, GEOS-Chem results

275 have been previously used for source contribution analysis similar to the analysis presented in this study (Meng et al. 2019). In order to examine the sensitivity of air pollutant concentrations to contributions from source regions, we perform a base-case simulation and three sensitivity simulations, each with anthropogenic emissions from a geographic region turned off: noQC, noCA, and noUS. In the noQC simulation, we do not allow any anthropogenic emissions within the borders of the province of Quebec. In the noCA simulation, we do not allow any anthropogenic emissions within the borders of Canada,

280 except for emissions from the province of Quebec (Rest of Canada, RoC). In the noUS simulation, we do not allow any anthropogenic emissions within the borders of the contiguous US. Emissions from shipping and aircraft are removed within the boundaries of the specified region, but we have not changed emissions from biomass burning or natural sources. We note that for the purposes of masking emissions, each model grid cell is considered to be entirely within one province or country; the resolution of the provincial or national masks is the same as the model resolution. By calculating the differences in the

285 concentrations of PM components in the sensitivity simulations compared to the base-case simulation, we qualitatively evaluate the proportions of air pollutants in Quebec due to sources within Quebec, sources in the RoC, and sources in the contiguous US.

3 Results and discussion

3.1 PM$_{2.5}$ concentrations

290 The average PM$_{2.5}$ concentration (and standard deviation) at the MTL site was 4±3 µg/m^3. The concentration of PM$_{2.5}$ in all samples collected at MTL site was lower than the daily standard set by the World Health Organization (WHO) (15 µg/m^3) (WHO, 2021) and the Canadian daily standard of 27 µg/m^3 (EAR, 2019) (**Fig. 1**). The PM$_{2.5}$ levels at the MTL site can be compared against nearby government monitoring stations to understand if there are large differences in concentrations and how concentrations have changed over recent years in this area of Montréal. The average concentrations at MTL were lower

295 than that reported during the same sampling period at Décarie station (6.6 µg/m^3) located ~5 km South-West of the MTL site near an intersection of two major highways (**Fig. 2**). Given that the Décarie station is strongly impacted by vehicle emissions, this difference is not surprising. In contrast, the average PM$_{2.5}$ concentration at the MTL site is similar to that recorded at the Molson station (NAPS ID: S50134; ~4 km North-East of MTL) (4.7 µg/m^3), which is located in a mixed residential/industrial zone for the same sampling period. Furthermore, there is a general decreasing trend between 2017 and

300 2020 in PM$_{2.5}$ levels at the government monitoring stations. Since the concentrations of PM$_{2.5}$ in 2020 was not too different

in comparison with the previous years (2018 and 2019), the sources of $PM_{2.5}$ of this study could be generally applicable to other years.

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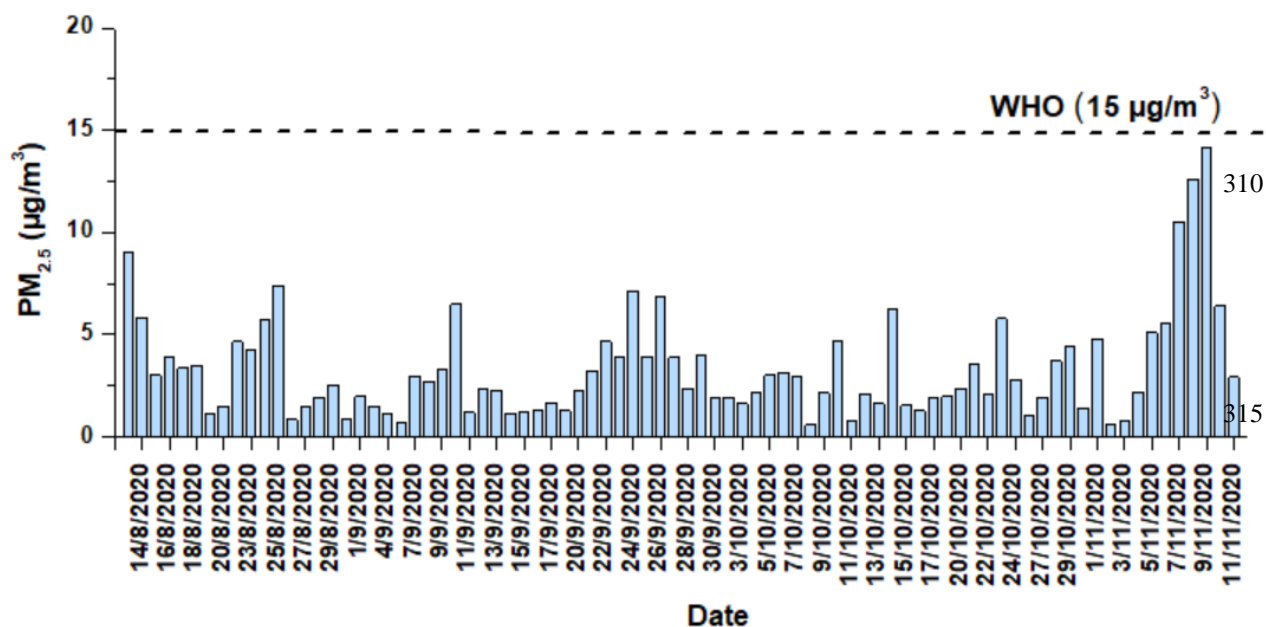

320

Figure 1. The temporal variation of $PM_{2.5}$ concentrations for the sampling period (13 August to 11 November 2020).

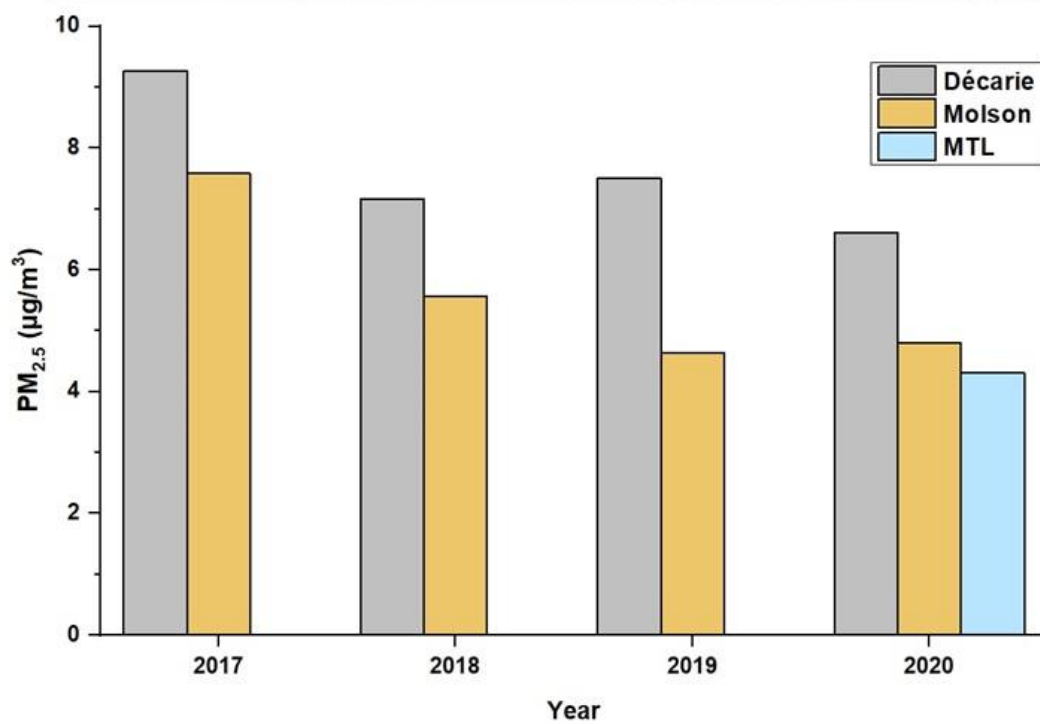



Figure 2. $PM_{2.5}$ concentrations for the sampling period (13 August to 11 November 2020) at MTL, Décarie and Molson sites between 2017 and 2020 along with the location of the sampling sites (© Google Earth®).

3.2 Carbonaceous matter

The average OC and EC concentrations (± standard deviation) were 1.31±0.76 μg/m^3 and 0.17±0.15 μg/m^3, respectively (**Table 2**). While EC originates from combustion sources and has a primary origin, OC can be directly emitted from combustion of fossil fuels, biomass burning, cooking activities, and can also be formed in the atmosphere through chemical reactions (Hallquist et al., 2009). The OC/EC ratio is a useful diagnostic ratio that provides information on the sources in PM$_{2.5}$. An OC/EC ratio ranging between 0.3 and 1 was reported for diesel vehicles, between 1.4 and 5 for gasoline operated vehicles while a larger OC/EC ranging between 4.1 and 14.5 for biomass burning (Khan et al., 2021; Salameh et al., 2015). In this study, the ratio of OC/EC was 7.42±3.12, which is larger than those associated with vehicular emissions and consistent with the presence of biomass burning. Indeed, wood burning may be an important source of air pollutants in Quebec and wood-burning stoves and fireplaces are used in both residential and businesses settings (e.g., pizzerias and bagel factories). The production of secondary organic carbon will also increase OC/EC ratios beyond values measured for primary sources. Indirect methods have been developed for identifying primary (POC) or secondary organic carbon (SOC) (Shivani et al., 2019).

$$ SOC = OC_{total} - EC \times \left(\frac{OC}{EC}\right)_{min} \quad (Eq. 13) $$

One such method is summarized in Eq. 13, OC$_{total}$ is the measured OC and (OC/EC)$_{min}$ is the minimum ratio observed in the samples. Using this method, the average contribution of SOC to the total OC and the standard deviation was 61±15% at the MTL site indicating a strong SOC contribution.

3.3 Organic species

Some organic compounds are specific to a certain source and have been used in source apportionment studies as molecular markers. The average concentrations of selected organic compounds in PM$_{2.5}$ measured at the MTL site are summarized in **Table 3**. Levoglucosan, generated by the pyrolysis of cellulose and often utilized as a particular marker of biomass burning (Simoneit, 2002), was the most abundant compound among the organic tracers examined. Due to its presence in lubrication oil used in both gasoline and diesel vehicles, 17α(H)-21β(H)-Hopane is a specific marker of traffic emissions, and it was the least prevalent measured organic species in the PM$_{2.5}$ (El Haddad et al., 2009; Fadel et al., 2021). Arabitol and mannitol were well correlated (R=0.98; *p<0.001*) and are commonly described as markers for primary biogenic emissions, more specifically with fungal spores (Petit et al., 2019). Alkanes, specifically acyclic saturated hydrocarbons, can originate from both biogenic and anthropogenic sources. The n-alkane with the highest concentration was C29. In the literature, low molecular weight n-alkanes (<C27) are primarily associated with traffic emissions, whereas high molecular weight n-alkanes (C27, C29, C31) are associated with plant detritus because they are abundant in the epicuticular wax of plants (Rogge et al., 1993a, 1993b).

To further evaluate the contribution of the anthropogenic and the biogenic sources to n-alkanes, the carbon preference index (CPI) was calculated (Fadel et al., 2021; Esmaeilirad et al., 2020). Two CPI parameters were adopted: the Overall CPI for the whole range of n-alkanes (C15-C30), and the High CPI for the higher molecular weight n-alkanes (C25-C30). The detailed description of the calculation method is included in the supplementary material. The average Overall CPI value was 0.86±0.21, indicating the contribution of petrogenic sources. The High CPI values during the entire campaign were between 0.74 and 2.81, with a majority of the measurements in the anthropogenic range and the rest in the mixed anthropogenic/biogenic range (**Fig. 3**). The average High CPI was 1.56±0.48, indicating that larger n-alkanes at the MTL site are predominately anthropogenic with a lesser biogenic contribution.

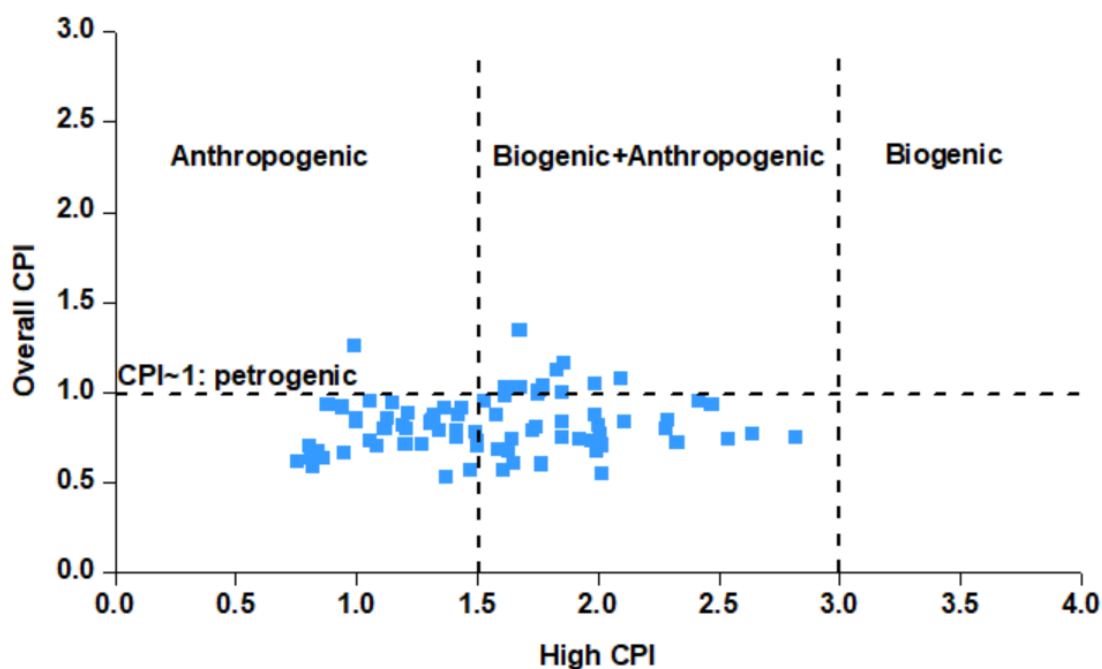



Figure 3. The n-alkanes source identification using the carbon preference index (CPI).

Table 2: Concentrations of major and trace components of PM$_{2.5}$ measured at MTL site.

	Mean	Stdev	Range
			µg/m³
OC	1.31	0.76	0.64-4.23
EC	0.17	0.15	0.05-0.85
SO$_4^{2-}$	0.56	0.40	0.09-2.34
NO$_3^-$	0.18	0.29	0.01-2.21
NH$_4^+$	0.36	0.23	0.03-1.32
Na$^+$	0.04	0.02	0.003-0.13
Cl$^-$	0.03	0.03	0.003-0.13
Mg^{2+}	0.01	0.007	0.001-0.06
K$^+$	0.03	0.03	0.002-0.19
Ca^{2+}	0.11	0.21	0.019-1.90
			ng/m³
Na	109.44	54.52	33.62-335.33
Mg	42.62	44.04	10.79-380.38
Ti	2.57	4.34	0.13-36.11
Al	111.17	62.45	4.93-405.3
K	69.68	36.63	21.72-283.02
Mn	2.97	2.76	0.79-24.72
Fe	76.07	101.66	0.69-932.46
Zn	39.53	38.52	14.04-240.40
Ni	1.21	0.93	0.33-6.35
Sr	1.05	1.41	0.25-11.95
Cu	15.26	19.45	0.44-101.8
Co	3.81	5.76	0.026-27.8
Cr	3.05	0.12	0.05-0.72
V	0.31	0.35	0.03-2.68
Cd	0.13	0.17	0.0004-1.21
Mo	0.30	0.13	0.13-0.99
Sb	0.25	0.21	0.04-1.20
Pb	5.66	5.41	0.63-33.4

380

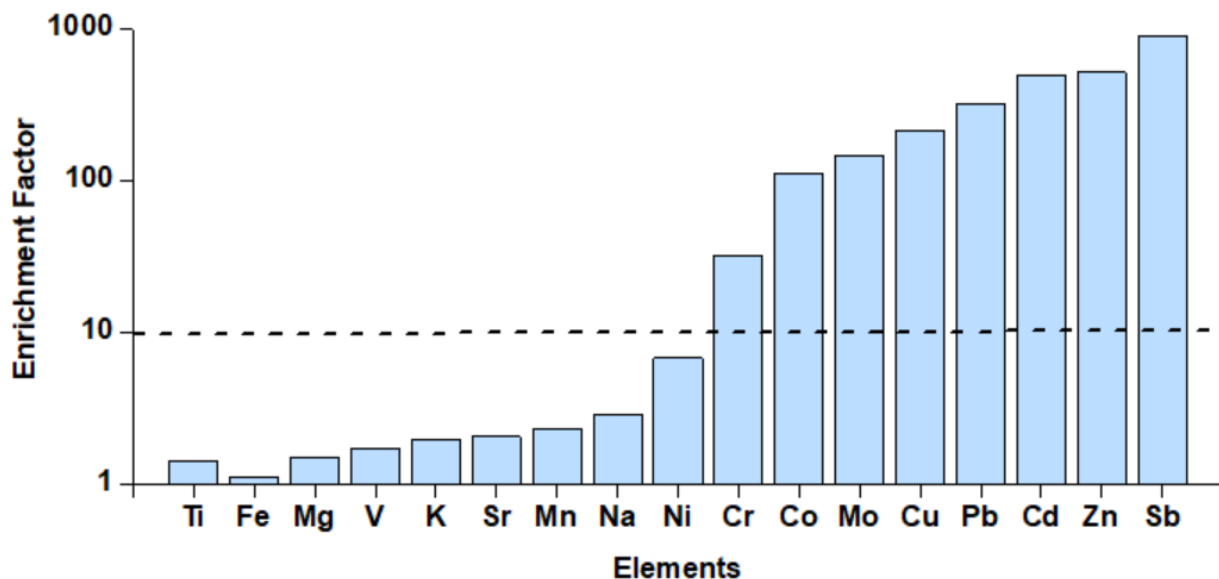
Table 3: Average concentrations (ng/m^3) of organic compounds in PM$_{2.5}$.

	Mean	Stdev	Range
17α(H)-21β(H)-Hopane	0.18	0.01	0.06-0.70
n-Alkanes			
Tetradecane (C14)	0.58	0.31	0.20-1.73
Pentadecane (C15)	0.48	0.66	0.28-4.27
Hexadecane (C16)	0.75	0.37	0.34-2.04
Heptadecane (C17)	0.71	0.67	0.22-5.20
Octadecane (C18)	0.99	1.69	0.18-8.29
Nonadecane (C19)	0.46	0.24	0.17-1.26
Eicosane (C20)	1.82	1.20	0.73-7.90
Heneicosane (C21)	0.99	0.35	0.37-2.14
Docosane (C22)	0.96	1.15	0.37-8.49
Tricosane (C23)	1.02	0.42	0.40-2.16
Tetracosane (C24)	2.24	1.61	0.82-11.16
Pentacosane (C25)	1.97	1.02	0.83-4.97
Hexacosane (C26)	1.51	0.84	0.48-3.96
Heptacosane (C27)	2.52	2.89	0.74-23.82
Octacosane (C28)	1.79	2.84	0.45-23.20
Nonacosane (C29)	3.84	3.78	0.73-3.37
Triacontane (C30)	1.12	1.41	0.12-7.07
Hentriacontane (C31)	1.56	0.96	0.34-6.72
Sugars			
Levoglucosan	33.72	6.45	6.45-126.40
Mannosan	1.03	0.94	0.15-4.59
Mannitol	2.14	3.22	0.23-18.91
Arabitol	3.14	4.29	0.29-39.00
Glucose	2.92	3.01	0.17-24.47
Fatty acids			
Tetradecanoic acid	4.17	1.40	1.66-7.97
Hexadecanoic acid	51.12	13.09	28.39-87-43
Octadecanoic acid	37.06	9.41	18.05-64.90
Oleic acid	4.43	1.65	2.51-13.05
Dicarboxylic acids (DCAs)			
Oxalic acid (diC2)	7.79	1.58	0.28-15.03
Adipic acid(diC6)	1.60	4.18	0.31-3.42
Azelaic acid (diC9)	5.93	2.18	1.12-15.01
Biogenic SOA Tracers			
Pinic acid	4.73	1.78	0.21-8.93
Cis-pinonic acid	3.17	1.71	0.62-9.73

3.4 Elemental composition

To differentiate between the anthropogenic and natural origins of the various elements, the EF was determined. As shown in **Fig. 4**, Ti, Fe, Mg, V, K, Sr, Mn, Na and Ni presented EF values lower than 10, indicating that these elements mainly originate from crustal sources. In contrast, Cr, Co, Mo, Cu, Pb, Cd, Zn and Sb exhibited high enrichment factors, indicating that these elements are predominately from anthropogenic sources. Moreover, a significant correlation ($R>0.95$, $p<0.05$) was observed among Ti, Fe, Mg, V, K, Mn and Na, indicating a common crustal source.

The relationship between trace metals provides qualitative information on the sources of the measured elements. Numerous studies have analyzed the chemical composition of traffic-related PM and have reported that Cu, Sb and Cd are linked to non-exhaust emissions, more precisely from vehicular brake wear (Thorpe and Harrison, 2008; Lin et al., 2015; Pio et al., 2013; Mancilla et al., 2012; Pant et al., 2013). In this study, a correlation of $R=0.82$ ($p<0.05$) was found between Sb and Cd indicating that Sb and Cd originate from the same sources, most probably brake wear. Studies in other Canadian cities, namely Toronto and Vancouver, have also associated the elements Sb and Cd with non-exhaust emissions from road traffic (Celo et al., 2021). No correlation was found between Cu and the elements Cd and Sb ($R<0.01$, $p<0.05$); indicating that brake wear debris was not an important source of Cu in Montréal.

Additionally, Co was correlated with Cr ($R=0.79$, $p<0.01$) and Cu ($R=0.86$, $p<0.05$), suggesting a common source from industrial emissions, similar to observations in Edmonton, Canada (Bari and Kindzierski, 2016). The Canadian Copper Refinery and Suncor Energy refinery can be identified as potential sources of Cr and Co in the Montréal region based on the National Pollutant Release Inventory (NPRI) data published by the Government of Canada (NPRID, 2022). It is important to mention that Cu, Cr and Co could also originate from other sources such as traffic-related emissions and coal combustion (Riffault et al., 2015; Bari & Kindzierski, 2016; Thorpe & Harrison, 2008; Celo et al., 2021). However, these possibilities seem less important given the correlations between the elements as well as the lack of coal combustion in the province of Québec. Lastly, no correlation was found between Zn, Pb and Sb with Cl⁻ ($R<0.09$, $p<0.05$) revealing that incinerators are not a potential source of these trace elements.

410   **Figure 4.** Enrichment factor of selected elements in $PM_{2.5}$. An EF higher than 10 indicates an anthropogenic source.

3.5 Water-soluble ions

Among the water-soluble ions, SO_4^{2-} presented the highest concentration followed by NH_4^+, NO_3^-, Ca^{2+}, Na^+, Cl^-, K^+, and the
415   species with the lowest concentration was Mg^{2+}. The secondary inorganic aerosol components (sulfate, ammonium, and
nitrate) accounted for 83% of the total water-soluble ions and 32% of the total $PM_{2.5}$ mass (**Fig. S5**). The presence of
secondary sulfate is supported by the strong correlation between sulfate and ammonium with a Pearson coefficient of 0.90
($p<0.005$). This result, and the weak correlation between ammonium and nitrate (R=0.27, $p<0.002$), suggests that a
significant fraction of ammonium in $PM_{2.5}$ was associated with ammonium sulfate with a limited amount of ammonium
420   nitrate. Nitrate concentrations were higher in the end of October and November in comparison with the warmer months (**Fig.
S6**) consistent with a shift in equilibrium partitioning from gas-phase nitric acid to the particle-phase nitrate due to colder
temperatures (Geng et al., 2013; Mantas et al., 2014). The Total Ammonium/Total Sulphate (TA/TS) molar ratio was used to
evaluate if the site conditions were ammonia-rich (>2) or ammonia-poor (<2) (Joseph et al., 2012; Remoundaki et al., 2013).
The TA/TS molar ratio was 1.24, highlighting that the concentrations of ammonium are not sufficient to neutralize the
425   concentrations of sulfate and nitrate. Therefore, the latter anions could be associated to different cations such as Na^+, Mg^{2+},
K^+ and Ca^{2+} and the formation of salts with these cations (e.g., $NaNO_3$, $MgSO_4$). Moreover, when considering the
neutralization of all the cations (Na^+, Mg^{2+}, NH_4^+, K^+, Ca^{2+}) by all the anions (SO_4^{2-}, NO_3^-, Cl^-), the scatter plot (**Fig. S7**)
presented a slope of 0.98, indicating a charge balance between the anions and cations.

3.6 Source apportionment of PM$_{2.5}$

430 **3.6.1 Source identification**

The source profiles obtained from the PMF model are presented in **Fig. 5**. Eleven sources were identified at MTL site namely SOA, secondary inorganic aerosol, crustal dust, marine, biomass burning, cooking, traffic exhaust, road dust, industrial, plant wax and biogenic SOA. The species with the highest loadings were used to identify each factor, and comparison to source profiles found in the literature served as confirmation.

435 The SOA factor was distinguished with high loading of oxalic acid (75% of the total concentration of oxalic acid) and contributed to 22% of the PM$_{2.5}$ mass concentration. Oxalic acid is a byproduct of oxidation from various precursors including biogenic (e.g., isoprene) and anthropogenic (e.g., cycloalkanes) compounds, and it is also generated from the photochemical oxidation of larger acid homologues (Srivastava et al., 2019).

The secondary inorganic aerosol (SIA) factor was distinguished by the presence of the water-soluble ions SO$_4^{2-}$ (58%) and

440 NH$_4^+$ (59%). This factor accounted for 17% of the total PM$_{2.5}$. No trend was observed in the time series of this factor and this source can originate from both local emissions and long-range transport (LRT) originating from the rest of Canada (e.g., Ontario) and the United States (Seinfeld and Pandis, 2016; NPRID, 2022). Aluminum production and industrial processes related to metallurgy and all other minor sources contributed to ~ 90 000 tons of SO$_2$ in Québec in 2020, which consists of 15% of the total Canadian emissions (583 008 tons) (NPRID, 2022).

445 The crustal dust factor was identified by high loadings of Al (68%), Fe (76%) and Ti (63%). This factor accounted for 12% of the total PM$_{2.5}$ and is likely associated with crustal dust sources such as wind-driven resuspension, construction and agricultural activities (Bari and Kindzierski, 2016). All of these crustal dust sources are plausible given that construction is omnipresent in Montréal, and the surrounding St. Lawrence Valley has a large amount of agriculture.

A marine factor was characterized by the ions Na$^+$ (46%), Cl$^-$ (69%) and NO$_3^-$ (30%), contributing to 11% of the PM$_{2.5}$. The

450 Cl$^-$/Na$^+$ calculated for this factor was 0.95, which is lower than the ratio of 1.80 reported for fresh sea-salt and is indicative of aged sea-salt (Petit et al., 2019; Seinfeld and Pandis, 2016). The presence of high nitrate loading in the profile further confirms the presence of aged marine salt. The observed chloride depletion is due to the reaction of nitric and sulfuric acid with NaCl particles (Seinfeld and Pandis, 2016).

Biomass burning was identified by high loadings of levoglucosan (70%). The OC/EC in this factor was 8.4, consistent with

455 biomass burning (Khan et al., 2021). This source accounted for 9% of the total PM$_{2.5}$ mass. Levoglucosan is a major pyrolysis product of cellulose and hemicellulose (Simoneit, 2002), and has been used as a molecular marker of biomass burning aerosols in several source apportionment studies (Gadi et al., 2019; Shivani et al., 2019). No trend was observed in the time series of this factor with season or temperature, indicating that levoglucosan originates from both residential burning and forest fires.

460   A cooking emissions factor was identified based on the contribution of hexadecanoic (65%) and octadecanoic acids (68%) in the profile and accounted for 9% of the total $PM_{2.5}$ mass. These carboxylic acids have been used in source apportionment studies to distinguish cooking activities (Gadi et al., 2019; Lv et al., 2021; Shivani et al., 2019).

The traffic exhaust factor was identified by the presence of 17α[H]-21β[H]-Hopane and lower molecular weight n-alkanes (C20 to C25) and accounted for 6% of total $PM_{2.5}$ mass concentration. Hopanes are specific markers of traffic emissions due

465   to their presence in lubrication oil (Rogge et al., 1993a; Schauer et al., 2002). Furthermore, dynamometer tests results showed that the most abundant n-alkanes were C20 and C21 for diesel vehicle emissions and C24 – C25 for gasoline-powered vehicle emissions (Rogge et al., 1993a), and these compounds are commonly associated with motor vehicle emissions. This traffic exhaust factor contributed around 72% of the hopane mass in the model, 59% of the C24 mass and 62% of the C25 mass. We suggest that the traffic emission factor is comprised principally of primary exhaust emissions

470   given the lack of secondary tracers in the factor profile.

The road dust factor was characterized by high loadings of Cd (69%) and Sb (58%) and accounted for 2% of $PM_{2.5}$. These elements are linked to non-exhaust vehicle emissions, particularly from brake-wear debris (Thorpe and Harrison, 2008; Lin et al., 2015).

The industrial emissions factor was dominated by Cu and Co and contributed 70% and 90% of the mass of these elements,

475   respectively, and accounted for 6% of $PM_{2.5}$. These elements are emitted from metal-industry related sources and coal combustion (Riffault et al., 2015; Bari and Kindzierski, 2016; Sharma and Mandal, 2017), but coal is not used for electricity generation in Québec and thus industrial sources seem more likely to be responsible for this factor.

The plant wax factor was characterized by high loadings of C27 and C29 with 55% of the C27 and 58% of the C29 apportioned to this factor. These compounds have been previously linked to primary biogenic emissions (Rogge et al.,

480   1993b). This factor contributed to 2% of the total $PM_{2.5}$.

Finally, the biogenic SOA factor accounted for 75% of the measured pinic acid and 66% of the measured pinonic acid and accounted for 4% of $PM_{2.5}$. α-Pinene is one of the most atmospherically important compounds in the monoterpene family, and pinic acid and pinonic acid are derived from the photooxidation of α-pinene with ozone (O_3) and hydroxyl (OH) radicals (Fadel et al., 2021). Although it is uncommon to see these species included in PMF models, doing so provides insight into

485   how much biogenic SOA contributes to $PM_{2.5}$ mass concentration.

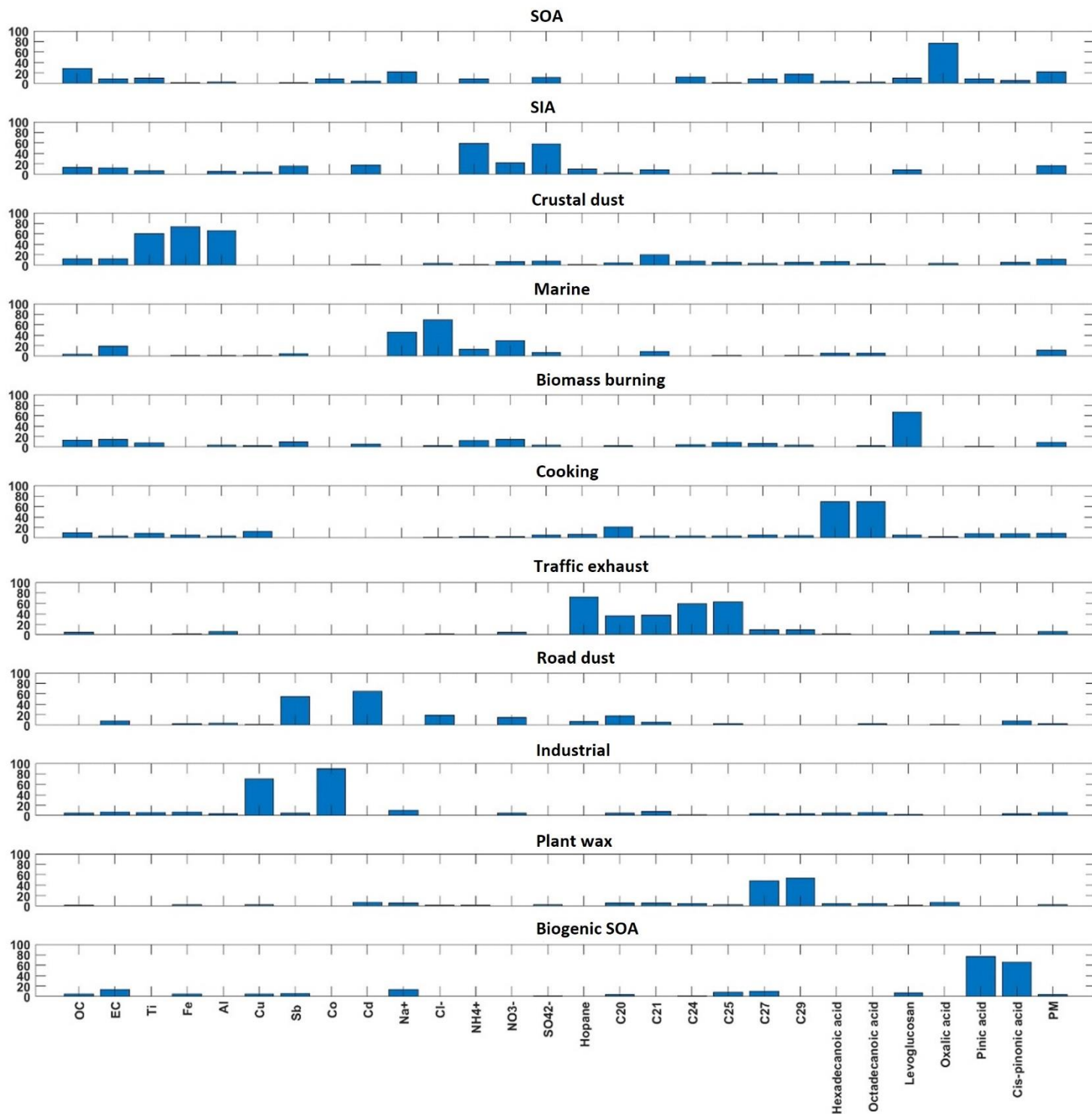



Figure 5. Profiles of the eleven factors identified from the PMF model. Loading (in percentage) is indicated on the vertical axes.

3.6.2 Source contribution to PM$_{2.5}$

490 One of the originalities of the present study relies on the identification of primary and secondary biogenic and anthropogenic sources based on the inclusion of selected organic markers in the PMF model namely n-alkanes, anhydrosugars, a hopane, fatty acids, dicarboxylic acids, and biogenic secondary organic aerosols tracers. Of a total of 11 sources, the addition of organic markers allowed the identification of 4 of them, namely SOA, cooking, plant wax, and biogenic SOA.

When the PM$_{2.5}$ sources identified in this study were compared to other source apportionment studies conducted in major

495 urban areas in Canada (Bari & Kindzierski, 2016; Jeong et al., 2011; Celo et al., 2021) where NAPS PM$_{2.5}$ chemical speciation datasets were used as inputs, this work resolved additional primary and secondary biogenic and anthropogenic sources due to the inclusion of a large suite of organic markers in the PMF model that were not available previously. The additional sources identified, namely SOA, BSOA, plant wax, cooking emissions are also rarely apportioned in the literature (Gadi et al., 2019; Lv et al., 2021).

500 There are also important differences between the source profiles for vehicular emissions in this study versus previous source apportionment studies conducted in Canada. In Montréal for example, Jeong et al. (2011) identified a traffic emission factor based on the contributions of OC, EC and oxalate. On the other hand, the traffic factor was identified in Edmonton based on the contribution of Ba, Sb, EC, Cu and Co (Bari and Kindzierski, 2016). Since trace elements and carbonaceous matter could be emitted from a variety of sources, this study refined the evaluation of vehicular sources by incorporating two source-

505 specific organic tracers in the PMF model, namely n-alkanes and a hopane. This allowed the differentiation of exhaust and non-exhaust emissions.

The PMF results indicate that SOA and SIA were the largest contributors to fine PM and together constituted 39% (1.68 µg/m^3) of the measured PM$_{2.5}$ mass (**Fig. 6**). The primary local urban anthropogenic sources, namely traffic exhaust, road dust, industrial and cooking emissions contributed to 23% (0.99 µg/m^3) of the measured PM$_{2.5}$ mass. These sources along

510 with crustal dust, biomass burning, and plant wax comprise the primary aerosol fraction that is 44% (1.94 µg/m^3) of the measured PM$_{2.5}$ mass. It should also be noted that residential burning likely contributes to the biomass burning factor, but this factor is not included with the primary local urban anthropogenic sources listed above since it is not possible to distinguish residential burning from wildfires in our PMF analysis.

The chemical transport model GEOS-Chem was used to qualitatively evaluate the relative contributions from three different

515 source regions, namely Québec, RoC, and United States to the sources (**Fig. S4**). To link the modelling results to the PMF factors, we focus on modelled concentrations of SOA, of dust in particles smaller than 2.5 µm in diameter, and of the sum of NH$_4$ and SO$_4$. As most of the NH$_4^+$ and SO$_4^{2-}$ was observed to be in the SIA PMF factor, we expect the sum of the simulated concentrations of NH$_4$ and SO$_4$ from GEOS-Chem have similar sources as the SIA PMF factor. Similarly, the concentrations of SOA from GEOS-Chem would be analogous to the sum of the SOA and biogenic SOA factors, although we note that only

520 anthropogenic sources were altered in the sensitivity simulations. The dust species in GEOS-Chem comprises not only road dust and crustal dust, but all elements not included in the other model aerosol species (primary and secondary organic

aerosol, elemental carbon, sulfate, nitrate, ammonium, and sea-spray aerosol). It is therefore most comparable to the sum of the crustal dust, road dust, and industrial PMF factors. Together, the SIA, SOA, biogenic SOA, crustal dust, road dust, and industrial PMF factors comprise 61% of the total observed PM$_{2.5}$ mass.

525   According to the findings of the chemical transport modelling, Montréal air pollution concentrations are influenced by all three of the regions that were considered. As presented in **Fig. 7**, the US makes an important contribution to SOA and ammonium sulfate concentrations. The concentrations of SOA dropped by 22% between the base case and the sensitivity simulation without Quebec emissions and by 36% when the US emissions were not included. The concentrations of ammonium sulfate decreased by 33% when US emissions were excluded and by 35% when emissions from Quebec were
530   excluded. Thus, GEOS-Chem simulations reveal an important contribution from US emissions to ammonium sulfate and SOA concentrations.

On the other hand, anthropogenic dust emissions from Québec presented the highest contribution to total dust concentrations and the concentrations dropped by 16% when emissions from Quebec were excluded and by 10% when US emissions were excluded. The sum of the anthropogenic fractions is 30% for dust in GEOS-Chem, which is close to the ratio of the PM$_{2.5}$
535   mass in the industrial and road dust PMF factors to the sum of the industrial, road dust, and soil dust factors (40%). The similarity in the two approaches (modeling versus PMF) increases confidence that the dust sources are being correctly apportioned in our study. In general, emissions from the RoC for all pollutants presented a smaller contribution to local concentrations than Quebec or US emissions (**Fig. 7**). Therefore, GEOS-Chem emphasized the important role of transboundary input from the US during our sampling period. PM$_{2.5}$ can be reduced through local mitigation strategies, but
540   the effectiveness of such strategies will be limited without updating international agreements to further reduce transboundary pollution.

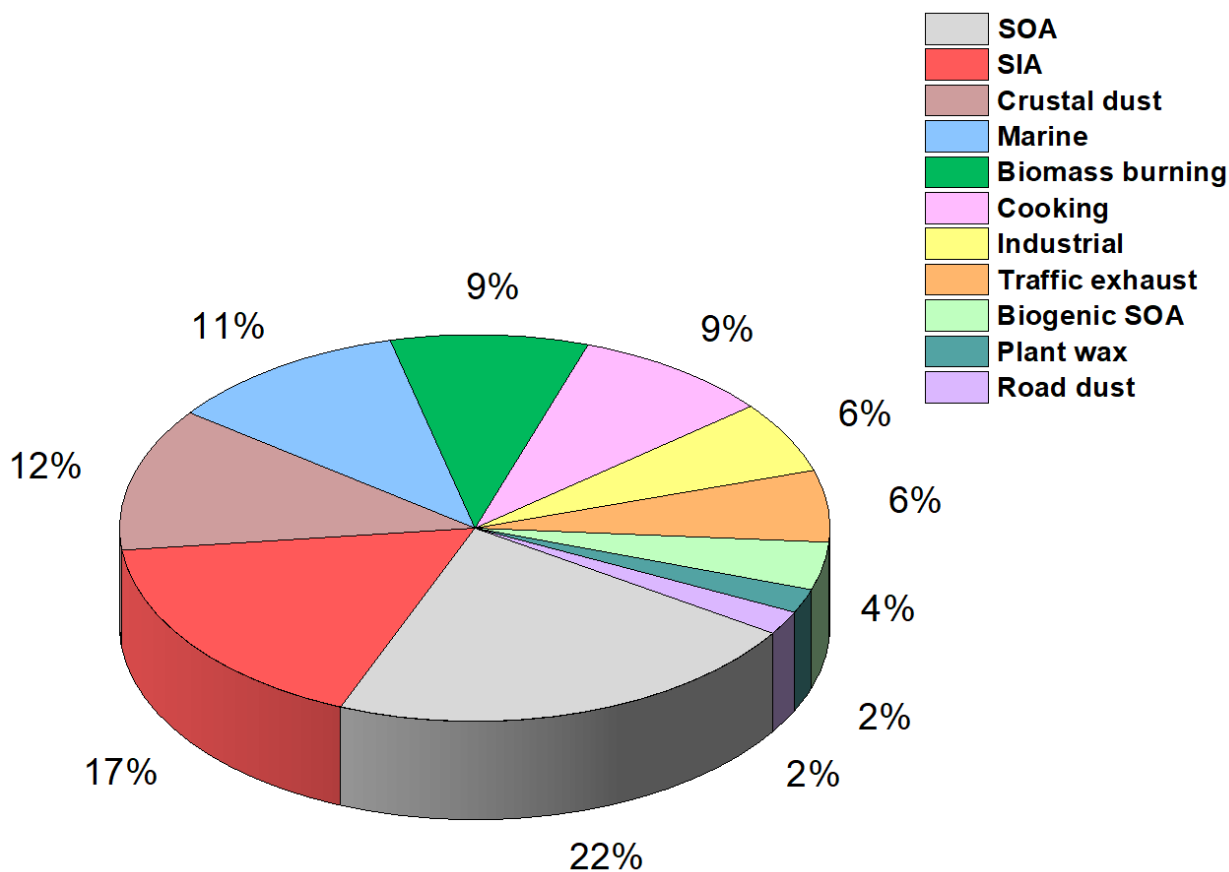



Figure 6. Contributions of the eleven identified sources to the total PM$_{2.5}$ mass.

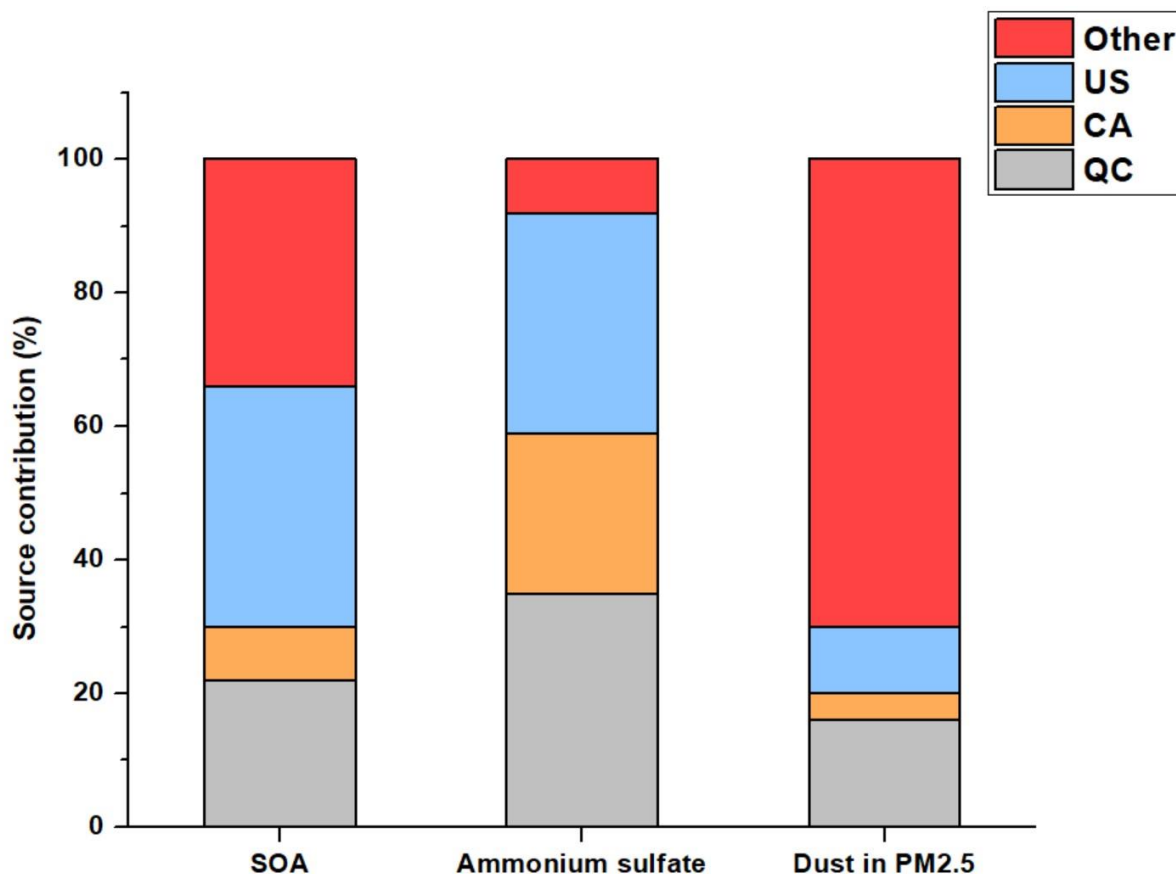



Figure 7. Contribution of anthropogenic emissions from three different source regions, namely Quebec (QC), United States (US) and the rest of Canada (CA) to concentrations of SOA, ammonium sulfate, and dust in PM$_{2.5}$ between August and November 2020, as predicted by GEOS-Chem.

3.7 Health risk assessment of PM$_{2.5}$ elements

The non-carcinogenic health risks from airborne elements through inhalation, ingestion and dermal contact were estimated. The HI exhibited the same trend for both children and adults and followed a decreasing order of Co > Mn > Pb > Cu > Cd > Ni > Cr(VI) > Sb > Zn> Al > Fe > V. Among the three exposure pathways, inhalation contributed the most to the total non-carcinogenic risk (HI$_{total}$). Overall, inhalation contributed 98% for adults and 97% for children to HI$_{total}$, ingestion contributed 1% (adults) and 2% (children) while dermal absorption was the remainder. Co was the largest contributor to the HI$_{inhalation}$, with a contribution of 61% for both adults and children. An HI value higher than one implies that adverse effects other than cancer such as cardiovascular and respiratory diseases are expected (Fadel et al., 2022a). In this study, HI and HI$_{total}$ (HI$_{total}$ = 0.24 for adults and 0.36 for children) were below the level of 1, highlighting limited non-carcinogenic health hazards from PM$_{2.5}$-metals.

The carcinogenic risk of each carcinogenic metal (i.e., Cr(VI), Co, Ni, V, Cd and Pb) from the three exposures pathways was also calculated. Inhalation was the exposure pathway with the highest cancer risk to which 99% and 98% of the overall carcinogenic risk (CR_{total}) for adults and children was ascribed, respectively. According to the USEPA, a cancer risk value

565   between 10^{-6} (one additional case per one million people) and 10^{-4} (one in a ten thousand) indicates that the carcinogenic risk is considered as tolerable, while a value higher than 10^{-4} indicates that a serious risk of cancer exists (Bari and Kindzierski, 2016; Dahmardeh Behrooz et al., 2021).

In this study, the carcinogenic risk of V, Ni, Cd and Pb was between 1.18×10^{-8} and 6.11×10^{-7}, which is lower than 10^{-6}. However, Co and Cr(VI) presented a cancer risk higher than 10^{-6} (**Fig. 8**), highlighting that more attention should be given

570   to these trace metals. Based on PMF analysis, Co was associated with industrial emissions and the correlation between Co and Cr (R=0.79, *p<0.01*) (section 3.4) suggests a common source from industrial emissions for these two trace elements (Cr was not added in the PMF analysis because it was not well modeled). The sum of the risk levels posed by the six metals was 1.77×10^{-5} and 5.87×10^{-6} for adults and children, respectively, which is between the range of 10^{-6} - 10^{-4}, indicating that the carcinogenic risk is considered as tolerable.

575   These results show that even though industrial emissions presented a very small contribution in term of mass (0.26 µg/m³), the health risks associated with this source cannot be fully determined by the $PM_{2.5}$ mass concentration alone, and the trace elements emitted from industrial sources source were found to have a potential health risk. Thus, this study highlights that mitigation strategies should also prioritize reduction in metals in addition to PM.

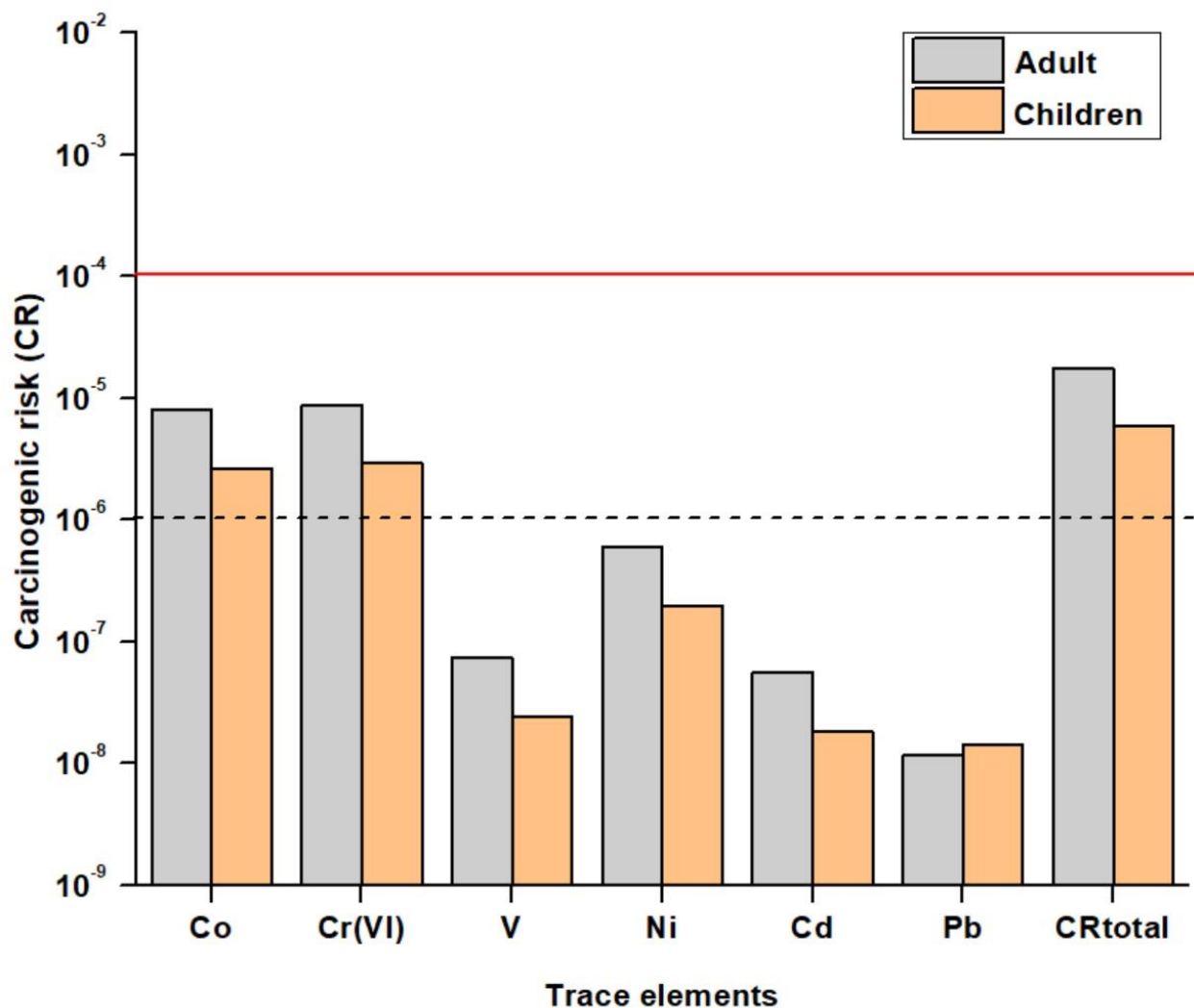



Figure 8. The carcinogenic risk (CR_{total}) from trace metals in $PM_{2.5}$. A cancer risk value between 10^{-6} and 10^{-4} indicates that the CR is considered tolerable while a value higher than 10^{-4} indicates that cancer risk exists seriously.

4 Conclusion

This work examines $PM_{2.5}$ sources in Montréal using detailed chemical speciation data collected over a 3-month period (August-November 2020). The chemical composition data included concentrations of the major components such as OC, EC, water-soluble ions, and elements. These species, along with a large suit of organic tracers were used as inputs in a source apportionment model (PMF) to identify and quantify the sources of $PM_{2.5}$. This source apportionment study, which used a wide range of organic molecular markers to investigate the main sources of $PM_{2.5}$, is the first of its kind in Montréal

590 and Canada. SOA and SIA were major sources and constituted 39% of the measured $PM_{2.5}$ mass. The local primary anthropogenic sources, namely traffic exhaust, road dust, industrial and cooking emissions contributed to 23% of the measured $PM_{2.5}$ mass. These sources along with crustal dust and biomass burning represented the total primary aerosol and accounted altogether for 44% of $PM_{2.5}$. According to the chemical transport model GEOS-Chem, both local (from Québec) and transboundary pollution (from the United States) contribute to the observed concentrations of SOA and SIA in Montréal,

595 but the transboundary contribution is greater than the local contribution, indicating the need to update international agreements to further limit transboundary pollution.

One of the novel aspects of the present study was the inclusion of specific organic tracers which allowed the identification of 4 sources in addition to those that are usually identified using chemical speciation datasets from government monitoring alone. Specifically, these sources (tracers) are plant wax (high MW n-alkanes), BSOA (α-pinene oxidation products),

600 secondary organic aerosols (dicarboxylic acids) and cooking emissions (fatty acids). Moreover, the distinction between exhaust and non-exhaust vehicular emissions was achieved by incorporating two source-specific organic tracers in the PMF model, namely n-alkanes and hopane.

Evaluation of the health risk associated with exposure to metals revealed that Co and Cr(VI) presented a cancer risk (CR) higher than 10^{-6}, highlighting that more attention should be given to these trace metals, which originate principally from

605 industrial emissions according to the PMF analysis. While industrial emissions are the dominant source of Co and Cr(VI), they only contribute a small amount to the total PM2.5 (6%) indicating that the prioritization of sources and sectors for mitigation strategies will be different when considering the concentrations of individual contaminants or total $PM_{2.5}$ concentration.

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Data availability: Data used in this study can be accessed here: https://doi.org/10.5683/SP3/96IVPX. More details on the analyses are available upon request to the contact author Nansi Fakhri (nansi.fakhri@umontreal.ca).

Author contributions.

Nansi Fakhri: field campaign and collection of the filters; chemical characterization of the collected filters; analyzing the

615 data and writing the manuscript, **Robin Stevens:** application of GEOS-chem software; review and editing the manuscript, **Arnold Downey:** chemical characterization of the collected filters by ICP-MS, **Konstantina Oikonomou**: resources, **Jean Sciare:** resources, review and editing the manuscript, **Patrick L. Hayes**: supervision, review and editing the manuscript, project administration and resources, **Charbel Afif:** supervision, review and editing the manuscript.

620 *Competing interests.* The authors declare that they have no conflict of interest.

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