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# Ambient volatile organic compounds (VOCs) in Calgary, Alberta: Sources and screening health risk assessment

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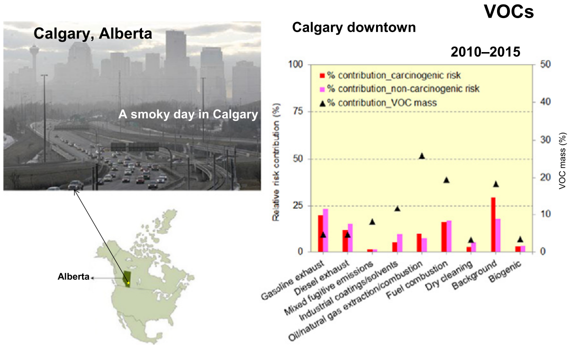
## HIGHLIGHTS

- Sources and health risks of ambient VOCs were assessed at Alberta's largest city Calgary.
- Industry, fuel combustion and traffic emissions contributed to ~80% of total VOCs.
- Contribution of background and biogenic emissions was ~20% of total VOCs.
- Traffic, background and fuel combustion sources were important to cancer risk.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Exposure to ambient volatile organic compound (VOCs) in urban areas is of interest because of their potential chronic and acute adverse effects to public health. Limited information is available about VOC sources in urban areas in Canada. An investigation of ambient VOCs levels, their potential sources and associated risks to public health was undertaken for the urban core of Alberta's largest city (downtown Calgary) for the period 2010–2015. Twenty-four hour arithmetic and geometric mean concentrations of total VOCs were 42 μg/m$^3$ and 39 μg/m$^3$, respectively and ranged from 16 to 160 μg/m$^3$, with winter levels about two-fold higher than summer. Alkanes (58%) were the most dominant compounds followed by halogenated VOCs (22%) and aromatics (11%). Mean and maximum 24 h ambient concentrations of selected VOCs of public health concern were below chronic and acute health risk screening criteria of the United States regulatory agencies and a cancer screening benchmark used in Alberta equivalent to 1 in 100,000 lifetime risk. The Positive matrix factorization (PMF) model revealed nine VOC sources at downtown Calgary, where oil/natural gas extraction/combustion (26%), fuel combustion (20%), traffic sources including gasoline exhaust, diesel exhaust, mixed fugitive emissions (10–15%), and industrial coatings/solvents (12%) were predominant. Other sources included dry cleaning (3.3%), biogenic (3.5%) and a background source (18%). Source-specific health risk values were also estimated. Estimated cancer risks for all sources were below the Alberta cancer screening benchmark, and estimated non-cancer risks for all sources were well below a safe level.

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## 1. Introduction

Urban air pollution is generally caused by a wide variety of emission sources and is comprised of a complex mixture of inorganic and organic

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compounds including volatile organic compounds (VOCs). While concentrations of many VOCs tend to be higher indoors (up to ten times higher) than outdoors (USEPA, 2017), there is ongoing interest in understanding levels and sources of ambient VOCs in urban areas and the corresponding risk to public health (Otto et al., 1992; Delfino et al., 2003; Metzger et al., 2004; Huang et al., 2014; Gałęzowska et al., 2016). Numerous VOC species including benzene, ethylbenzene, and oxygenated- and halogenated-VOCs (e.g., acetaldehyde, 1,2-dichloroethane) are treated as carcinogens and potentially toxic substances by Canadian, the United States and other international agencies (CEPA, 1999; ATSDR, 2011; IARC, 2015). VOCs can also act as precursors of photochemically formed secondary pollutants such as ozone and peroxyacetyl nitrate and may contribute to stratospheric ozone layer depletion (Chameides et al., 1992; Finlayson-Pitts and Pitts, 2000; Heard and Pilling, 2003). Understanding VOCs sources and associated risk to public health can aid in developing targeted management strategies for specific sources in order to minimize their release into the urban environment.

Ambient VOCs are ubiquitous in urban air and they are emitted from a wide variety of natural (e.g., emissions from trees, wildfires) and anthropogenic sources (e.g., vehicle exhaust, refineries, residential combustion, vehicular and industrial evaporation, paints/solvent usage) (Conner et al., 1995; McLaren et al., 1996; Watson et al., 2001; Na et al., 2004; Liu et al., 2008; Barletta et al., 2009; Dumanoglu et al., 2014). Multivariate source apportionment models e.g., positive matrix factorization (PMF) have been widely used to determine potential ambient sources of VOCs in urban areas. Source-risk apportionment – which couples the risk assessment process and the source apportionment model, can provide valuable information for understanding the relative importance of particular emission source categories (Mukerjee and Biswas, 1992) and has been applied in several studies (e.g., Wu et al., 2009; Bari and Kindzierski, 2016a, 2017a).

The City of Calgary, located about 300 km south of Alberta's capital Edmonton, is the largest urban area and most populous city (area 825 km$^2$, population 1,246,337, Municipal census, 2017) in the oil and natural gas-rich province of Alberta and third-largest municipality in Canada (Statistics Canada, 2016). It is located within the southern edge of Alberta's oil and gas extraction activities (Supplemental information-SI, Fig. S1). Because of its diversified economy including oil and gas, film and television industries, transportation and logistics, technology, manufacturing, retail, and tourism sectors, Calgary plays a key role in supporting the economic growth of Alberta and Canada. Limited source apportionment studies for ambient VOCs have been carried out in Canada including Alberta; for example in Edmonton (McCarthy et al., 2013), Fort Saskatchewan (Mintz and McWhinney, 2008) and the Athabasca oil sands region (Bari and Kindzierski, 2017b) as well as in Ontario e.g., Ottawa (Kuntasall, 2005) and Windsor (Li, 2012). In a recent study, Ladha et al. (2014) used the United States Environment Protection Agency (USEPA)'s PMF model (EPA PMF3.0) to investigate VOC sources in downtown Calgary for the time period of 2004–2011. However, Ladha et al. (2014) did not present any analysis to verify sources identified in their model. In this present study, we used the current version of the USEPA PMF model (PMF 5.0) to investigate probable local and distant sources that affect ambient levels of VOCs in downtown Calgary for a more recent time period (2010 to 2015). We also undertook several approaches e.g., correlation analysis between PMF-derived factors and criteria air pollutant concentrations, conditional bivariate probability function (CBPF) and backward trajectory analysis to assist in verifying the sources. In addition, we performed a screening health risk assessment to understand potential risks to the public from ambient VOCs and the PMF-derived sources in downtown Calgary.

## 2. Methodology

### 2.1. Sampling strategies

As part of Environment and Climate Change Canada's (ECCC) National Air Pollution Surveillance (NAPS) initiatives, Alberta Environment and Parks has been responsible for routinely monitoring VOCs in Calgary downtown. Calgary has a humid continental climate with wide fluctuations in temperatures throughout the seasons e.g., long cold winters and warm summers and no dry season. Due to close proximity to the Rocky Mountains, Calgary's air quality can be influenced by warm and dry Chinook winds that blow over the mountains during winter months (Hicks and Mathews, 1979). Early morning ground-based temperature inversions are common throughout the whole year in Alberta with deeper and stronger inversions observed during winter months (Hicks et al., 1977; Myrick et al., 1994), thus limiting the dispersion of air pollutants and potentially increasing pollutants levels in winter (e.g., Munn et al., 1970; Nkemdirim, 1988; Cheng et al., 1997; Kossmann and Sturman, 2004).

Topography for the City of Calgary and the immediate surrounding area (Fig. S2a), locations of major roadways and average daily (24 h) weekday traffic volume for all roadways in 2016 (Fig. S2b) and designated truck routes (Fig. S2c) are shown in the SI. Calgary is located in the Calgary Regional Airshed Zone (CRAZ), which is one of 10 airshed regions in Alberta (Fig. S2d). According to 2008 emission inventories (Novus Environmental, 2013), major sources of VOC emissions in the Calgary Regional Airshed Zone are biogenic, traffic, agriculture including field burning, several upstream oil and gas facilities, solvent use, and retail gas stations as well as some contributions from residential and commercial heating and other industries. Within the City of Calgary, contributions to total VOC emissions were noteworthy for transportation (30%), solvent use (22%), agriculture (17%), and retail gas stations (14%) (Table S1). Residential- and industrial-zoned districts in the City of Calgary are shown in Fig. S3. National Pollutant Release Inventory (NPRI) (ECCC, 2017a) reported annual releases of volatile organic compounds (VOCs) to the air from major industrial facilities within 50 km of downtown Calgary are shown in Table S3. Over the 10-year period 2004–2014 the city added 261,700 residents to its population (City of Calgary, 2015) and 287,790 more registered vehicles using its roadways (Alberta Transportation, 2015).

The study was performed using historical VOCs data collected from an available air monitoring station in downtown Calgary i.e., Calgary central (51.0459°N, 114.0747°W) (Fig. 1). The downtown core of the city lies in the Bow River Valley and surrounding residential areas are elevated to 30 to 60 m above the floor of the valley. The study was carried out using publicly available 24 h VOC data for 153 VOC species over a 6-year period (2010–2015) at Calgary central and accessed via ECCC (2017b).

VOC samples were collected at a frequency of once every 6 days using 6-L evacuated Summa canisters (Scientific Instrumental Specialists, Inc., Moscow, ID) and analyzed by gas chromatograph-mass spectrometer (GC–MS) at Environment Canada's lab in Ottawa, ON. Details of VOCs sampling and analysis methods are described elsewhere (Wang et al., 2005; Galarneau et al., 2016). Meteorological parameters (wind speed and direction) are not monitored at the Calgary central station.

### 2.2. Source identification methods

The USEPA multivariate receptor model positive matrix factorization (EPA PMF5.0) (USEPA, 2014) was used to determine possible emission sources of measured ambient VOC concentrations at Calgary Central. The model description and data treatment procedures are described in the SI. The input file for PMF analysis of the period 2010–2015 consisted of 349 daily (24 h) samples. Out of 153 measured VOC species, initially 38 species which were detected in >80% of the samples above the method detection limit were chosen for PMF analysis. An additional 24 species (where 17 and 7 species detected in >50% and in 28%–46% of the samples above the detection limit, respectively) were incorporated in PMF analysis based on their potential toxicity (e.g., 1,3-butadiene, tetrachloroethylene, naphthalene) and being source-specific tracers (e.g., biogenic tracer isoprene) (Tables 1, S3).

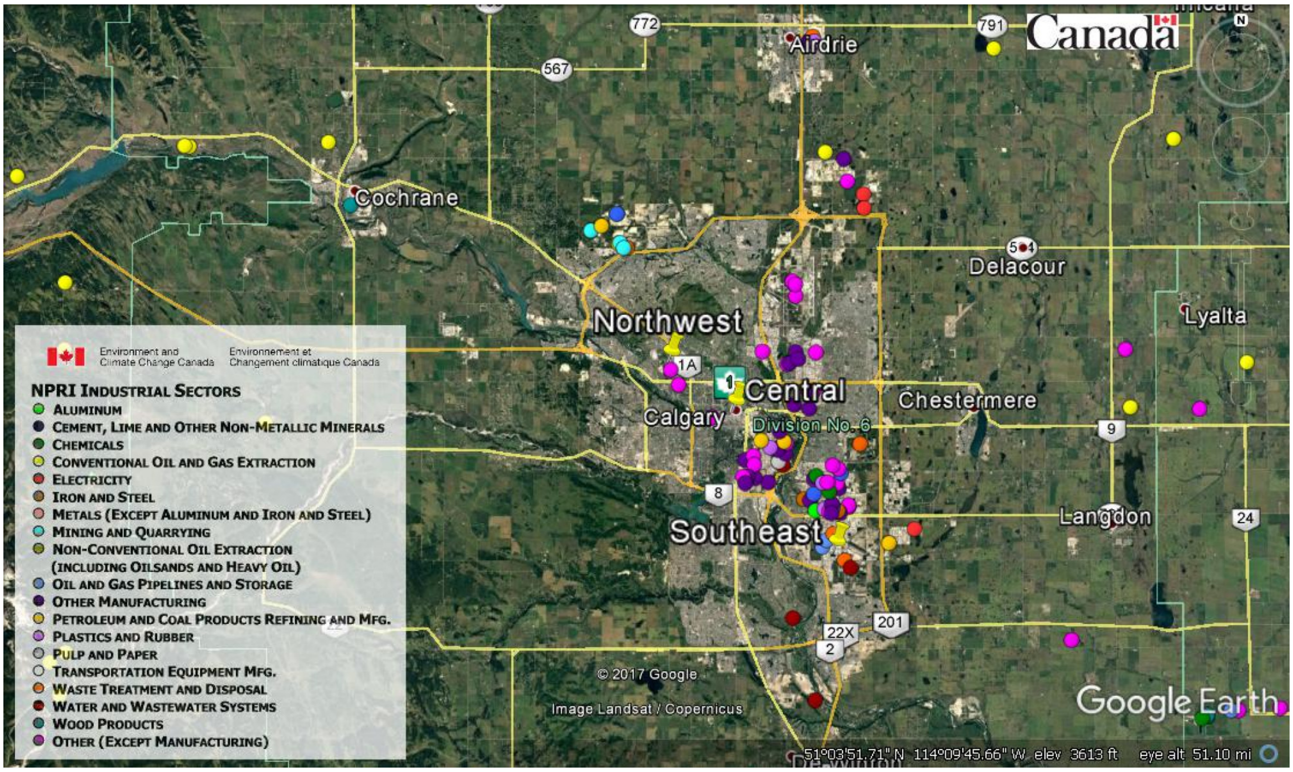

**Fig. 1.** Locations of three air monitoring stations (yellow stick pins) including VOC monitoring station in Calgary central and industries in and surrounding the monitoring stations that report to NPRI during 2015 using Google Earth (Image © 2017 DigitalGlobe © 2017 Google). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

In this study, the total measured VOC was included as an input variable in the PMF model to directly obtain source contribution instead of using post-hoc regression analysis. Different approaches were applied to verify source assignments from the PMF analysis. Correlation analysis was performed between PMF-derived source contributions and criteria air pollutant concentrations. Hourly concentration data for fine particulate matter ($PM_{2.5}$), nitric oxide (NO), nitrogen dioxide ($NO_2$), oxides of nitrogen ($NO_X$), ozone ($O_3$), total hydrocarbon (THC), carbon monoxide (CO) and non-methane hydrocarbons (NMHC) were accessed for the study period from AEP (2016a). For local source identification, a conditional bivariate probability function (CBPF) – developed by Uria-telelaetxe and Carslaw (2014) – was calculated using available meteorological data from the Calgary northwest station to characterize potential local emission sources using PMF-derived factor contributions. This was accomplished by coupling a conditional probability function (CPF) with bivariate polar plots in order to show the direction and relative location of potential local contributions for the different sources through wind speed dependence. Here one is trying to identify potential sources within one hour wind travel time from the air monitoring station. In addition, to identify the influence of potential long-range sources (if any), backward trajectory analysis was conducted using the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (Draxler and Rolph, 2003). Forty eight-hour backward trajectories starting at noon local time at a height of 500 m above the ground level were calculated for every sample day using gridded meteorological data combined with the Geographic Information System (GIS) based software TrajStat (Wang et al., 2009). The geographic region covered by the air trajectories was divided into 8800 grid cells of 0.5° × 0.5° latitude and longitude. In this study, the concentration-weighted trajectory (CWT) model was used where each grid cell was assigned a weighted concentration by averaging the sample concentrations that have associated trajectories crossing the grid cell (Seibert et al., 1994; Hsu et al., 2003). CWT is a function of contributions of PMF-resolved source factors and the residence time of a trajectory arriving at Calgary central station in each grid cell. Further details on trajectory analysis are provided in the SI.

### 2.3. Screening human health risk assessment

A deterministic screening human health risk assessment of the inhalation exposure pathway was performed to identify substances and/or derived emissions sources that may pose the greatest health risks. For assessing risks associated with long-term (chronic) and short-term (acute) inhalation exposures, dose-response criteria of the USEPA's Office of Air Quality Planning and Standards (OAQPS) were used to screen ambient VOC concentrations for the study period. Carcinogenic and non-carcinogenic risks of all risk-posing VOC species were estimated. In this study, out of all detected species, only 16 VOC species with known toxicity values were considered (benzene, toluene, ethylbenzene, xylenes, *n*-hexane, cyclohexane, 1,3-butadiene, styrene, chloroform, chloromethane, dichloromethane, 1,2-dichlorobenzne, 1,4-dichlorobenzene, tetrachloroethylene, carbon tetrachloride and naphthalene). Health risks posed by PMF-derived VOC sources was also screened by summing carcinogenic and non-carcinogenic risks of all available risk-posing species in a particular source. Further details on the health risk estimate procedures are presented in the SI.

## 3. Results and discussion

### 3.1. Ambient VOC levels

Summary statistics for 71 detected VOCs for the time period 2010–2015 at Calgary central is shown in Table 1 and data quality for low and non-detect VOC species (n = 82) is presented in Table S3. The geometric mean concentration of total VOCs was 38.6 $\mu g/m^3$ (median = 36.6 $\mu g/m^3$, interquartile range, IQR = 29–50 $\mu g/m^3$, range = 15.7–160 $\mu g/m^3$) based on the detected

**Table 1**
Summary statistics of selected VOCs (μg/m$^3$) for the time period 2010–2015 at Calgary central.

| | >MDL | <MDL | Missing | Arithmetic mean | Geometric mean | Median | 25th percentile | 75th percentile | Minimum | Maximum |
|---|---|---|---|---|---|---|---|---|---|---|
| | % | % | % | | | | | | | |
| Benzene | 100 | 0 | 0 | 0.59 | 0.52 | 0.51 | 0.39 | 0.72 | 0.13 | 2.38 |
| Toluene | 100 | 0 | 0 | 1.79 | 1.44 | 1.46 | 0.91 | 2.12 | 0.36 | 14.79 |
| Ethylbenzene | 98 | 2 | 0 | 0.26 | 0.21 | 0.21 | 0.13 | 0.29 | 0.04 | 1.41 |
| *m*,*p*-Xylene | 99 | 1 | 0 | 0.87 | 0.69 | 0.71 | 0.44 | 1.00 | 0.09 | 5.40 |
| *o*-Xylene | 97 | 3 | 0 | 0.30 | 0.25 | 0.25 | 0.16 | 0.35 | 0.04 | 1.68 |
| 3-Ethyltoluene | 88 | 12 | 0 | 0.16 | 0.12 | 0.12 | 0.08 | 0.18 | 0.002 | 1.14 |
| 4-Ethyltoluene | 79 | 21 | 0 | 0.08 | 0.06 | 0.06 | 0.04 | 0.09 | 0.002 | 0.57 |
| 1,2,4-Trimethylbenzene | 78 | 22 | 1 | 0.25 | 0.19 | 0.20 | 0.13 | 0.29 | 0.001 | 2.06 |
| Ethane | 100 | 0 | 0 | 6.33 | 5.57 | 5.11 | 3.84 | 7.72 | 1.40 | 20.98 |
| Propane | 100 | 0 | 0 | 5.19 | 4.25 | 3.85 | 2.76 | 6.23 | 0.79 | 23.06 |
| *n*-Butane | 100 | 0 | 0 | 4.07 | 3.37 | 3.27 | 2.12 | 5.15 | 0.57 | 17.47 |
| Isobutane | 100 | 0 | 0 | 1.83 | 1.48 | 1.39 | 0.92 | 2.34 | 0.27 | 7.15 |
| 2,3-Dimethylbutane | 100 | 0 | 0 | 0.11 | 0.09 | 0.09 | 0.06 | 0.13 | 0.02 | 0.82 |
| *n*-Pentane | 100 | 0 | 0 | 1.20 | 0.95 | 0.90 | 0.60 | 1.42 | 0.21 | 16.99 |
| Isopentane | 100 | 0 | 0 | 2.07 | 1.76 | 1.76 | 1.18 | 2.49 | 0.43 | 11.02 |
| 2-Methylpentane | 99 | 1 | 0 | 0.49 | 0.40 | 0.39 | 0.26 | 0.59 | 0.08 | 6.60 |
| 3-Methylpentane | 94 | 6 | 0 | 0.34 | 0.28 | 0.28 | 0.18 | 0.42 | 0.06 | 2.91 |
| 2,3-Dimethylpentane | 100 | 0 | 0 | 0.31 | 0.26 | 0.26 | 0.17 | 0.36 | 0.05 | 1.68 |
| 2,4-Dimethylpentane | 99 | 1 | 0 | 0.12 | 0.10 | 0.10 | 0.07 | 0.15 | 0.02 | 0.86 |
| 2,2,4-Trimethylpentane | 100 | 0 | 0 | 0.45 | 0.37 | 0.36 | 0.25 | 0.52 | 0.06 | 2.52 |
| 2,3,4-Trimethylpentane | 91 | 9 | 0 | 0.10 | 0.08 | 0.07 | 0.05 | 0.11 | 0.01 | 0.53 |
| Cyclopentane | 98 | 2 | 0 | 0.09 | 0.08 | 0.07 | 0.05 | 0.11 | 0.02 | 0.43 |
| Methylcyclopentane | 100 | 0 | 0 | 0.26 | 0.22 | 0.21 | 0.14 | 0.32 | 0.04 | 2.19 |
| *n*-Hexane | 99 | 1 | 0 | 0.51 | 0.40 | 0.39 | 0.25 | 0.62 | 0.09 | 3.91 |
| 2-Methylhexane | 100 | 0 | 0 | 0.23 | 0.19 | 0.19 | 0.13 | 0.28 | 0.04 | 1.49 |
| 3-Methylhexane | 100 | 0 | 0 | 0.28 | 0.23 | 0.22 | 0.15 | 0.33 | 0.05 | 1.96 |
| Cyclohexane | 94 | 6 | 0 | 0.11 | 0.09 | 0.09 | 0.06 | 0.14 | 0.02 | 1.20 |
| Methylcyclohexane | 98 | 2 | 0 | 0.15 | 0.12 | 0.11 | 0.08 | 0.18 | 0.02 | 0.73 |
| *n*-Heptane | 72 | 27 | 0 | 0.26 | 0.21 | 0.21 | 0.13 | 0.32 | 0.04 | 1.61 |
| 2-Methylheptane | 67 | 33 | 0 | 0.07 | 0.06 | 0.06 | 0.04 | 0.09 | 0.02 | 0.36 |
| 3-Methylheptane | 78 | 22 | 0 | 0.06 | 0.05 | 0.05 | 0.03 | 0.07 | 0.01 | 0.35 |
| *n*-Octane | 68 | 32 | 0 | 0.08 | 0.07 | 0.07 | 0.05 | 0.10 | 0.02 | 0.36 |
| *n*-Nonane | 85 | 15 | 0 | 0.08 | 0.07 | 0.06 | 0.04 | 0.09 | 0.01 | 0.47 |
| *n*-Decane | 87 | 13 | 0 | 0.12 | 0.09 | 0.09 | 0.06 | 0.14 | 0.01 | 0.79 |
| *n*-Undecane | 85 | 14 | 1 | 0.12 | 0.09 | 0.09 | 0.06 | 0.16 | 0.002 | 0.85 |
| Ethylene | 100 | 0 | 0 | 1.54 | 1.29 | 1.19 | 0.89 | 1.86 | 0.28 | 8.42 |
| Propylene | 100 | 0 | 0 | 0.45 | 0.39 | 0.36 | 0.28 | 0.51 | 0.09 | 2.68 |
| Acetylene | 100 | 0 | 0 | 0.93 | 0.74 | 0.70 | 0.47 | 1.17 | 0.16 | 5.05 |
| 1,3-Butadiene | 62 | 38 | 0 | 0.07 | 0.05 | 0.05 | 0.04 | 0.07 | 0.01 | 0.43 |
| 1-Butene/isobutene | 79 | 21 | 0 | 0.28 | 0.25 | 0.24 | 0.18 | 0.32 | 0.07 | 1.70 |
| 2-Methyl-1-butene | 79 | 21 | 0 | 0.07 | 0.06 | 0.05 | 0.04 | 0.08 | 0.01 | 0.37 |
| 2-Methyl-2-butene | 70 | 30 | 0 | 0.07 | 0.05 | 0.05 | 0.03 | 0.07 | 0.003 | 0.51 |
| *trans*-2-Pentene | 74 | 26 | 0 | 0.06 | 0.05 | 0.04 | 0.03 | 0.06 | 0.01 | 0.42 |
| Freon11 | 100 | 0 | 0 | 1.63 | 1.62 | 1.60 | 1.50 | 1.72 | 1.31 | 4.86 |
| Freon12 | 100 | 0 | 0 | 2.60 | 2.60 | 2.58 | 2.48 | 2.71 | 2.09 | 3.36 |
| Freon22 | 100 | 0 | 0 | 0.99 | 0.95 | 0.88 | 0.80 | 1.04 | 0.61 | 7.23 |
| Freon113 | 67 | 0 | 33 | 0.60 | 0.59 | 0.59 | 0.56 | 0.63 | 0.39 | 0.78 |
| Carbon tetrachloride | 100 | 0 | 0 | 0.53 | 0.52 | 0.52 | 0.49 | 0.57 | 0.24 | 0.75 |
| Chloromethane | 100 | 0 | 0 | 1.17 | 1.17 | 1.17 | 1.09 | 1.25 | 0.80 | 1.85 |
| Dichloromethane | 100 | 0 | 0 | 0.36 | 0.33 | 0.31 | 0.26 | 0.38 | 0.18 | 3.90 |
| Chloroform | 68 | 32 | 0 | 0.10 | 0.10 | 0.10 | 0.09 | 0.11 | 0.06 | 0.18 |
| Tetrachloroethylene | 67 | 32 | 0 | 0.22 | 0.14 | 0.12 | 0.07 | 0.26 | 0.02 | 2.23 |
| Isoprene | 74 | 26 | 0 | 0.21 | 0.10 | 0.09 | 0.05 | 0.19 | 0.01 | 2.42 |
| 2-Ethyltoluene | 45 | 54 | 0 | 0.06 | 0.05 | 0.05 | 0.03 | 0.07 | 0.002 | 0.44 |
| 1,2,3-Trimethylbenzene | 42 | 57 | 1 | 0.06 | 0.05 | 0.05 | 0.03 | 0.07 | 0.001 | 0.45 |
| 1,3,5-Trimethylbenzene | 55 | 44 | 1 | 0.07 | 0.06 | 0.06 | 0.04 | 0.08 | 0.001 | 0.55 |
| *n*-Dodecane | 44 | 54 | 1 | 0.08 | 0.06 | 0.07 | 0.04 | 0.11 | 0.004 | 0.71 |
| Naphthalene | 43 | 57 | 0 | 0.09 | 0.06 | 0.07 | 0.04 | 0.11 | 0.002 | 0.83 |
| 1,2-Dichloroethane | 46 | 54 | 0 | 0.07 | 0.07 | 0.07 | 0.06 | 0.08 | 0.04 | 0.16 |
| 1,4-Dichlorobenzene | 54 | 46 | 0 | 0.06 | 0.05 | 0.05 | 0.03 | 0.07 | 0.004 | 0.36 |
| Styrene | 29 | 68 | 3 | 0.05 | 0.03 | 0.03 | 0.02 | 0.06 | 0.001 | 0.97 |
| α-Pinene | 28 | 69 | 3 | 0.08 | 0.05 | 0.05 | 0.03 | 0.10 | 0.002 | 0.93 |
| 4-Methylheptane | 53 | 47 | 0 | 0.03 | 0.02 | 0.02 | 0.01 | 0.03 | 0.005 | 0.14 |
| 2,4-Dimethylhexane | 46 | 54 | 0 | 0.05 | 0.04 | 0.04 | 0.03 | 0.05 | 0.01 | 0.29 |
| 2,5-Dimethylhexane | 52 | 48 | 0 | 0.04 | 0.03 | 0.03 | 0.02 | 0.04 | 0.004 | 0.19 |
| *trans*-2-Butene | 49 | 51 | 0 | 0.06 | 0.05 | 0.04 | 0.03 | 0.07 | 0.01 | 0.46 |
| *cis*-2-Butene | 47 | 53 | 0 | 0.05 | 0.04 | 0.04 | 0.03 | 0.06 | 0.01 | 0.37 |
| *cis*-2-Pentene | 33 | 67 | 0 | 0.03 | 0.03 | 0.03 | 0.02 | 0.04 | 0.004 | 0.23 |
| 1-Propyne (Propyne) | 46 | 21 | 33 | 0.04 | 0.03 | 0.03 | 0.02 | 0.04 | 0.01 | 0.19 |
| *cis*-1,3-Dimethylcyclohexane | 32 | 36 | 33 | 0.07 | 0.06 | 0.05 | 0.04 | 0.08 | 0.02 | 0.29 |
| *n*-Propylbenzene | 30 | 69 | 0 | 0.05 | 0.04 | 0.04 | 0.03 | 0.05 | 0.01 | 0.28 |
| VOCs | | | | 41.99 | 38.57 | 36.56 | 29.04 | 50 | 15.68 | 160 |

species (this included 57 and 14 species detected in ≥50% and 30% of the samples, respectively). Significantly higher VOCs concentrations (Kruskal Wallis test, $p \leq 0.01$) were observed during winter (median = 51 μg/m$^3$) compared to other seasons i.e., summer (median = 32 μg/m$^3$), spring (median = 33 μg/m$^3$) and fall (median = 40 μg/m$^3$) and no variation was found between summer and spring months (Kruskal Wallis test, $p = 0.09$). The observed VOCs levels at Calgary downtown (arithmetic mean 42 μg/m$^3$) were comparable with Edmonton downtown (43 μg/m$^3$) for the same study period 2010–2015 (ECCC, 2017b) (Table 2). As reported earlier similar to Calgary, Edmonton downtown is also influenced by transportation (40% of total ambient VOCs) followed by natural gas/carry over (20%), fugitive evaporative emissions (17%) and it has less industrial impact (17%) from the east (McCarthy et al., 2013). VOC levels at Calgary downtown were also comparable with a big city like Toronto (36 μg/m$^3$) influenced by transportation and Hamilton downtown (39 μg/m$^3$) influenced by industry (ECCC, 2017b) but relatively higher than reported levels at an urban oil sands community Fort McMurray (33 μg/m$^3$) (Bari and Kindzierski, 2017b) and national capital Ottawa downtown (22 μg/m$^3$) (ECCC, 2017b), and lower than the City of Fort Saskatchewan (~50 μg/m$^3$) (Mintz and McWhinney, 2008) (Fig. S4).

Out of measured VOC species, the most dominant compounds found at Calgary central were alkanes (median contribution: 58% of total VOCs) followed by halogenated VOCs (22%), aromatics (11%), alkenes (6%), alkynes (2%) and terpenes (e.g., isoprene and $\alpha$-pinene) (0.4%). Alkanes are generally emitted from fuel evaporation, fossil-fuel combustion in industry and industrial processes such as oil and gas development, petrochemical production and petroleum refining (Sexton and Westberg, 1983; Cheng et al., 1997; Watson et al., 2001). For example, elevated levels of alkanes were also observed in industrial areas of the City of Edmonton influenced by the Strathcona petroleum refineries (Cheng et al., 1997), Athabasca oil sands communities (Bari et al., 2016) and near the Peace River oil sands deposit (AEP, 2015). Due to their higher emission rates and longer atmospheric lifetime (Atkinson and Arey, 2003), abundance of observed alkane levels may suggest an influence of emissions from natural gas combustion in local industries and conventional oil and gas development in surrounding Calgary. Average and geometric mean concentrations of individual BTEX compounds (benzene, toluene, ethylbenzene, xylenes) ranged from 0.3 to 1.8 μg/m$^3$ with maximum concentrations up to 15 μg/m$^3$. Yearly average benzene concentrations at Calgary central over the study period 2010–2015 (ranged from 0.51 μg/m$^3$ to 0.67 μg/m$^3$) and were below the annual Alberta Ambient Air Quality Objective (AAAQO) of 3 μg/m$^3$ (AEP, 2016b). In this study, notable concentrations (median = 6.4 μg/m$^3$, range = 2.7–32 μg/m$^3$) of sixteen hazardous VOC species considered as CEPA toxic substances (reported earlier) were observed. These species contributed 18% to the total VOCs, where BTEX and seven halogenated VOCs (chloroform, chloromethane, dichloromethane, 1,2-dichlorobenzne, 1,4-dichlorobenzene, tetrachloroethylene, and carbon tetrachloride) accounted for 9% and 7% of total VOCs, respectively.

### 3.2. VOC sources at Calgary downtown

In this study, a 9-factor PMF solution was chosen to best represent VOC sources at Calgary downtown for 2010–2015. Model input data statistics, performance criteria and error estimates are shown in the SI (Tables S4–S6). Fig. 2 shows source profiles i.e., chemical composition of emission sources of each of the identified source factors from the base and bootstrap runs and the average contributions (in μg/m$^3$ and percentage) of PMF-derived sources to total VOCs. The time series plots of 24 h contributions of the sources are depicted in Fig. 3 and annual average contributions along with yearly variations in identified sources are shown in the SI (Fig. S5, Table S7). Spearman rank correlation coefficients for PMF-derived factor and criteria air pollutant concentrations are shown in Table S8. Seasonal (summer and winter) CBPF plots of important PMF-resolved local sources at Calgary central are shown in Fig. 4. Other CBPF plots are shown in the SI, including seasonal plots for distant sources (Fig. S6) and plots for all sources for the whole study (Fig. S7). The spatial distribution of summer and winter CWT values for potential contribution of two dominant distant sources characterized by long-lived species e.g., oil/natural gas extraction/combustion and fuel combustion is presented in Fig. 5 (CWT plots for mixed fugitive emissions and background sources are shown in SI Fig. S8). The regression relationship between modeled and measured total VOCs concentrations (Fig. S9) showed a good fit with square of the correlation coefficient ($R^2$) of 0.98 suggesting that statistically, observed VOC concentrations at Calgary central were well represented by the PMF model-resolved source factors.

#### 3.2.1. Factor 1 gasoline exhaust

The key characteristics species found in factor 1 were benzene, ethylene, propylene, 1,3-butadiene, ethyltoluene isomers, trimethylbenzene isomers, xylene isomers, trimethylpentane isomers explaining from 20% to 41% of the variation. Some contributions of methylpentane, alkenes, styrene and naphthalene (representing from 17% to 27% of the explained variation) were also present in this factor. Benzene, ethylene, propylene, 1,3-butadiene are typically emitted from exhaust of gasoline vehicles (Watson et al., 2001; Schauer et al., 2002). This factor was interpreted as gasoline exhaust and it contributed 4.8% (1.97 μg/m$^3$) to measured total VOCs at Calgary central. In general, characteristic emission ratios of toluene/benzene (T/B) and *m,p*-xylene/ethylbenzene (X/EB) in the range of 1.5–3.0 (Miller et al., 2010) and 3.3–4.3 (Nelson and Quigley, 1983), respectively have been used as an indicator of vehicle exhaust emissions. In this factor, the observed ratios of T/B (1.6) and X/EB (4.1) suggest an influence of downtown traffic at the Calgary central air monitoring station. In this study, contributions of this factor showed significant correlation with traffic-related gaseous pollutants i.e., NO, $NO_2$, $NO_X$, CO (Spearman rank coefficient, r = 0.50–0.64, $p < 0.01$) and some association with $PM_{2.5}$, THC and $CH_4$ (r = 0.20–0.26) (Table S8). The time series plot of daily contributions of this factor (Fig. 3) showed significantly higher average contribution during winter (Kruskal Wallis test, $p < 0.0001$) compared to summer. The observed

**Table 2**
Comparison of VOC levels at selected major urban areas in Canada.

| TVOCs | Study period | Average (μg/m$^3$) | Min–max (μg/m$^3$) | Reference |
|---|---|---|---|---|
| Calgary downtown | 2010–2015 | 42 | 16–160 | This study |
| Edmonton downtown | 2010–2015 | 45 | 15–167 | ECCC, 2017b |
| Fort McMurray | Jan. 2010–Mar. 2015 | 33 | 2–240 | Bari and Kindzierski, 2017b |
| Fort Saskatchewan | Sep. 2004–Mar. 2006 | ~50 | | Mintz and McWhinney, 2008 |
| Toronto[a] | 2010–2014 | 36 | 15-167 | ECCC, 2017b |
| Hamilton downtown | 2010–2015 | 39 | 15–177 | ECCC, 2017b |
| Ottawa downtown | 2010–2015 | 22 | 11–131 | ECCC, 2017b |

[a] Measured in Gage Institute.

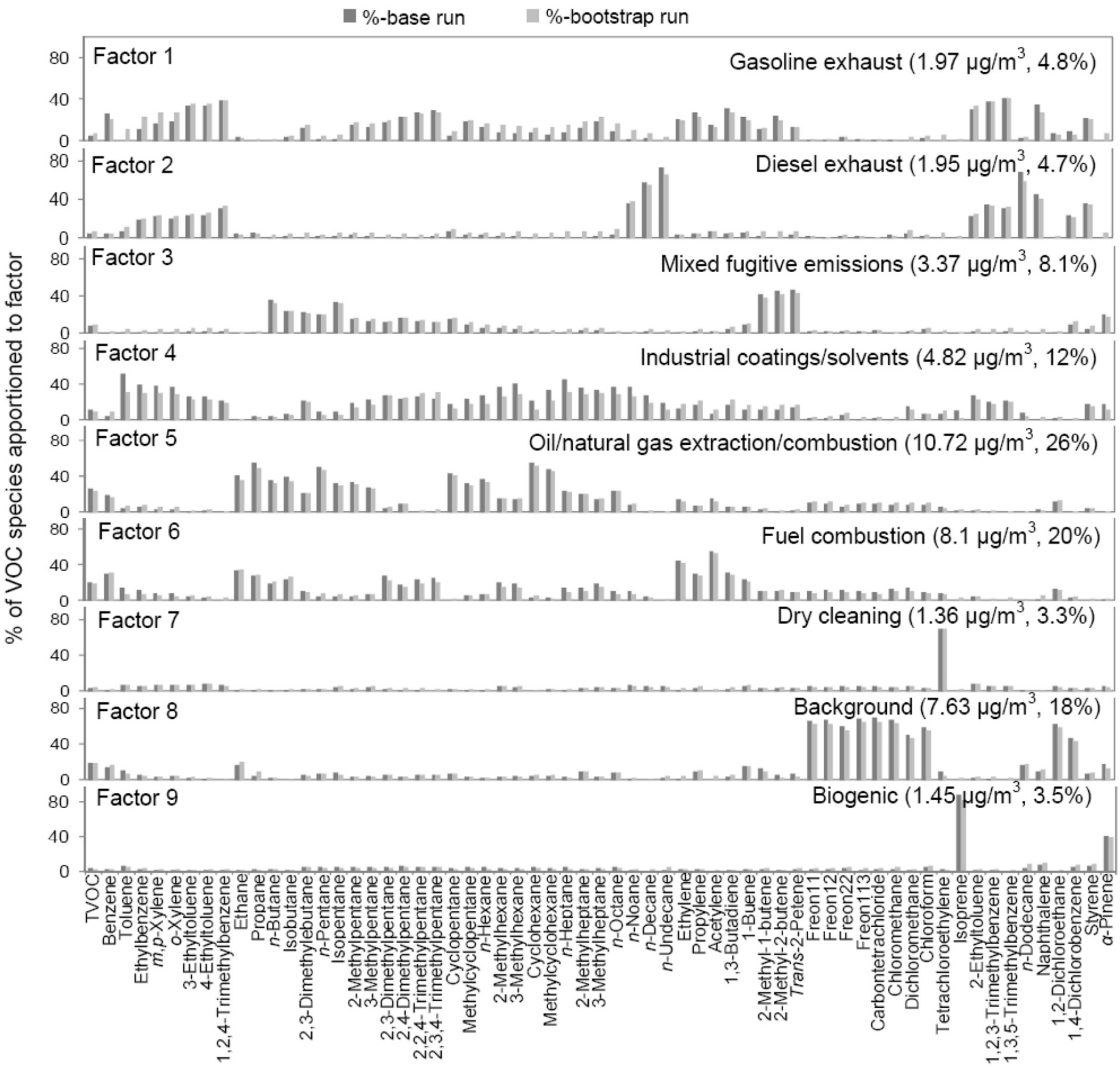

**Fig. 2.** PMF-derived source profiles from base and bootstrap runs (% of species apportioned to each factor) and average contributions of each sources to total VOCs (in the parentheses) at Calgary central for study period 2010–2015.

winter-high pattern may be associated with occurrence of stable atmospheric conditions (low temperature, wind speed, and surface inversions with low mixing layer heights) (Hicks et al., 1977), cold-start emissions and increased car idling during winter months. CBPF plots of this factor revealed northwest (summer and winter) and easterly (summer) (Fig. 4). With respect to potential sources, these locations suggest traffic-related emissions from major roadways within Calgary (Figs. S2b, c) and from the downtown core. A similar source type 'gasoline combustion' was also suggested for Calgary downtown by Ladha et al. (2014) for the study period 2004–2011 contributing 9% to reconstructed VOC mass. The observed decrease in contributions of gasoline exhaust during 2010–2015 agrees with the decreasing trends in traffic-related pollutants i.e., $NO_2$ (3.6% decrease per year) and CO (4.9% decrease per year) from 1998 to 2014 in Calgary downtown, suggesting a decline of traffic emission contributions over the 17-year period (Bari and Kindzierski, 2016b).

### 3.2.2. Factor 2 diesel exhaust

Factor 2 was distinguished by high concentrations of heavier alkanes i.e., *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane (explaining 38% to 67% of the variation), typically known as tracers for diesel combustion (Schauer et al., 1999; Watson et al., 2001). Some contributions of ethylbenzene, xylene isomers, ethyltoluene isomers, trimethylbenzene isomers, trimethylpentane isomers, naphthalene, 1,4-dichlorobenzene and styrene (representing from 20% to 40% of the explained variation) were also observed in this factor. This factor was positively correlated with traffic-related gaseous pollutants and showed no clear seasonality (Kruskal Wallis test, $p = 0.15$) with peaks during winter and summer/fall months over the study period 2010–2015 consistent with previous findings for 2004–2011 (Ladha et al., 2014). The ratios of T/B and X/EB were 4.5 and 4.0, respectively. The CBFP plots indicated southeast under low to high wind speed (5–25 km/h) and southwest/west under high wind speed (20–30 km/h) (Fig. 4, summer and winter) as dominant source directions. Diesel vehicle emissions from designated truck routes within Calgary (Fig. S2c) and from industrial-zoned districts to the southeast (Fig. S3) are likely associated with this factor. Therefore, factor 2 was interpreted as diesel exhaust source and the contribution of this factor was 4.7% (1.95 μg/m$^3$) to measured total VOCs at Calgary central.

### 3.2.3. Factor 3 mixed fugitive emissions

Factor 3 was characterized by *n*-butane, isobutane, isopentane, *trans*-2-pentene, 2-methyl-2-butene, and 2-methyl-1-butene explaining from

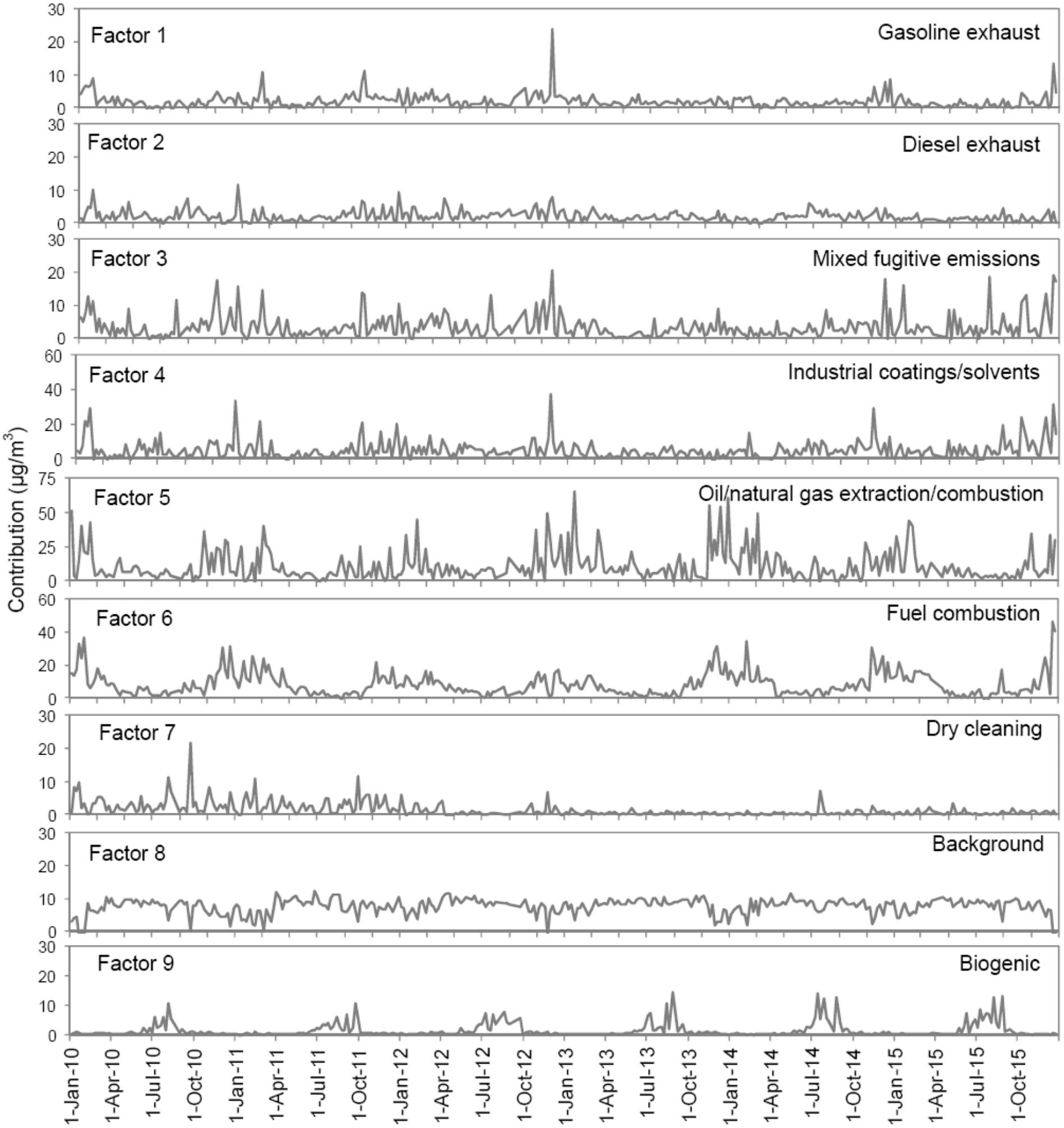

**Fig. 3.** Time series of PMF-derived source contributions at Calgary central for study period 2010–2015.

23% to 43% of the variation. Some associations with *n*-pentane, 2,3-dimethylbutane, methylpentane, cyclopentane were also observed (explaining 15% to 21% of the variation). The contribution of this factor was 8.1% (3.37 μg/$m^3$) to measured total VOCs. Typically, emission ratios of isobutane/*n*-butane are 0.2–0.3, 0.46 and 0.6–1.0 representing vehicular traffic, liquefied petroleum gas (LPG) and natural gas, respectively (Russo et al., 2010). In addition, emission ratios of isopentane/*n*-pentane have been reported by others for vehicle/tunnel emissions (2.2–3.8), liquid gasoline emissions (1.5–3.0) and fuel evaporation emissions (1.8–4.6) (Harley et al., 1992;Conner et al., 1995; Watson et al., 2001). In this study, the ratios of isobutane/*n*-butane and isopentane/*n*-pentane for this factor were 0.30 and 3.1, respectively suggesting an influence of mixed fugitive emissions from vehicles and industries. Evaporative gasoline emissions are generally associated with various industrial fugitive emissions due to leaks, process venting and flaring, and evaporation losses from hydrocarbon storage facilities (i.e., fuel, diluent or final product storage tanks) (CEMA, 2012) as well as motor vehicle emissions from resting losses, running loses due to liquid and vapor leaks in the fuel system, hot soak emissions, and liquid fuel spillage during refueling at gas stations (Fujita and Campbell, 2003; Harley and Kean, 2004; Na et al., 2004).

This factor showed notable associations with NO, $NO_2$, $NO_X$ and CO (0.44–0.54, $p < 0.01$) (Table S8). Several peaks were observed in both summer and winter months (Fig. 3), while concentrations were about two-fold higher during winter (4.3 μg/$m^3$) compared to summer (2.4 μg/$m^3$) (Kruskal Wallis test, $p < 0.01$). A similar winter-high trend was also observed for a fugitive butane source (contribution 8%, 5 μg/$m^3$) at Edmonton downtown in the capital city of Alberta (McCarthy et al., 2013). CBPF plots showed southeast and downtown sources during summer and southwest and north as dominant directions during winter (Fig. 4). The most plausible local emission sources could include traffic from heavily used roadways (Fig. S2b) and designated truck routes within Calgary (Fig. S2c), and emissions from commercial/industrial activities in the industrial-zoned districts to the northeast and southeast

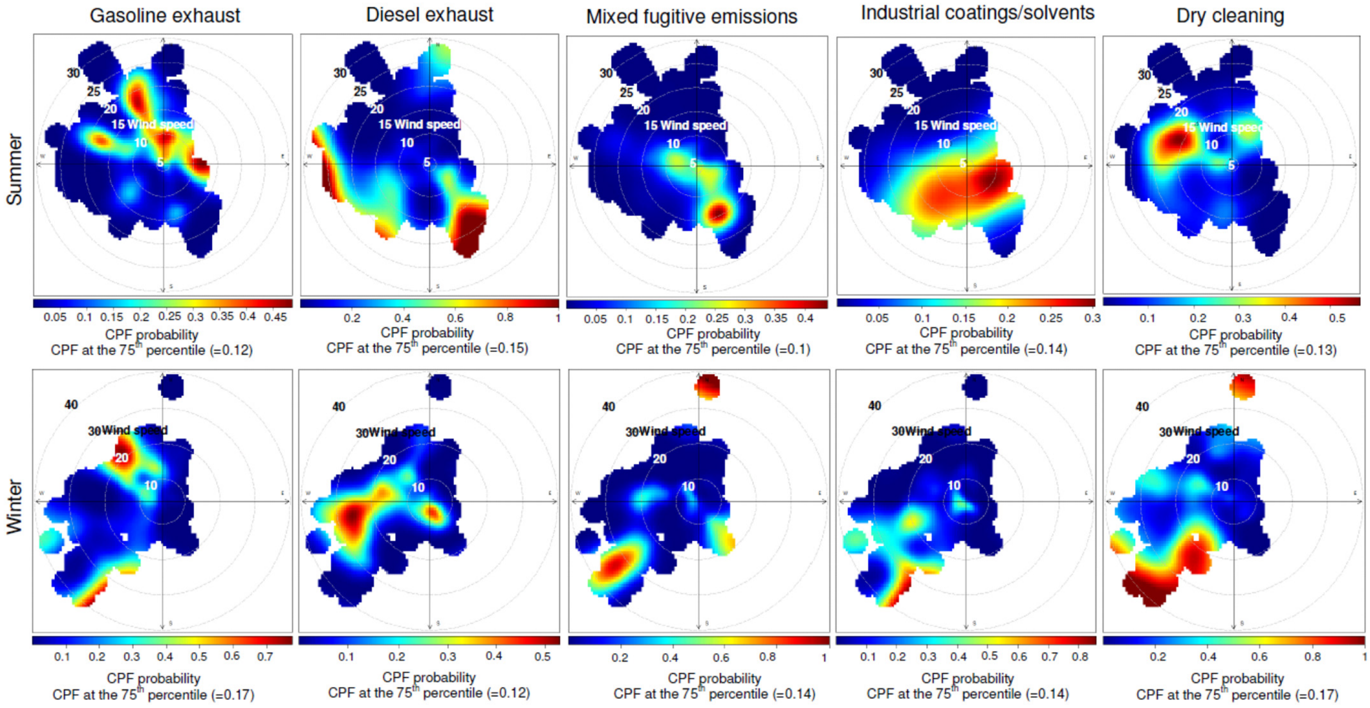

**Fig. 4.** Summer and wintertime CBPF plots of local VOC sources at Calgary central for study period 2010–2015.

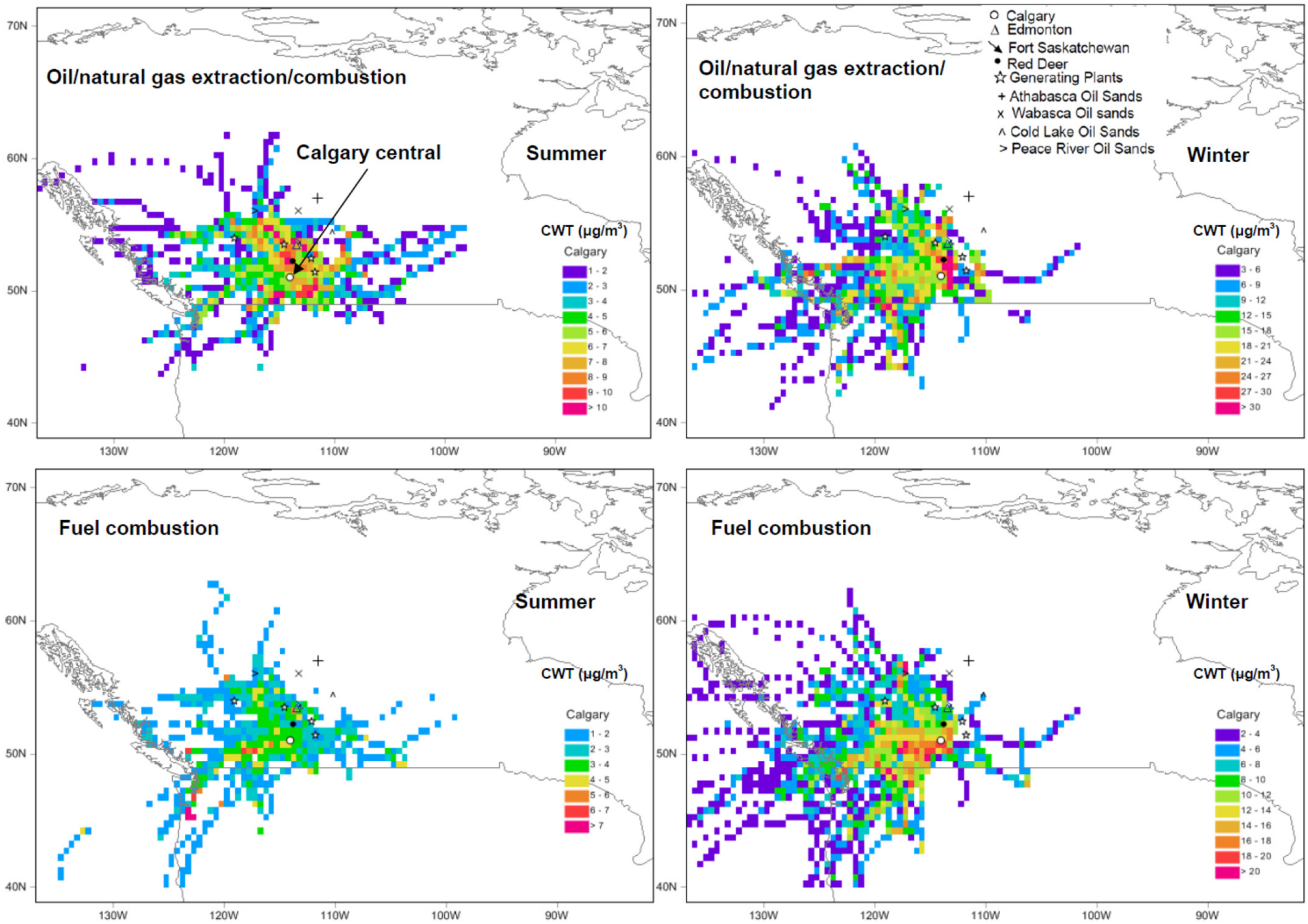

**Fig. 5.** CWT plots of oil/natural gas extraction/combustion and fuel combustion at Calgary central for 2010–2015.

(Fig. S3). Backward trajectory analysis (CWT plots, Fig. S8) indicated potential long-range source regions in and southeastern Alberta (summer) and from the southwest (winter) suggesting an influence from conventional oil and gas extraction. Therefore, factor 3 was assigned as mixed fugitive emissions from vehicle and industrial activities.

#### 3.2.4. Factor 4 industrial coatings/solvents

The key species detected in factor 4 were toluene (51% of total mass), ethylbenzene (39%), xylenes (37%), *n*-hexane (27%), 3-ethylhexane (41%), *n*-heptane (45%), *n*-octane (37%), *n*-nonane (36%) and *n*-decane (28%). Notable contributions of other isoalkanes and cycloalkanes e.g., 2,3-dimehtylbutane, dimethyl- and trimethylpentanes, methylcyclohexane, methylheptanes (22% to 35% of their total mass) were also present in this factor. Toluene and heavier alkanes (e.g., *n*-nonane, *n*-decane) are widely used as solvents for architectural coatings, degreasing/painting operations, printing inks and other industrial applications (TRC Environmental Corporation, 1994; Watson et al., 2001; Liu et al., 2008). The observed higher ratio of T/B (>10) in this factor indicates the influence of industrial applications including solvents, consistent with ratios observed in urban and industrial areas elsewhere (Tang et al., 2007). Contributions of this factor showed positive associations with criteria pollutants e.g., NO, $NO_2$, $NO_X$, CO and $PM_{2.5}$ ($r = 0.30–0.45$, $p < 0.01$) (Table S8). The time series plot (Fig. 3) showed some peak concentrations particularly during winter months, however no significant seasonal variation was observed (Kruskal Wallis test, $p = 0.16$). CBPF plots (Figs. 4, S6) clearly showed southeast and southwest as dominant source directions during summer under low wind speeds and only southwest during winter under high wind speed. Several paint and coating industries located in southwest, south and southeast Calgary are likely associated with this factor (Fig. S10). Therefore, factor 4 was interpreted as industrial coatings/solvents and it contributed 12% (4.82 μg/$m^3$) to measured total VOCs at Calgary central.

#### 3.2.5. Factor 5 oil/natural gas extraction/combustion

Factor 5 was identified as the largest contributor (26%, 10.72 μg/$m^3$) to ambient VOCs at Calgary central. It was characterized by notable abundances of ethane, propane, *n*-butane, isobutane, *n*-pentane, cyclopentane, *n*-hexane, cyclohexane, and methylcyclohexane explaining from 32% to 51% of the variation. Some contributions of benzene, isopentane, methylpentanes, heptanes, methylheptanes, and *n*-octane (representing from 17% to 30% of the explained variation) and *n*-pentane, methylcyclopentane, and methylcyclohexane (representing from 26% to 34% of the explained variation) were also present in this factor. Ethane, propane, *n*-butane, isobutane are typical fingerprints for natural gas (Thijsse et al., 1999; Na et al., 2004). The key abundance species found in petroleum-related emissions are ethane, propane, *n*-butane, *n*-pentane, cyclopentane, *n*-hexane, cyclohexane, methylcyclohexane, *n*-octane and benzene (Watson et al., 2001; Liu et al., 2008). In this factor, the mean ratio of isobutane/*n*-butane (0.5) was within the range of reported emission ratio for natural gas (~0.6) (Thijsse et al., 1999; Na et al., 2004) and consistent with ambient measurement ratios observed in conventional and non-conventional oil and gas extraction operations in Fort Saskatchewan (0.56), in Alberta oil sands communities (0.40–0.43), in Houston, Texas (0.46–0.85) and in Colorado (0.56) (Xie and Berkowitz, 2006; Mintz and McWhinney, 2008; Bari et al., 2016; Swarthout et al., 2015). This factor showed significant correlations with THC ($r = 0.51$, $p < 0.01$) and $CH_4$ ($r = 0.53$, $p < 0.01$) (Table S8). THC can be emitted from a variety of sources including petroleum and chemical industries, natural gas combustion and other sources. Significantly higher average contribution (Kruskal Wallis test, $p < 0.0001$) was observed during winter (16.5 μg/$m^3$) compared to summer (5.7 μg/$m^3$). The higher contributions in winter months may be associated with numerous factors including higher atmospheric residence time of alkanes, seasonality of atmospheric removal of hydroxyl (OH) radical reactions (Penkett et al., 1993) and more frequent stable weather and inversion conditions during winter (Hicks et al., 1977).

The CBPF plots of this factor indicated moderate northwest and dominant southwest directions during summer under low to moderate wind speeds (Fig. S6), while strong contributions were observed from the northwest during winter under wind speed > 20 km/h. Natural gas combustion related to industries located within 5 to 15 km south/southeast and 15 to 45 km northwest (e.g., Inter pipeline extraction plant, Wildcat Hills gas plant in Cochrane) may contribute to this factor. CWT plots (Fig. 5) revealed potential long range source regions to the north and southeast during summer and easterly and north/northeast during winter. Conventional oil/natural gas extraction activities in southeastern Alberta and within the Calgary-Edmonton Corridor region are likely associated with this factor.

Local sources for this factor (i.e., within Calgary) would be consistent with emissions from industrial facility natural gas combustion. Industry is a large consumer of natural gas which is used as an energy source. Whereas, distant emission sources are more likely associated with conventional oil/natural gas extraction. Therefore, factor 5 was best interpreted as an oil/natural gas extraction/combustion signal. It is noteworthy that annual contributions of this factor at Calgary central showed no significant variation over the 6-year study period ($p = 0.075$), consistent with a background regional secondary sulfate signal attributed to oil and gas production activities in Alberta (Schulz and Kindzierski, 2001; Bari and Kindzierski, 2017c, 2016a).

#### 3.2.6. Factor 6 fuel combustion

Factor 6 was the second largest source in Calgary contributing 20% (8.1 μg/$m^3$) to ambient total VOCs on average. The key species found in this factor were ethylene, propylene, acetylene, 1,3-butadiene, benzene, ethane and propane representing 41%, 27%, 53%, 29%, 31%, 34%, and 28% of the explained variation, respectively. Some contributions of butane (22%), isobutane (26%), 2,3-dimethylpentane (22%), 1-butene (22%), 1,2-dichloroethane (12%) and chloromethane (10%) were also found. Ethylene, propylene, acetylene, 1,3-butadiene, benzene, ethane and propane are typical combustion products primarily emitted from biomass burning (Schauer et al., 2001; Liu et al., 2008). Contributions of this factor showed good correlations with typical combustion gases like NO, $NO_2$, $NO_X$, CO ($r = 0.68–0.78$, $p < 0.01$) and positive associations with THC, $CH_4$ and NMHC ($r = 0.23–0.34$, $p < 0.01$) (Table S8). CO is released to the atmosphere primarily from incomplete combustion of carbon-containing fuels such as biomass, natural gas, gasoline, oil. THC, $CH_4$ and NMHC can also be emitted from natural (e.g., forest fires) and anthropogenic sources including oil and gas industry and residential/commercial heating (Ferek et al., 1998; Sauvage et al., 2009; Bari and Kindzierski, 2017d). The time-series plot of daily source contributions of this factor (Fig. 3) showed a clear seasonality with significantly higher concentrations in winter (14.2 μg/$m^3$) than in summer (2.9 μg/$m^3$) (Kruskal Wallis test, $p < 0.0001$), suggesting a possible influence of emissions from residential and commercial heating combustion. No significant year to year variations ($p = 0.306$) in contributions of this factor was observed (Table S7). Factor 6 was identified as fuel combustion (e.g., wood, natural gas, oil).

As reported previously, according to CRAZ 2008 emission inventories, >10,000 tonnes/year of CO along with VOCs (>1500 tonnes/year), $NO_X$ (>5000 tonnes/year) and $PM_{2.5}$ (~2000 tonnes/year) are released to the atmosphere in the CRAZ region and the City of Calgary from the commercial and residential heating sector (Table S1). The winter CBPF plot of this factor (Fig. S6) indicated northwest as dominant and west and northeast as moderate directions for local sources. Combustion of natural gas for commercial/residential heating and wood stove/fireplace use among residences within the city and surrounding rural Calgary, respectively during winter are likely associated with this factor. Several elevated concentrations (e.g., May 27, 2011; July 16, 2014; June 30, 2015; August 28, 2015) were also observed during spring and summer months, suggesting that this factor may be associated with smoke emissions from wildfires that occurred in Alberta and other western provinces such as British Columbia, Saskatchewan and in Western United States during the study period 2010–2015. The summer CWT plot suggest an influence of wildfire smoke coming from British Columbia, northern and southern Alberta, Saskatchewan and the Western United States (Figs. 5, S11). The winter CWT plot indicated potential source regions surrounding Calgary and easterly suggesting the possible influence of residential wood-burning, open wood burning (e.g., agricultural slash burning) that can occur during winter as found in our Edmonton source apportionment study for $PM_{2.5}$ (Bari and Kindzierski, 2016a).

### 3.2.7. Factor 7 dry cleaning

Factor 7 was highly enriched with tetrachloroethylene explaining 69% of the variation. Tetrachloroethylene, also known as perchloroethylene (PERC) is a commonly used solvent typically emitted from dry cleaning shops (Wallace, 1989). Historically, higher ambient levels of PERC have been reported near dry cleaning facilities (Verberk and Scheffers, 1980; Howie, 1981). The 24 h source contributions of this factor showed no seasonal variation (Kruskal Wallis test, $p = 0.09$) over the study period and were positively correlated with $PM_{2.5}$, $NO_X$ and CO ($r = 0.51$, $p < 0.01$). The annual contribution of this factor showed significant variation ($p < 0.0001$) over the study period and a declining trend in recent years (Fig. S5, Table S7). CBPF plots of this factor indicated west (summer), southwest and north (winter) as dominant source directions and moderate influence from the northwest (summer). Several dry cleaning shops and facilities located west, southwest and north of the monitoring station are likely associated with this factor (Fig. S12). Therefore, factor 7 was assigned as dry cleaning and it contributed 3.3% (1.36 $\mu g/m^3$) of total measured VOCs on average.

### 3.2.8. Factor 8 background

Factor 8 was characterized by an abundance of halogenated VOCs e.g., Freon groups, chloroform, chloromethane, dichloromethane, tetrachloroethylene, carbon tetrachloride, 1,2-dichloroethane and 1,4-dichlorobenzene explaining from 43% to 65% of the variation. These species have long atmospheric lifetimes (e.g., Godish, 1991; Ramamoorthy and Ramamoorthy, 1997) and can be considered global background pollutants. It is noteworthy that some of these species' commercial production (e.g., carbon tetrachloride) was phased out and is well controlled in Canada and the United States since the Montreal Protocol (1989). This factor showed negative correlation with all criteria pollutants except ground level $O_3$, where a significant correlation was observed ($r = 0.59$, $p < 0.01$) (Table S8). The time series plot of this factor indicated an apparent seasonality with higher contributions in summer months compared to winter (Kruskal Wallis test, $p < 0.0001$). While annual yearly contributions showed no significant variation ($p = 0.08$) over the study period (Fig. S5, Table S7).

It is noteworthy that residual halogenated VOCs may originate from global sources, leading to background mixing ratios of halocarbons in the atmosphere and can be unaffected by local or regional sources (Shao et al., 2011). Most halogenated VOC species are released into the atmosphere from natural sources in trace amounts; while a substantial portion can also be emitted from industrial point sources and area sources such as fossil fuel combustion, waste incineration, and wastewater treatment plants, consumer and commercial products (Wallace et al., 1987; Harkov et al., 1987; McCulloch et al., 1999; Rosenbaum et al., 1999). Given these origins, it is plausible that both local and distant (global) sources can contribute to this signal. Both CBPF plots of this factor (Fig. S6) and CWT plots (Fig. S8) support this. Factor 8 was represented as a background source and it accounted for 18% (7.63 $\mu g/m^3$) of total measured VOCs. A similar global background source was also observed in Edmonton and contributed 12% (7 $\mu g/m^3$) to total VOCs (McCarthy et al., 2013).

### 3.2.9. Factor 9 biogenic

Factor 9 was identified as biogenic emissions and it was distinguished by a high abundance of isoprene (explaining 82% of the variation) along with some contributions of $\alpha$-pinene (39%). Isoprene, an important ozone precursor, is a common marker for biogenic emissions (Altshuller, 1983; Fuentes et al., 2000), despites its high reactivity (Carter, 1994) and it contains about 35% of the total carbon in non-methane ambient VOCs (Guenther et al., 2000). Monoterpenes like $\alpha$-pinene can be emitted from vegetation, trees and forest leaves (Singh et al., 1994; Guenther, 1997). Since isoprene emissions are associated with increasing photosynthesis, contributions of this factor are expected to be highest in summer and lowest in winter (Monson et al., 1992). Accordingly, significantly higher contributions of this factor were observed in summer months compared to winter (Kruskal Wallis test, $p < 0.0001$). Vehicle exhaust in urban areas is usually the most important source of anthropogenic isoprene (Borbon et al., 2001). CBPF plots indicated dominant contributions from the northwest/north and moderate influences from the west suggesting probable influence from local sources. The contribution of this factor was 3.5% (1.45 $\mu g/m^3$) to measured total VOCs at Calgary central. This is consistent with findings from emission inventories conducted by Environment Canada 2006 and CRAZ 2008, where the contribution of biogenic emissions was 2.5% to total VOC emissions for the City of Calgary (Novus Environmental, 2013).

## 3.3. Human health risk of VOCs and associated sources via inhalation exposure

For deterministic health risk screening, arithmetic and geometric mean concentrations of detected VOCs at Calgary central were compared to cancer risk criteria (inhalation unit risk-IUR, $(\mu g/m^3)^{-1}$) and non-cancer risk criteria (reference concentrations-RfC, $mg/m^3$) for potential chronic end-points. Whereas, maximum concentrations were compared to available acute limits (United States Agency for Toxic Substances and Disease Registry (ATSDR) minimal risk levels (MRLs) and California EPA reference exposure levels (RELs)) (Table S9). Concentrations of carcinogens were also compared to an equivalent cancer benchmark target used for Alberta (1 in 100,000) (Health Canada, 2004). Arithmetic and geometric means of all hazardous VOCs were well below USEPA screening risk criteria and the cancer benchmark for Alberta. Carcinogenic and non-carcinogenic risks of hazardous VOC species via inhalation exposure are shown in Fig. 6. At Calgary central, carcinogenic risks of benzene (means and 95th percentile), carbon tetrachloride and naphthalene (95th percentiles) were above the acceptable level of $1 \times 10^{-6}$ but below a tolerable risk of $1 \times 10^{-4}$. In Alberta, potential lifetime exposures corresponding to these risk values are deemed acceptable if it increases a person's chance of developing cancer by 1 in 100,000 ($1 \times 10^{-5}$) or less (Health Canada, 2004; Kindzierski et al., 2011). This level is judged to be reasonable when compared to an estimated average background risk of all cancers (34,000 in 100,000 over a lifetime) that Albertans carry (Kindzierski et al., 2011). For non-carcinogens, means and 95th percentile values of hazard quotients (HQs) of all potentially toxic VOC species were below a safe level ($= 1$).

Health risk from inhalation exposure was apportioned to the nine identified sources at Calgary downtown by summing carcinogenic and non-carcinogenic risks of all available risk-posing VOC species in a particular source. This point estimate approach for ‘source risk apportionment’ has been applied in several other studies (Wu et al., 2009; Li et al., 2015; Khan et al., 2016; Bari and Kindzierski, 2017a). The source specific carcinogenic and non-carcinogenic risk values are shown in Fig. 7. Carcinogenic risks of different sources ranged from $8.2 \times 10^{-8}$ to $1.5 \times 10^{-6}$ and all risk values were below the USEPA acceptable level ($1 \times 10^{-6}$) except for the background source, where the risk value was above the acceptable level but below the tolerable risk ($1 \times 10^{-4}$). Carcinogenic risks of gasoline exhaust and fuel combustion

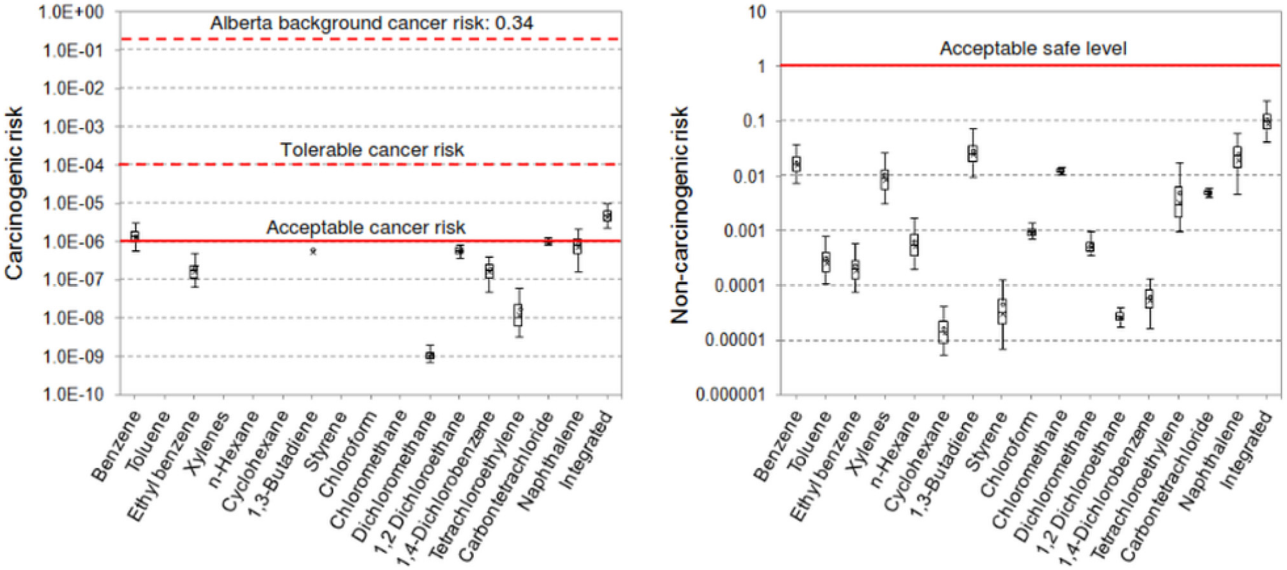

**Fig. 6.** Carcinogenic and non-carcinogenic risks of hazardous VOC species at Calgary central for 2010–2015. Boxes represent 25th (lower quartile) and 75th (upper quartile) percentile values, with median values as lines across the boxes, geometric and arithmetic mean values as cross and circles as well as 5th and 95th percentile concentrations as whiskers.

were close to the acceptable level. Source specific non-carcinogenic risk values (HIs) ranged from 0.002 to 0.03 and were below the safe level (= 1).

We also evaluated the relative contribution to risk for each source after Wu et al. (2009) to understand which sources may pose more risk to public health. In general, sources consisting of more hazardous air pollutants or air toxics may contribute to greater health risk, while sources with less contribution from air toxics pose relatively less health risk. The relative contribution to carcinogenic and non-carcinogenic inhalation risk of the sources is also shown in Fig. 7. As reported previously (Fig. 1), traffic related sources (gasoline and diesel exhausts, mixed fugitive emissions) showed notable contribution (combined 10–15%) to total measured VOCs and at the same time they posed greater risk to public health (33% and 40% of carcinogenic and non-carcinogenic risks, respectively) compared to the other sources. For other sources, the background source showed a notable contribution to cancer risk (30%), while fuel combustion posed 16% and 17% of cancer and non-cancer risk, respectively. The most dominant VOC source – oil/natural gas extraction/combustion posed relatively low carcinogenic (10%) and non-carcinogenic (7%) risks to public health. This is consistent with our previous cancer risk estimates for Edmonton, Alberta for $PM_{2.5}$-derived secondary sulfate and secondary nitrate sources (<10%) for the period 2010–2015 (Bari and Kindzierski, 2016a, 2016b) as well as a HAPs-derived fossil fuel combustion source (13%) for the period 2019–2013 (Bari and Kindzierski, 2017a). The screening risk assessment study undertaken here is based on an assumption that the potential for receptor exposure to VOCs is the same from all sources. However, in reality VOCs emitted for specific sources in the near-field of a receptor (e.g., from transportation emissions generated at street level) will be much more important for personal exposure compared to VOCs emitted from sources in the far-field (e.g., from oil/natural gas extraction/combustion emissions generated outside the City of Calgary).

We acknowledge some limitations in our health risk assessment. It was only screening-level and provides an initial assessment about

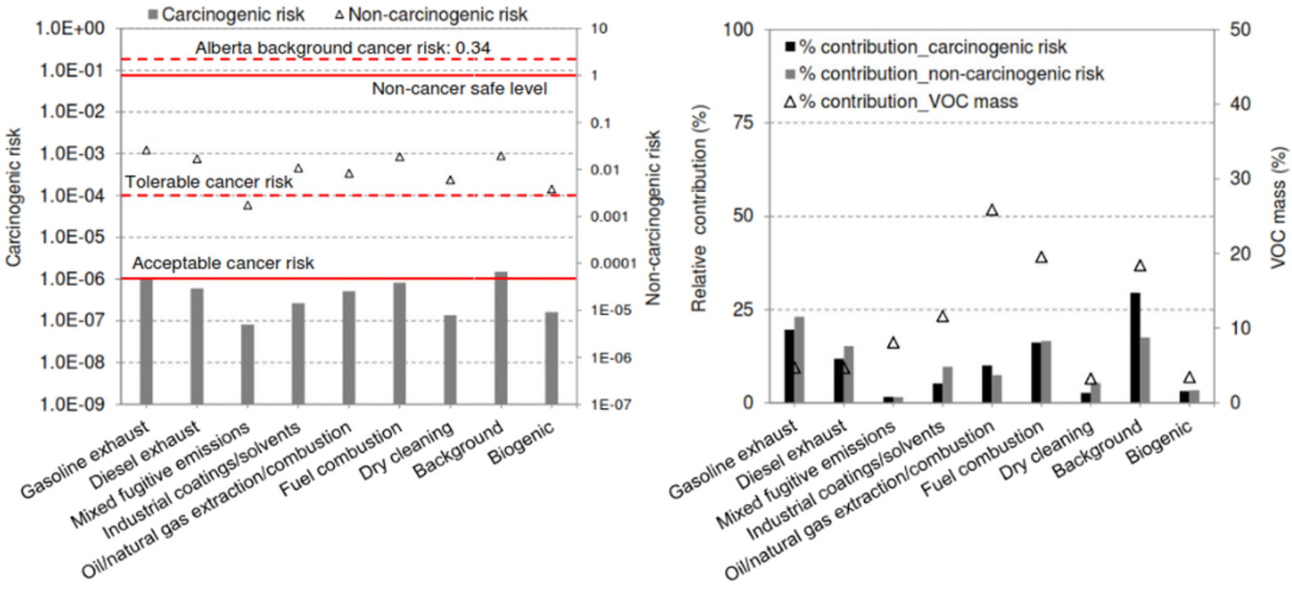

**Fig. 7.** Carcinogenic and non-carcinogenic risks of predicted VOC sources at Calgary downtown for 2010–2015.

whether individual VOCs or specific sources are likely to pose a risk to public health. We characterized human health risk based on available toxicity data for measured VOCs species and this may underestimate total risk values. For those species with available toxicity data, most of the uncertainty is related to assumptions in the quantitative derivation of inhalation unit risk (IUR) and/or reference concentration (RfC) values. Carcinogenic and non-carcinogenic risks of VOC sources were calculated based on 16 detected hazardous VOCs used in the PMF analysis. However, other potentially important hazardous VOCs in the USEPA list of 187 air toxics and 30 urban air toxics (USEPA, 2016a, 2016b) were not measured in this study – for example, acrolein, formaldehyde, acetaldehyde. Notwithstanding these limitations, the resultant inhalation cancer and non-cancer risks estimated here is a reasonable first step for understanding ambient VOC source-specific risks to public health in Calgary.

## 4. Conclusion

A study was carried out at Calgary downtown using VOCs air monitoring data for the period 2010–2015 to better understand current levels and sources of ambient VOCs and their associated risk to public health. Total VOCs levels at Calgary downtown (arithmetic mean 42 μg/m$^3$) were comparable with Edmonton downtown (43 μg/m$^3$) but higher than Alberta oil sands communities (33 μg/m$^3$) and lower than the City of Fort Saskatchewan, Alberta (~50 μg/m$^3$). The most dominant compounds were alkanes, followed by halogenated VOCs and aromatics. Source apportionment analysis identified nine sources where industrial emissions (41%), commercial/residential fuel combustion (20%) and traffic-related emissions (10–15%) contributed to about 80% of total VOCs mass. A screening health risk assessment indicated that carcinogenic risks of benzene, carbon tetrachloride and naphthalene were above the acceptable level of $1 \times 10^{-6}$ but below a tolerable risk of $1 \times 10^{-4}$. Estimated cancer risks for all sources were below the Alberta cancer screening benchmark of 1 in 100,000 and estimated non-cancer risks for all sources were well below a safe level.

There are some limitations in the current study. Some potential VOC species of public health interest, including aldehydes (e.g., formaldehyde, acetaldehyde, acrolein), alcohols (e.g., methanol) and ketones (e.g., acetone) were not measured in downtown Calgary. Future monitoring of these additional VOC species (which are currently measured in Edmonton and oil sands communities of Alberta) would be needed to better understand their potential sources and contribution to public health risk in Calgary.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.03.023.

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