



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



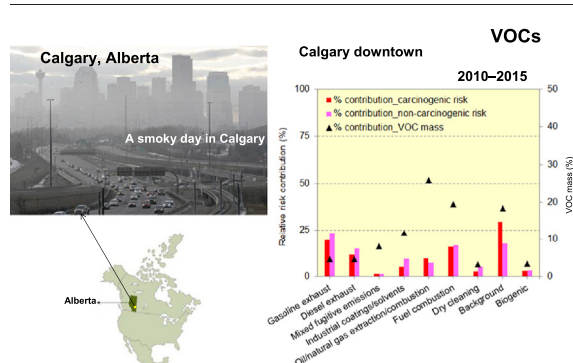
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HIGHLIGHTS

- 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 $42 \mu\text{g}/\text{m}^3$ and $39 \mu\text{g}/\text{m}^3$, respectively and ranged from 16 to $160 \mu\text{g}/\text{m}^3$, 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 km², 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).

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