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Estimation of indoor and outdoor ratios of selected volatile organic compounds in Canada

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HIGHLIGHTS

- A unique approach was developed to the calculation of the ratios of VOCs in indoor and outdoor air (I/O).
- Data used for the calculation of I/O were from two independent large surveys, one for indoor air and the other outdoor air.
- Two calculation methods produced similar I/O ratios boosting confidence for the calculated I/O ratios for selected VOCs.
- Rank of VOC sources was similar to ranks reported based on traditional paired indoor and outdoor air samples.

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ABSTRACT

Indoor air and outdoor air concentration (I/O) ratio can be used to identify the origins of volatile organic compounds (VOCs). I/O ratios of 25 VOCs in Canada were estimated based on the data collected in various areas in Canada between September 2009 and December 2011. The indoor VOC data were extracted from the Canadian Health Measures Survey (CHMS). Outdoor VOC data were obtained from Canada's National Air Pollution Surveillance (NAPS) Network. The sampling locations covered nine areas in six provinces in Canada. Indoor air concentrations were found higher than outdoor air for all studied VOCs, except for carbon tetrachloride. Two different approaches were employed to estimate the I/O ratios; both approaches produced similar I/O values. The I/O ratios obtained from this study were similar to two other Canadian studies where indoor air and outdoor air of individual dwellings were measured. However, the I/O ratios found in Canada were higher than those in European cities and in two large USA cities, possibly due to the fact that the outdoor air concentrations recorded in the Canadian studies were lower. Possible source origins identified for the studied VOCs based on their I/O ratios were similar to those reported by others. In general, chlorinated hydrocarbons, short-chain (C5, C6) *n*-alkanes and benzene had significant outdoor sources, while long-chain (C10–C12) *n*-alkanes, terpenes, naphthalene and styrene had significant indoor sources. The remaining VOCs had mixed indoor and outdoor sources.

1. Introduction

Volatile organic compounds (VOCs) are organic compounds having a boiling point below 250 degree Celsius (°C) at ambient atmospheric pressure (WHO, 1989). These include a large number of chemicals such as benzene and its derivatives, simple aliphatic hydrocarbons (e.g., hexane and decane), chlorinated hydrocarbons (e.g., chloroform and trichloroethylene), and terpenes (e.g., limonene). They also include alcohols, aldehydes and ketones with low carbon numbers such as isopropanol, hexanal and butanone (Cometto-Muñiz and Abraham, 2015). VOCs are emitted from a variety of building materials and consumer products such as carpets, ceiling tiles, paints, solvents, cleaning products and furniture. Emissions from transportation and from combustion, including cigarette smoking, also contribute to the presence of VOCs in indoor air (Palot et al., 2008). Due to their relatively high vapour pressure,

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VOCs in products can escape into the ambient air in homes, offices, schools and transportation vehicles (Guo et al., 2004).

Since people spend the majority of their times in indoor environments, indoor air pollutants can potentially have negative health impacts on building occupants (Rumchev et al., 2007; Casset and de Blay, 2008; Choi et al., 2010). Indoor air quality (IAQ) continues to be a major environmental health concern (Luengas et al., 2015; de Gennaro et al., 2014; Zhang and Smith, 2003). Short- and long-term adverse health effects vary greatly among VOCs. Some are carcinogenic (e.g., benzene and 1,3-butadiene). Others have little or no known health effects (Khanchi et al., 2015). The extent and nature of the health effects also depend on environmental concentrations and exposure time. Acute effects may include eye and respiratory tract irritation, headaches, dizziness, visual disorders and memory impairment (USEPA, 2015).

VOCs in indoor air, and to some extent in outdoor air, have been measured in studies conducted during the past several decades, including a number of recent large scale surveys on the prevalence of VOCs in residential homes (Edwards et al., 2001; Billionnet et al., 2011; Zhu et al., 2013). Both passive and active methods have been employed in sample collection. Common VOC sampling methods include evacuated canisters and sorbents such as activated charcoal, Carbopack B, Carboxen and Tenax TA. Gas chromatography coupled with mass spectrometry or other detectors is commonly used for analysis of the VOCs in the air samples.

Many studies of VOCs in indoor air have also simultaneously measured in outdoor air near the buildings where indoor air was measured. Paired indoor air and outdoor air measurements allow the calculation of ratios of indoor and outdoor VOC levels (I/O) (Bari et al., 2015; Kinney et al., 2002; Tang et al., 2005; Zabiegala, 2006; Zhu et al., 2005; Bruno et al., 2008; Solomon et al., 2007; Chikara et al., 2009; Fuselli et al., 2010; Liu et al., 2010; Otson and Zhu, 1997). I/O ratio is an important indicator in the identification of VOC source origin (indoors vs. outdoors); a higher I/O means greater contribution from indoor sources.

Recently, indoor air VOC levels were measured in approximately 4000 residential homes across Canada as part of the Canadian Health Measures Survey (CHMS) (Zhu et al., 2013). The time and locations of indoor air VOC sample collection in the CHMS overlapped with the collection of outdoor ambient air samples that were carried out under the National Air Pollution Surveillance (NAPS) network (NAPS, 2016). The objective of the present study is to estimate I/O ratios of selected VOCs measured in both programs.

2. Methods

2.1. Indoor VOC sampling and analysis

Indoor air data were obtained from the CHMS Cycle 2 data collection. CHMS is an ongoing Canadian national survey designed to provide comprehensive health measures data at the national level (StatsCan, 2016). Detailed description of the survey design and reporting on the indoor air VOC data in the CHMS Cycle 2 data collection can be found elsewhere (Zhu et al., 2013) and were briefly summarized here. Samples were collected over two years, between September 2009 and November 2011, at 18 collection areas across Canada. Each area included homes within a radius of 50 km, or up to 100 km for rural areas. Indoor air VOCs were collected using a passive sampling tube over a 7-day period. The tube was made of stainless steel with an internal diameter of 5.0 mm and a tube length of 90 mm and was packed with Carbopack B 60/80 sorbent. VOCs in the tube were thermally desorbed onto a gas chromatography/mass spectrometry (GC/MS) system (Zhu et al., 2013). Method detection limit (MDL) for each VOC was estimated from pooled 173 field blanks collected over the survey period (Patry-Parisien et al., 2013). Values below MDL were replaced by ½ MDL.

2.2. Outdoor VOCs sampling and analysis

Outdoor air VOC data were obtained from NAPS, including 42 urban and 9 urban-impacted rural air monitoring stations across Canada (NAPS, 2016). Outdoor air in NAPS was collected into evacuated Summa™ electro-polished stainless steel canisters. Samples were collected once every 6 day at urban monitoring stations over a 24-h period into 6-L canisters, and once every 3 day at rural stations over a 4-h period (noon to 4 p.m.) into 3-L canisters. Canisters were pressurized to just above atmospheric pressure to prevent ambient air being drawn into the canister following the sampling period and during transportation.

Outdoor air samples were analyzed following the US EPA TO-15 method (US EPA, 1999; Wang and Austin, 2006). Briefly, a 500-mL aliquot of air from the canister was pre-concentrated, thermally desorbed, then cryo-focused at the head of a GC capillary column and analyzed using GC/MS that was operated in selected ion monitoring (SIM) mode. Separate analytical instruments of the same type were used for the urban and rural samples in order to minimize carry-over contamination. MDLs were periodically determined from intra-day replicate analysis ($n = 7$) of a low level standard mixture of known concentration of the target VOCs in ultraclean air. Pooled MDLs calculated over time were used for the present study, calculated separately for the urban and rural GC-MSD analytical systems. Values below MDL were replaced by ½ MDL.

2.3. Data selection criteria

NAPS stations located in the sample collection areas of the CHMS Cycle 2 were found by the forward sortation area (FSA) identified by the first three characters of the 6-character alpha-numeric Canadian postal code (areas A to I, Table 1). The FSA was also available for each home included in the CHMS study. Postal codes of the NAPS stations were used to match NAPS monitoring stations with homes of CHMS in each CHMS collection area. Only

Table 1
Description of National Air Pollution Surveillance (NAPS) stations and sampling periods.

Study area	Land use[a]	Monitor[b]	Density[c]	Sampling period
A	R	NS	>50 K	2009-09-10 to 2009-10-16
B	O	NS	<10 K	2009-11-27 to 2010-01-29
B	na	na	na	2009-11-27 to 2010-01-29
C	A	NS	<10 K	2010-03-15 to 2010-04-23
D	R	T	>50 K	2010-04-26 to 2010-06-01
E	C	NS	>50 K	2010-07-31 to 2010-09-05
F	R	PS	>50 K	2010-09-17 to 2010-10-23
G	I	TPS	>50 K	2010-12-10 to 2011-01-21
H	P	NS	>50 K	2011-01-27 to 2011-03-10
H	R	T	>50 K	2011-01-27 to 2011-03-10
I	W	PS	>50 K	2011-11-05 to 2011-12-05
I	R	T	>50 K	2011-11-05 to 2011-12-05
I	I	PS	>50 K	2011-11-05 to 2011-12-05
I	R	PS	>50 K	2011-11-05 to 2011-12-05

[a] Dominant land use within a 400 m radius of the station: A = agricultural, C = commercial, F = forested, I = industrial, O = open land, P = parks, R = residential, W = water.

[b] Ambient environment surrounding the monitor: T = traffic (monitor within 100 m of a major road and located in an urban region), PS = point source (monitor within 400 m of a major industrial emissions source), PTS = both traffic and point source apply, NS = non-specific (not classified as traffic or point source influenced), na = information not available.

[c] Population density: population within a 4 km radius of the station.