

F O R T A I R P A R T N E R S H I P

We Monitor the Air You Breathe

**Bruderheim Volatile Organic Compound
Speciation Study Report**

September, 2021

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Executive Summary

The town of Bruderheim, with a population of 1,308, is located approximately 30 kilometres northeast of the city of Edmonton within an area identified as Alberta's Industrial Heartland. Over the years several odour complaints were reported to Fort Air Partnership (FAP), the Airshed organization operating an air monitoring network in the area. Furthermore, elevated concentrations of non-methane hydrocarbon (NMHC) concentrations were periodically measured at FAP's continuous air monitoring station located in Bruderheim.

This focused study was initiated to address, in part, one of FAP's monitoring objectives: to characterize emerging issues. One such emerging issue is the measured elevated concentrations of total hydrocarbons within the town of Bruderheim.

The Bruderheim air monitoring station is located near industrial facilities that report to the National Pollution Release Inventory (NPRI), a number of small oil and gas facilities consisting mostly of crude oil batteries, and a bulk petroleum loading rail terminal located approximately two kilometres to the east-southeast of the station. A complex set of hydrocarbon sources likely influence the measurements at the air monitoring station.

On average, NMHC concentrations at the Bruderheim station are higher than measured at a different regional station downwind and a nearby urban site, while being comparable to those measured near industrial operations in the area. Typically, NMHC concentrations at the Bruderheim station were higher during the colder months, in the early morning hours and were more frequently observed during low east-southeasterly winds.

In July 2017, a year long study was initiated to identify the specific volatile organic compounds (VOCs) measured at the Bruderheim station. While continuous monitoring of summative NMHC concentrations is informative on current state and trends, an in-depth investigation of the constituents of the measured summative NMHCs, as done in this study, was needed to gain better insight into the possible sources and potential impact of the periodically elevated NMHCs at the station.

To characterize the summative concentrations of NMHCs measured at the station, 24-hour integrated air samples were collected once every six days. In addition to this, 1-hour integrated air samples were collected each time the monitoring station reported NMHC concentrations equal to or greater than a set trigger. Both types of samples were analyzed for VOC constituents.

While the 24-hour integrated samples provided information on the general concentration of VOCs at the site, the 1-hour integrated samples were used to characterize VOC composition during periods of elevated concentrations. In general, notably contributing VOCs within the 1-hour integrated event samples were also found at higher concentrations in the 24-hour integrated samples, albeit the relative contribution of these VOCs in event samples were markedly higher. Almost all samples had enhanced concentrations of n- and i- pentane, n- and i- butane, propylene, n-hexane and methylcyclohexane.

These VOCs have in previous studies been associated with fugitive emissions from activities related to the production and storage of petroleum-based products. In addition to this general observation, few samples contained complex mixtures of VOCs or at times very few VOCs.

The observed variability in the 1-hour integrated event samples supports multiple possible source types. The monitoring site is located in an area with various sources that are known to emit hydrocarbon emissions into the atmosphere.

Continued evaluation of summative NMHC concentrations at the Bruderheim station should be used to examine trends and changes in the atmospheric concentration of NMHC going forward. In addition to identifying the components of summative NMHCs and meteorological conditions conducive to the periodic elevated concentrations of NMHC, concentrations were also compared to ambient air benchmarks.

Alberta does not have objectives in place for summative NMHCs but has ambient air quality objectives (AAQOs) for selected VOC species. Concentrations measured in this study did not exceed established AAQOs. Where available and in the absence of AAQOs, measured concentrations were compared to Texas Air Monitoring Comparison Values (AMCVs). VOCs measured during the study did not exceed the short and long-term published AMCVs.

Introduction

The town of Bruderheim is located within Alberta's Industrial Heartland. In the vicinity of the town are various industrial facilities, urban centres and numerous oil and gas wells. The surrounding area also includes forests, grassland and agricultural land. In 2010, FAP installed a continuous air monitoring station in the town, where elevated non-methane hydrocarbon (NMHC) concentrations were periodically measured. Due to a change in land use, the station was moved in the winter of 2016 to a new location 700 meters north of the initial site. Elevated concentrations of NMHCs continued to be observed at this new site albeit at a lower frequency.

The current study was initiated, in part, to address monitoring objectives for the area: to characterize emerging issues. The study sought to identify and fully characterize ambient VOC constituents in the Bruderheim area and better understand the periodic elevated NMHC concentrations observed at the site. In doing so, the aim was also to start addressing local concerns regarding the impact of emissions from sources related to oil and gas production, transport and storage. The impact of emissions from such sources have not been well characterized, particularly surrounding the Town of Bruderheim.

Volatile organic compounds (VOCs), emitted by anthropogenic and natural sources, are ubiquitous in the atmosphere and may be found even in remote areas (Hakola et al., 2006). The concentration and constituents of VOCs at a monitoring site will depend on the type of nearby sources and their intensity, the rate of atmospheric processing and atmospheric lifetime of the VOC, as well as factors influencing dispersion and deposition. A number of studies have used the composition of VOCs and key indicator compounds to provide insight into possible types of sources impacting a monitoring site (Hopke, 2016).

Within urban areas, vehicle exhaust can be a notable source of VOCs (Badol et al., 2008; Hellén et al., 2006) with alkanes and aromatics such as toluene and xylene being the predominant VOCs measured in vehicle exhaust (Hellén et al., 2003). Ambient concentrations of benzene, toluene, xylene and acetylene can also have contributions from evaporative loss and/or spillage of gasoline at filling stations (Srivastava et al., 2005). While in the summer these VOCs can be transformed to secondary pollutants in the atmosphere through photo-oxidation, in the winter, when photo-oxidation reaction rates are lower, urban VOC emissions may be transported further downwind (Borbon et al., 2004).

A number of studies have measured VOCs in the vicinity of industrial activities including refinery and petrochemical production (Badol et al., 2008; Buzcu and Fraser, 2006; McCarthy et al., 2013) and oil and gas wells (Field et al., 2015; Gilman et al., 2013; Schade and Roest, 2018; Warneke et al., 2014). Light alkanes (propane and butane) and light alkenes (ethylene and propylene) were associated with refinery and petrochemical production, respectively (Buzcu and Fraser, 2006).

Enhancement of light alkanes (<math><C_6</math>) have also been measured near oil and gas wells (Gilman et al., 2013; Petron et al., 2014). In addition, storage tanks can also be sources of fugitive VOC emissions (Chambers et al., 2008; Hendler and Nunn, 2009), the intensity and key VOCs emitted will vary with the product being stored and storage practices. Due to the similarity of key compounds in these source types, analysis using meteorological information can complement source apportionment to narrow down potential sources (Hopke, 2016).

In some regions of North America, emissions from vegetation can be a notable contributor to atmospheric VOCs (Guenther et al. 1995). Vegetation emits VOCs largely consisting of isoprene and monoterpenes (Fuentes et al., 2000 and references within; Kansal, 2009). Isoprene is thought to be emitted from vegetation in response to heat stress, and is dependant on foliar density and will vary by plant species (Sharkey et al., 2018). In the boreal region, atmospheric concentrations of VOCs emitted by vegetation are observed to have a distinct seasonal variation peaking in the summer months with minimal concentrations in the winter months (Guenther et al., 2000; Li et al., 2012; McCarthy et al., 2013). Since land use near Bruderheim includes forests, grassland, and agriculture, measured VOCs likely will have contributions from vegetation.

An additional, non-industrial VOC source in the region that contributes to both primary and secondary VOC concentrations are wildfires. Between 2006 and 2015, more than 1,000 fires were recorded annually in Alberta (Alberta Agriculture and Forestry, 2017). Various VOCs including oxygenated VOCs such as acetone and aromatics (benzene and toluene) have been measured in boreal wildfire plumes (Simpson et al., 2011). Wildfire season in Alberta can span several months, typically starting in March and continuing to October. During wildfire season, VOCs associated with biomass burning and their secondary products can contribute to the abundance of atmospheric VOCs in affected areas (Hsu et al., 2015; Landis et al., 2018; Simpson et al., 2011; Wentworth et al., 2018). The composition and contribution of wildfire associated VOCs to ambient air will likely vary depending on the biomass burned and distance to the fire front. Wildfire associated VOCs were not expected to have a significant contribution in Bruderheim during the study period.

The region encompassing Bruderheim, due to the varied potential sources of VOCs present, has been the focus of a few VOC studies in the past including a multi-site study conducted between 2001-2003 with additional samples collected between September 2004 and March 2006 (Environment Canada, 2006). This study found ambient VOC concentrations and composition were spatially variable and were affected by meteorology, seasonal and unique emission events. Among the most abundant VOCs in the 2006 study were light alkanes, selected aromatics (toluene, m,p-xylene, benzene and ethylbenzene) and propylene. While this regional study was comprehensive, VOC sources in the area most likely have changed since the study was conducted.

More recently, a VOC speciation investigative survey was conducted between the months of October 2014 and March 2015 within Bruderheim to verify occasionally observed elevated NMHC concentrations. Study average concentrations of light alkanes measured during this investigative survey were notably higher than those measured during the 2006 study, while study average concentrations of the most abundant aromatics and propylene were lower or comparable. These differences likely have contributions from seasonal variability of atmospheric concentration of various VOCs as the short survey was limited to a small number of samples (13) collected during the fall and winter months.

For this study, whole air canister samples were collected for a full year between July 2017 and July 2018. 24-hour integrated air samples were collected once every six days. In addition to this, 1-hour integrated air samples were collected each time the monitoring station reported NMHC concentrations equal to or greater than a set trigger. Both types of samples were analyzed for the same VOC constituents. While the 24-hour integrated samples provided information on the general concentration of VOCs at the site, the 1-hour integrated samples were used to characterize VOC composition during periods of elevated concentrations.

Sample Site

The monitoring station in Bruderheim is part of an air monitoring network operated by FAP. FAP's primary objective is to monitor ambient air quality in Alberta's Industrial Heartland, which includes Bruderheim. Bruderheim has a population of 1,308 (Census Canada, 2016). It is located approximately 30 kilometres northeast of the city of Edmonton, within the area identified as Alberta's Industrial Heartland.

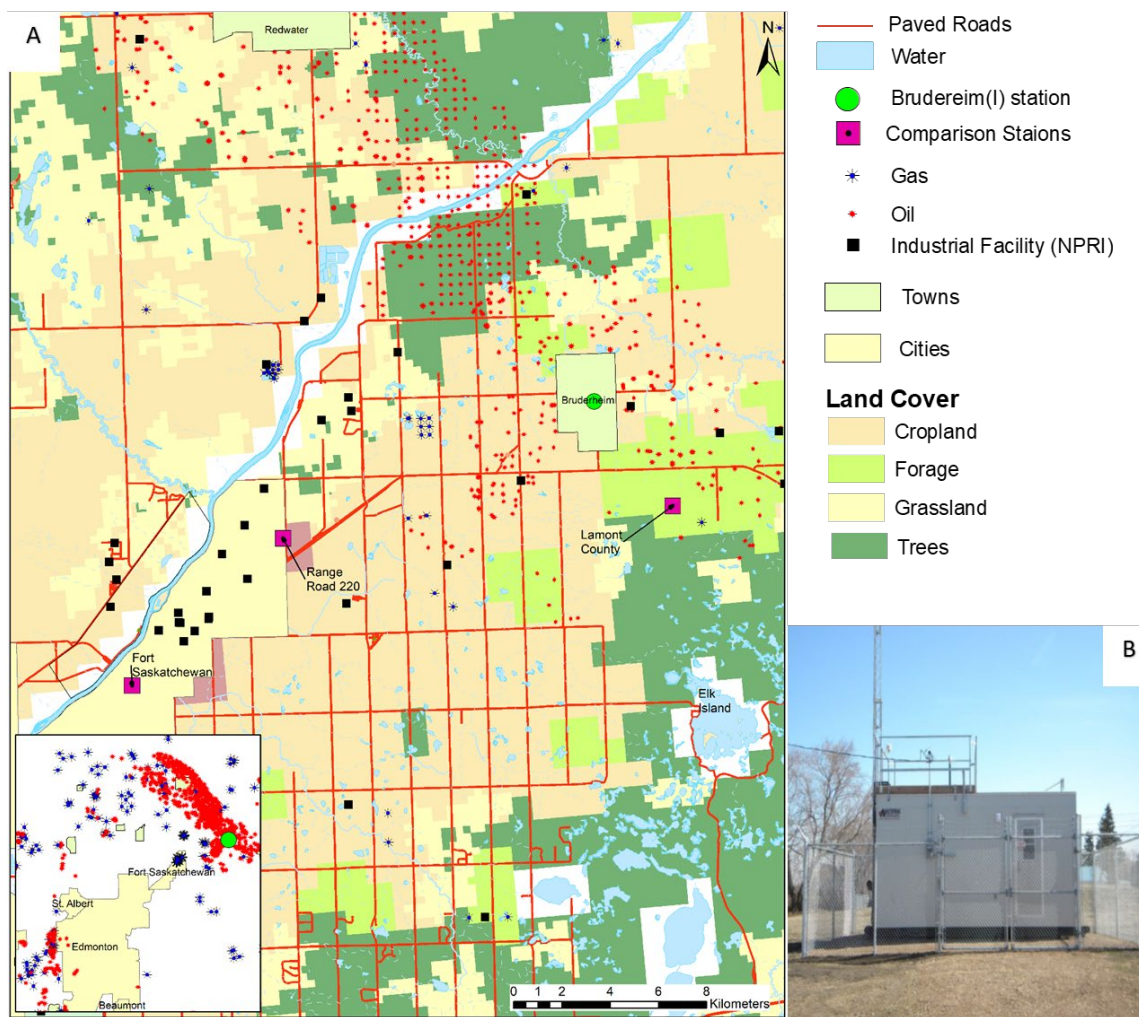
As illustrated in Figure 1, the Bruderheim air monitoring station is located near industrial facilities that report to the National Pollution Release Inventory (NPRI), a number of small oil and gas facilities consisting mostly of crude oil batteries, and a bulk petroleum loading rail terminal located approximately two kilometres to the east-southeast of the station. A complex set of hydrocarbon sources likely influence air quality in Bruderheim.

The land use in the surrounding area also includes forest, grasslands, and agriculture. The Bruderheim station was moved approximately 700 meters to the north from the original monitoring location in 2016 due to a change in land use. Hereafter, Bruderheim(I) refers to the current station location and Bruderheim refers to the initial station location.

The Bruderheim station was near two retail gas stations located 85 metres to the southeast and 350 metres to the north-northeast. Sporadic emissions from these nearby gas stations may have affected the initial Bruderheim station. The move from Bruderheim to Bruderheim(I) was not expected to noticeably change the magnitude of impact from regional or town scale sources. This assumed emissions from these sources would remain unchanged. However, the impact from nearby gas stations was expected to be lower, albeit the impact may be comparable in calm winds.

The siting of Bruderheim(I) meets the siting requirements outlined in the Air Monitoring Directive (Alberta Environment and Parks, 2016) and is located in the northwest corner of the Bruderheim school sports field. Monitoring equipment is housed in a temperature-controlled trailer equipped with a meteorological tower with a wind sensor that is three metres above ground. Data from three other stations in FAP's network are presented for comparison. The locations of these stations are indicated in Figure 1. The Lamont County station is located east and south of industrial and urban areas, the Fort Saskatchewan station is located within the City of Fort Saskatchewan and the Range Road 220 station is located northeast of a number of NPRI reporting industrial facilities.

Figure 1: (A) Location of Bruderheim(I) and comparison monitoring stations. Insert map illustrates large-scale location of Bruderheim(I) monitoring station relative to Edmonton and cluster of oil wells. (B) Bruderheim(I) station.



Sample Collection

The Bruderheim(I) station is outfitted with a number of continuous analyzers including a Thermo Fisher model 55i to monitor methane (CH₄) and non-methane hydrocarbons (NMHC). The CH₄/NMHC analyzer is calibrated using a mixture of methane and propane calibration gas. Other parameters monitored at the site include oxides of nitrogen (NO_x), fine particulate matter (PM_{2.5}), sulphur dioxide (SO₂), ozone, wind speed, wind direction and temperature. Zero and span checks for all gas-phase continuous monitoring are conducted daily; calibrations are performed monthly and analyzer performance audits are conducted annually. For the period in study, all calibration standards used met or exceeded the requirements outlined in the calibration chapter of the Air Monitoring Directive (Alberta Environment and Parks, 2018). Zero corrected data are stored as 1-hour average concentrations.

For the purpose of this study, the station was also outfitted with a system to collect air samples using evacuated canisters for VOC analysis. Two flow controllers were used for filling Summa™ canisters. One controller was programmed to sample for 24 hours every six days. The second controller was configured as an event sampler. Triggered event samples maximized the likelihood of sampling during periods of elevated NMHC concentrations. Event samples were triggered when ambient concentrations of NMHC as measured by the Thermo 55i analyzer were equal to or greater than a set trigger. The trigger level was set keeping in mind analysis cost and the study's budget. At the start of the study, a 1-hour sample was triggered whenever the NMHC concentration of any three-minute average was equal to or greater than 3.0 parts per million (ppm). However, at this trigger level, only one event sample was collected by January 1st, 2018.

Following a review of NMHC concentrations, a new trigger level using a 10-minute NMHC average at 1.0 ppm was set on January 3rd, 2018. This trigger level was anticipated to provide about 10 samples for the remainder of the study. This adjustment resulted in the collection of several event samples shortly after the adjustment. However, in order to ensure the collection of representative event samples with the available funds, the triggered samples were screened prior to analysis. Some of the events were short-lived (less than 15 minutes). These were deemed too short-lived to warrant laboratory analysis. The duration of each triggered event was examined using one minute average data shortly after the event sample collection. Five event samples were selected for analysis. This is a small sample size but is representative of events during the sample period. These samples were collected on September 7, 2017, March 8, April 30, July 12 and July 26 of 2018.

Once filled, canisters were stored at room temperature for no longer than 14 days and shipped to a Canadian Association for Laboratory Accreditation (CALA) accredited commercial laboratory in Ontario (Airzone One) for analysis. The same laboratory also provided the certified clean canisters for sample collection. Analyses of the VOC canister samples were done using a thermal desorption/gas chromatography/mass selective detector (TD/GC/MS) in accordance with USEPA's Toxic Organics -15 determination method for air collected in canisters (TO-15) (USEPA, 2018). Samples were analyzed for 73 VOCs.

Selection of VOCs from the standard laboratory's TO-15 analysis suite was informed by previous monitoring and reported emissions in the area. Canister samples collected as part of previous VOC studies in the region were analyzed by a federal government laboratory. Analysis at this laboratory was not possible for this study so the best available commercial laboratory was used.

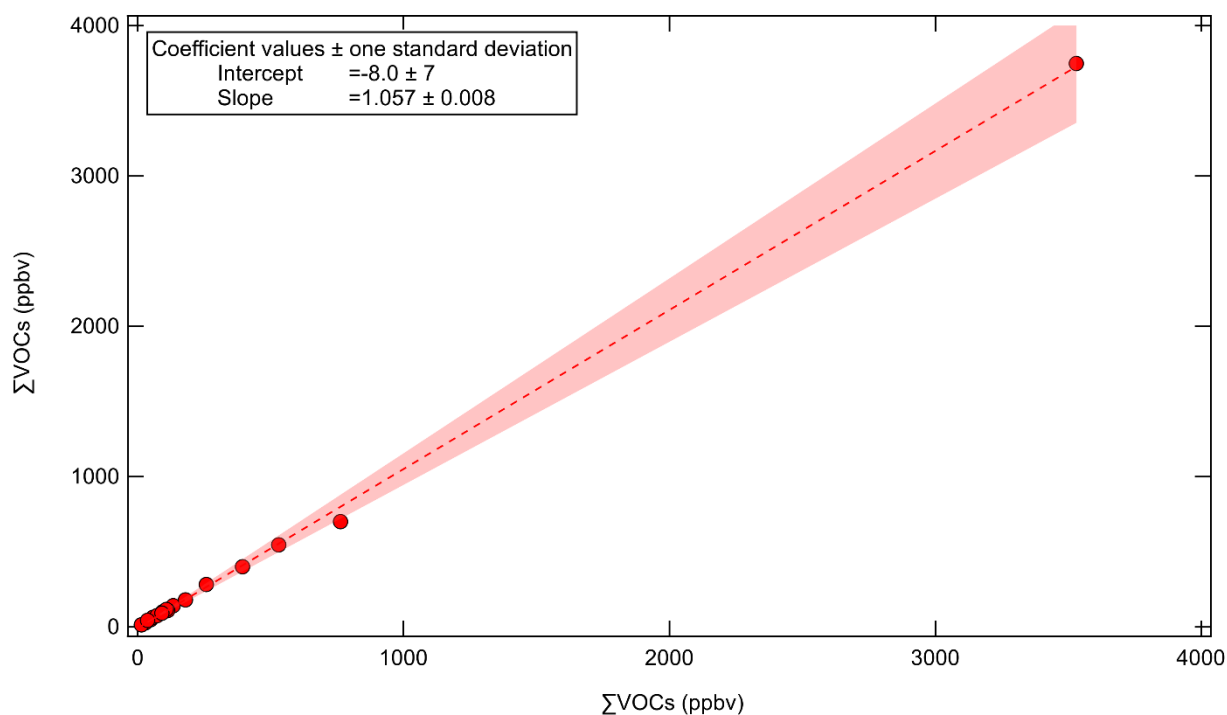
For this study, the laboratory reported the detection limit for all the compounds analyzed was 0.3 part per billion per volume (ppbv). Sample collection included nineteen duplicate samples and four field blanks. The laboratory method detection limit of 0.3 ppbv is an order of magnitude higher than those reported for the other studies in the region referenced in this report where the analyses were conducted by a Government of Canada laboratory.

Light alkanes such as ethane and propane have low and inconsistent recovery when using GC/MS and as a result, the concentration for ethane and propane are not reported for samples collected as part of this study. Laboratories used in previous studies used a combination of GC/MS and gas chromatography/flame ionization detector (GC/FID) and thus were able to report reliable concentration for light alkanes.

Duplicate and Blank Samples

Duplicate samples are used to assess variability in the total sample collection and analysis method. Nineteen duplicate samples were collected throughout the study. Duplicate samples consisted of two co-located independent canister samples collected at the sample time. The samples are collected, stored and analyzed similarly. Figure 2 illustrates a linear relationship between the total detected VOCs in duplicate samples. Total detected VOCs ranged from 13 to 3748 ppbv. The linear fit has a slope close to unity (1.057).

Figure 2: Total VOCs in duplicate samples. Total VOCs in all duplicate samples were comparable with the fitted line having a slope very close to one, the shaded line indicates 10% divergence. Table 1 lists the relative mean difference for each VOCs.



The mean relative percent differences for each detected VOC if detected in more than one sample pair are listed in Table 1. The relative percent difference (RPD) for a detected VOC is calculated as:

$$RPD = \frac{|C1 - C2|}{\left(\frac{C1 + C2}{2}\right)} \times 100$$

where *C1* and *C2* are the reported concentrations for duplicate canister samples. RPD for individual VOCs detected in duplicate samples ranged from 0-58%. USEPA's data reviewer guidance document for canister samples of air analyzed using method TO-15 identifies RPD greater than 50% for field duplicate samples as large and noteworthy (U.S. EPA, 2014). An RPD greater than 50% was noted for 3-methylhexane in one sample. An RPD greater than 30% was noted for ten VOCs in four duplicates, in most cases the measured concentrations were less than one ppbv.

The mean RPD was calculated by averaging all the RPD calculated for each VOC in each duplicate. The result and the number of times a VOC is above detection limit in a duplicate sample is indicated in Table 1. Generally, the RPD was well below 30% with the mean RPD for individual VOCs ranging from 5% to 19%. The concentrations of some VOCs were frequently close to or below the detection limit. As a result, fewer duplicate pairs were available to calculate the RPD. In these cases, values calculated would have a relatively higher uncertainty compared to VOCs with concentrations that were routinely above the detection limit.

The sum of total VOC concentrations (Σ VOC) in the four field blank samples were 5.0, 3.2, 48.4 and 10.0 ppbv. One field blank sample (Σ VOC=48.4 ppbv) collected on June 15 contained a number of VOCs above detection. VOCs that were above the detection limit in at least three of the four blanks included acetone, isopentane and n-pentane. The above detection limit average field blank concentrations for VOCs are listed in Table 2. The average concentrations of these four species in Table 2 were calculated by using 0.5DL for BDL samples.

Table 1: Mean relative difference (RPD) of VOC concentration for duplicate canisters.

VOC	Pairs above detection	Mean RPD	Median RPD	Max RPD
Propylene	17	7%	5%	31%
Isobutane	14	10%	9%	19%
n-Butane	16	7%	7%	20%
Isopentane	17	7%	8%	16%
n-Pentane	19	7%	4%	32%
Ethanol	18	9%	7%	27%
Isoprene	10	11%	7%	27%
2,3-Dimethylbutane	2	6%	6%	8%
2,2-Dimethylbutane	13	7%	7%	16%

VOC	Pairs above detection	Mean RPD	Median RPD	Max RPD
Acetone	19	8%	6%	21%
Methylenechloride	11	6%	4%	14%
2-Methylpentane	11	6%	5%	21%
Cyclopentane	11	8%	3%	34%
3-Methylpentane	8	8%	5%	23%
n-Hexane	15	9%	8%	21%
2,4-Dimethylpentane	1	N/A	N/A	3%
Methylcyclopentane	11	9%	7%	21%
Methylethylketone	12	8%	7%	18%
Chloroform	4	10%	9%	19%
Tetrahydrofuran	3	16%	14%	23%
2-Methylhexane	5	11%	9%	25%
2,3-Dimethyl pentane	2	19%	19%	28%
Cyclohexane	9	8%	8%	14%
3-Methylhexane	8	18%	11%	58%
1,2-Dichloroethane	2	8%	8%	11%
Benzene	12	10%	8%	33%
Isooctane	1	N/A	N/A	14%
n-Heptane	6	16%	13%	36%
Trichloroethylene	1	N/A	N/A	11%
Methylcyclohexane	9	17%	13%	31%
2,3,4-Trimethylpentane	1	N/A	N/A	15%
Toluene	12	7%	6%	13%
n-Octane	1	N/A	N/A	35%
Tetrachloroethylene	2	19%	19%	29%
Methylisobutylketone	4	16%	16%	27%
Ethylbenzene	2	5%	5%	7%
n-Nonane	1	N/A	N/A	14%
m,p-Xylene	4	5%	5%	9%
o-Xylene	2	11%	11%	18%
Styrene	2	18%	18%	19%
Isopropylbenzene	2	7%	7%	11%

VOC	Pairs above detection	Mean RPD	Median RPD	Max RPD
m,p-Ethyltoluene	1	N/A	N/A	41%
n-Decane	3	13%	13%	16%
1,2,4-Trimethylbenzene	1	N/A	N/A	4%
1,2,3-Trimethylbenzene	1	N/A	N/A	37%
m-Diethylbenzene	1	N/A	N/A	28%
Undecane	2	19%	19%	24%
n-Dodecane	1	N/A	N/A	13%

Table 2: Average field blank concentrations. Listed are concentrations that were greater than the detection limit of 0.3 ppbv. Concentrations reported as below the detection limit were replaced with half of the detection limit value.

VOC	Concentration (ppbv)
Isobutane	1.1
Isopentane	7.6
n-Pentane	5.4
Acetone	1.9

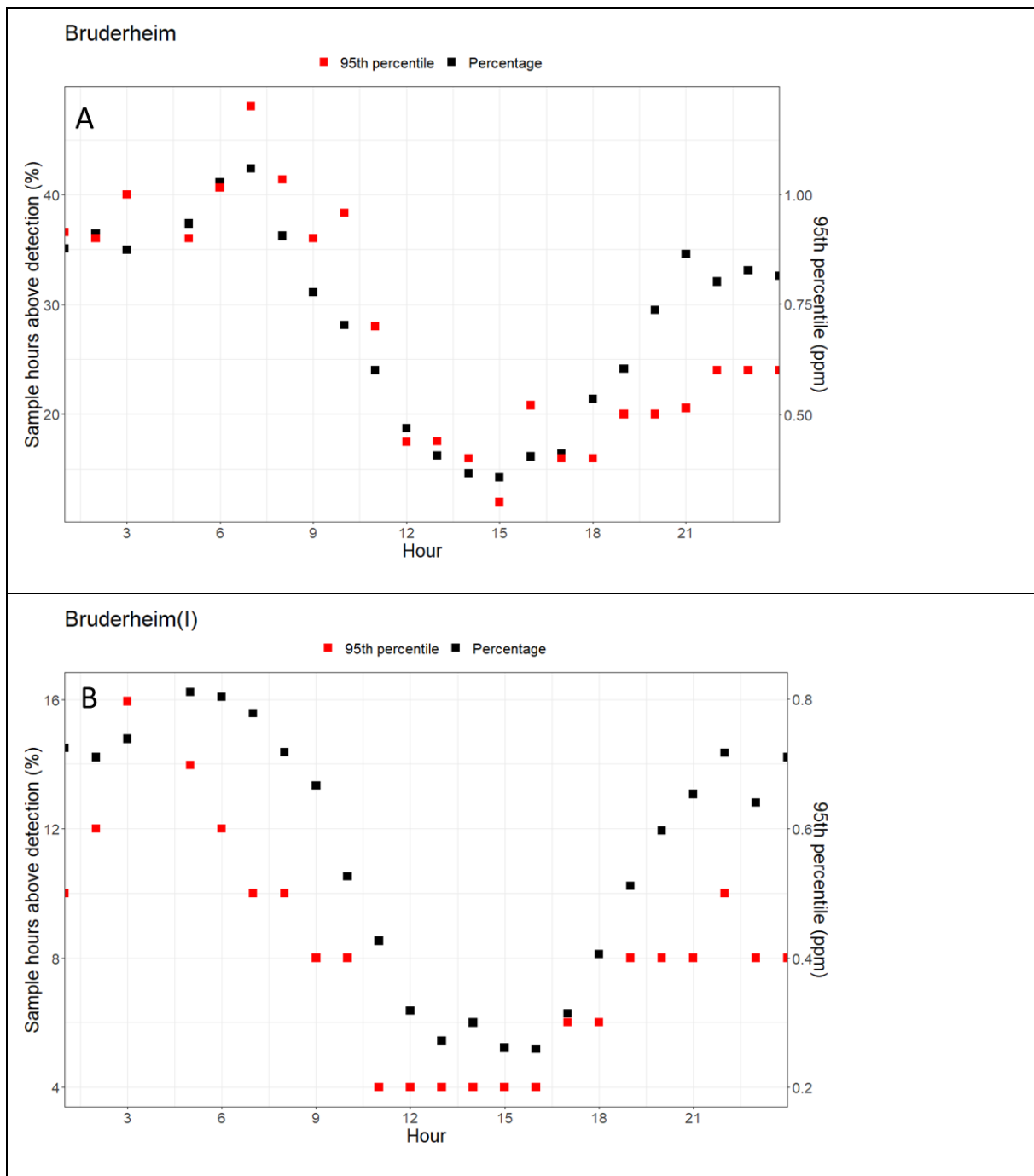
Non-methane Hydrocarbons

Elevated concentrations of NMHCs were measured at both Bruderheim stations. Figure 3 illustrates the 24-hour variability for data collected between January 2014 and February 2016 at the Bruderheim station and data collected at the Bruderheim(I) station between January 2017 and September 2018.

The number of sample hours with above detection NMHC concentrations and 95th percentile for each hour were higher for data collected at the Bruderheim station location (January 2014 and February 2016). This may be due to the change in monitoring location and/or change in emissions. That being said, elevated concentrations continued to be observed at Bruderheim(I) station.

At both locations, NMHC concentrations higher than the detection limit was most frequently observed overnight and during the early morning hours. A similar 24-hour variability is observed for the magnitude of measured concentration as illustrated by the 95th percentile for both Bruderheim sampling locations. This indicated impact from activities with emissions under the nocturnal boundary layer. Most of the triggered canister samples, initiated by elevated NMHC concentrations, were also collected during this time of day.

Figure 3: Percentage of sample hours with NMHC concentrations above the detection limit and 95th percentile concentration by hours of the day. (a) Data collected at Bruderheim station (January 2014 and February 2016). (b) Data collected at Bruderheim(I) station (January 2017 and December 2018). Daily zero and span are conducted during the fourth hour of the day, thus there is no data to determine values for this hour.



Comparison to nearby stations

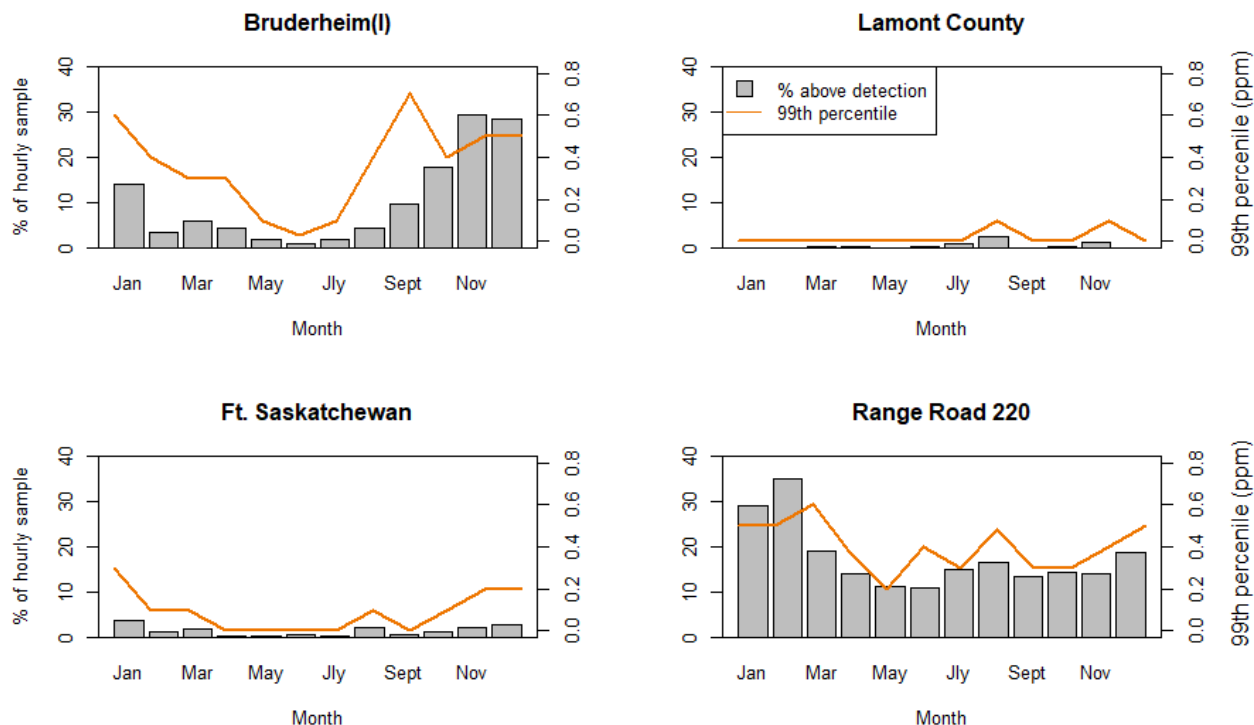
Non-methane hydrocarbon concentrations are measured at a number of air monitoring stations in Alberta. Unless monitored in the vicinity of hydrocarbon emissions, concentrations are often below the analyzer detection limit (0.1 ppb). Figure 4 presents a comparison of the percentage of 1-hour average concentrations above the detection limit and the 99th percentile 1-hour average concentration by month at four monitoring sites within Fort Air Partnership's monitoring network.

Concentrations measured at Fort Saskatchewan (an urban site) and Lamont County (a downwind regional site) are often below detection. NMHC concentrations at these two stations were above detection limit for less than 5% of the sample hours, for samples collected in 2017 and 2018.

The Range Road 220 air monitoring station is located in the vicinity of an industrial operation with reported VOC emissions to the National Pollution Release Inventory. NMHC concentrations were most frequently above detection limit at the Range Road 220 station, with the exception of the months of November and December.

The higher occurrence of above detection limit NMHC concentrations at the Bruderheim(I) station was observed in October, November and December. In general, at the Bruderheim(I) station, above detection NMHC concentrations and 99th percentile by month were higher in the colder months. These observations indicate that NMHC concentrations at the Bruderheim(I) station are higher than the downwind regional site (Lamont County) or the nearby urban site (Fort Saskatchewan) while being comparable to concentrations measured near an industrial operation (Range Road 220) for parts of the year.

Figure 4: Percent of hourly samples with NMHC concentrations above the detection limit (grey box left axis) and monthly 99th percentile concentration (solid line right axis) for data collected from January 2017 to December 2018.



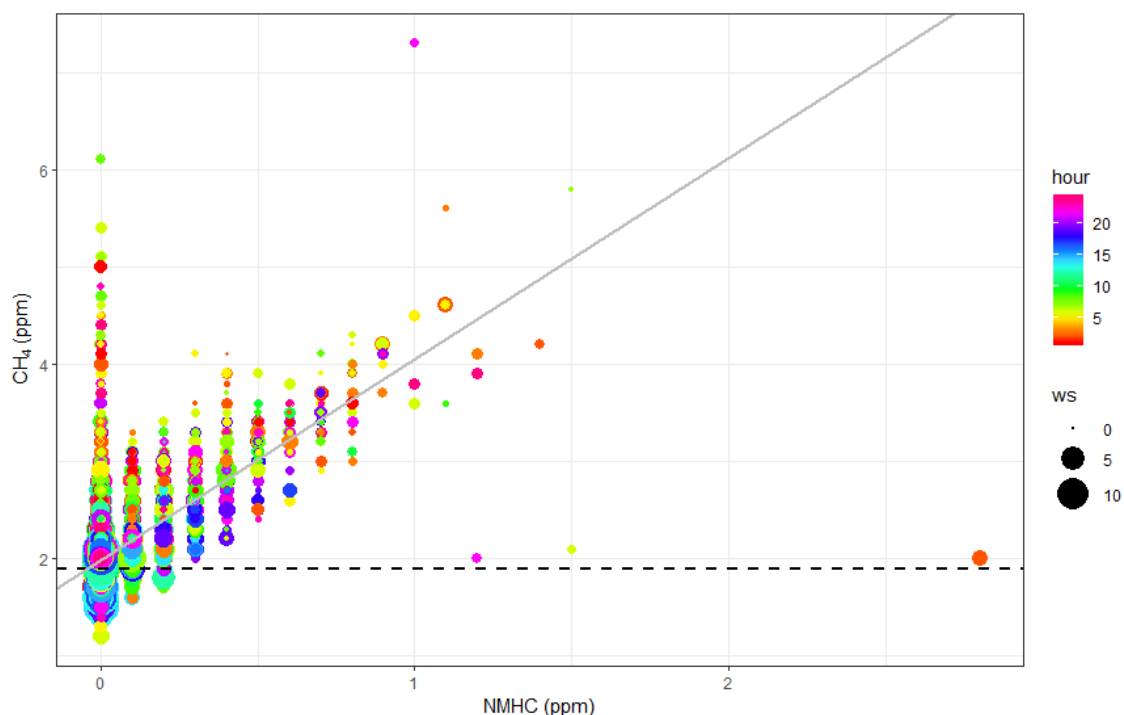
Comparison to co-monitored parameters

The linear relationship or association between NMHC concentrations and other continuously monitored parameters at Bruderheim(I) station was tested by calculating a Pearson correlation coefficient (r) for each pair of data. The highest correlation coefficient ($r=0.55$) was between NMHC and CH_4 concentrations. This coefficient increased ($r \geq 0.64$) for data collected in the fall and winter. Correlation coefficients between NMHC and all other parameters were notably lower ($r < 0.25$).

Figure 5 illustrates the relationship between CH_4 and NMHC at the Bruderheim(I) station. Two possible clusters of CH_4 and NMHC data are evident, possibly related to two types of sources or origins. The first cluster consists of a range of CH_4 concentrations measured for periods when NMHC concentrations were below the detection limit (indicated as zero ppm). In the second cluster, CH_4 increases with increasing NMHC concentrations.

In the case where the increase in NMHC is associated with increased CH_4 , a linear fit with an intercept of 2.0 ppm and slope of 2.1 was determined. The intercept of 2.0 ppm (the concentration of CH_4 when NMHC is below detection) is comparable to the northern hemisphere background CH_4 concentration of 1.9 ppm (Dlugokencky et al., 2011). The slope implies a 2.1 ppm increase in CH_4 for every one ppm increase in NMHC concentration. This observation implies that the source(s) leading to elevated NMHC concentrations likely also emits CH_4 . The figure also illustrates the relationship is not connected to the time of day.

Figure 5: Relationship between NMHC and CH₄. The size of the symbol represents wind speed (WS). The numerical values in the legend are in meters per second (m/s). The colour of the symbols represents time of day as illustrated in the legend. The broken line represents northern hemisphere background CH₄ concentrations and the solid line is a linear fit with slope = 2.1 and intercept of 2.0 ppm.



The lowest NMHC and CH₄ concentrations are measured during higher wind speeds (illustrated by the size of symbols in Figure 5). During these meteorological conditions, CH₄ concentrations are comparable to the background concentration and NMHC concentrations are below the detection limit.

Conditional probability function plots (Ropkins and Carslaw, 2012) for CH₄, NMHC, NO_x, PM_{2.5} and SO₂ are shown in Figure 6. These plots indicate the likelihood of observing a concentration higher than set criteria at various wind speeds and direction. The warmer colours in these plots illustrate a higher probability that the corresponding wind speed and direction results in a measured concentration equal to or higher than the set criteria (70th to 95th percentile depending on the parameter).

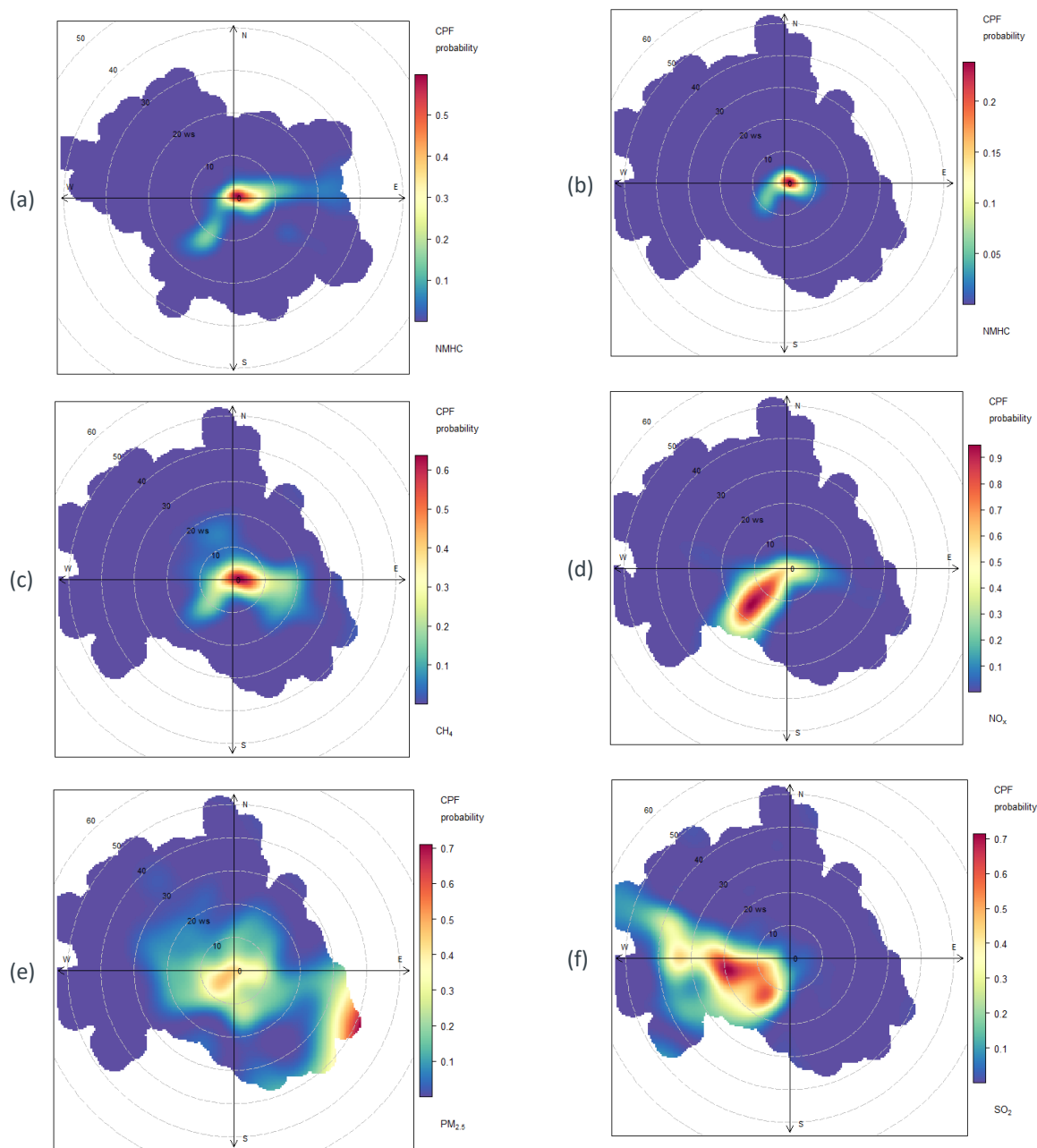
Figure 6 a and b illustrate the conditional probability function plot for Bruderheim and Bruderheim(I) stations, respectively. In both cases, there is a higher probability that NMHC concentrations greater than 0.1 ppm are measured during calm conditions and during low wind speeds with east or east-southeast winds. There is also a moderate probability of detectable NHMC for east and southwest winds.

There are similarities between the conditional probability function plots for NMHC and CH₄ concentrations (Figure 6 b and c) at the Bruderheim(I) station. One-hour averages greater than 2.1 ppm of CH₄ are observed for calm conditions and east-southeast winds. In addition, there is a moderate probability for south-westerly winds.

Condition probability function plots and thus meteorological conditions for periods of elevated PM_{2.5}, SO₂ and NO_x are notably different from conditions leading to elevated CH₄ concentrations and NMHC concentrations above the detection limit. For example, calm speeds and east winds with low wind speeds, associated with a high probability of elevated NMHC/CH₄, are associated with a moderate to low probability of elevated NO_x, SO₂ and PM_{2.5}. This observation, as well as the low Pearson correlation coefficient between NHMC and other parameters monitored, indicate a limited association between NMHC/CH₄ concentrations and the various gaseous and particulate matter concentrations measured at these monitoring locations.

The conditional probability function plots can at times show anomalous results at higher wind speeds as there are a limited number of observations. To ensure the observations for PM_{2.5} (high probability at high wind speed) are representative, outliers were excluded by limiting the plots to multiple observation (n>3). Even with such conditions, a high probability at high wind speeds from the southeast continue to be observed for elevated PM_{2.5} concentrations.

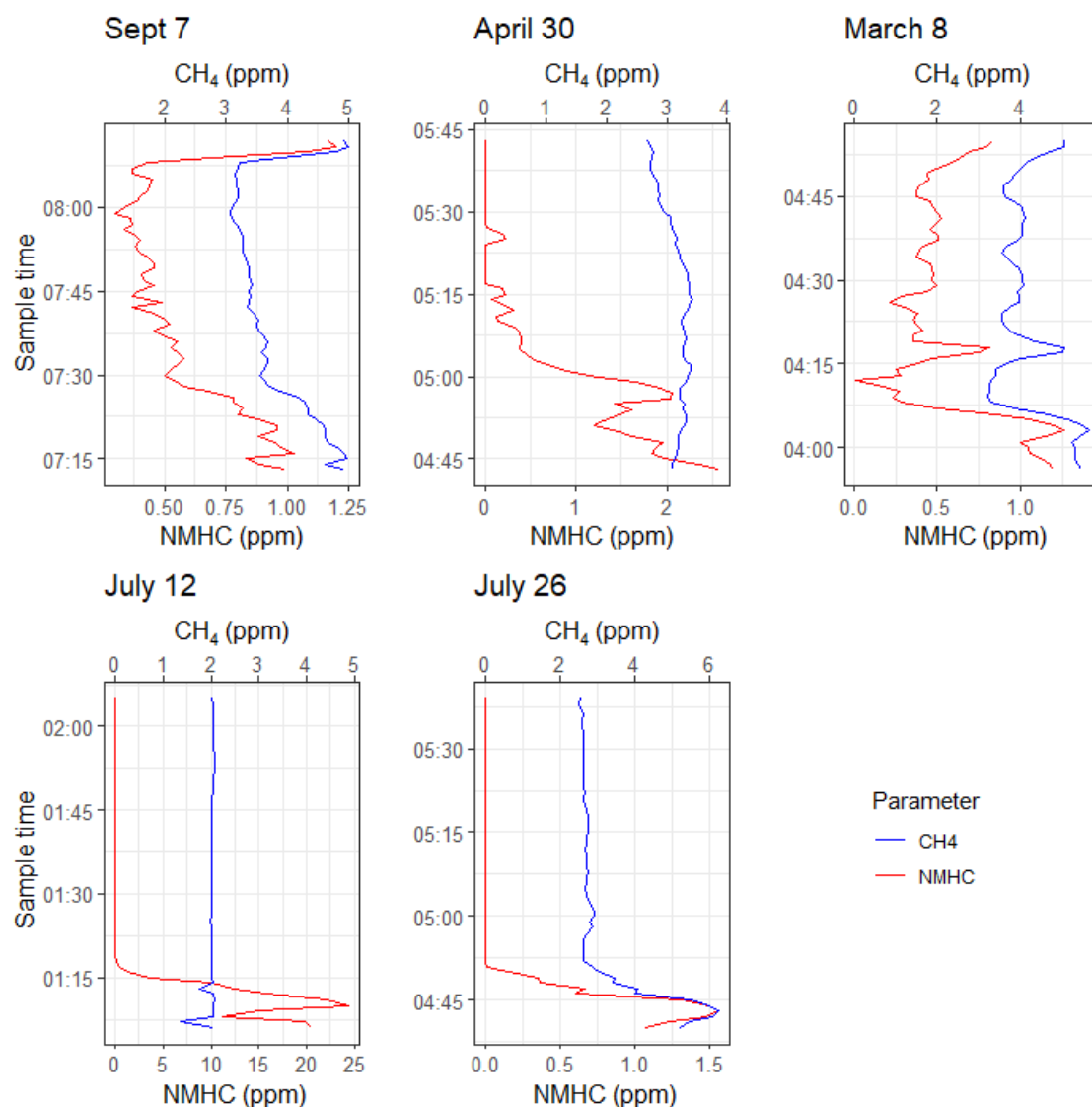
Figure 6: Conditional probability plots of concentration measured. The colour scale indicates the probability of measuring a concentration above a set criteria for the wind speed (km/hr) and direction indicated. (a) Conditional probability function for 75th percentile concentration of NMHC (0.1 ppm) at the Bruderheim station. Figures b to f are generated using data from the Bruderheim(I) station. (b) Conditional probability function for 95th percentile concentration of NMHC (0.1 ppm) at the Bruderheim(I) station. (c) Conditional probability function for the 70th percentile concentration of CH₄ (2.1 ppm). (d) Conditional probability function for the 70th percentile concentration of NO_x (7.6 ppb). (e) Conditional probability function for the 70th percentile concentration of PM_{2.5} (9 µg/m³). (f) Conditional probability function for the 80th percentile concentration of SO₂ (0.1 ppb).



Measured concentrations during event samples

The time series of one-minute NMHC and CH₄ concentrations for the analyzed event samples are illustrated in Figure 7. These event samples were selected because NMHC concentration remained elevated long enough to warrant lab analysis. However, even for this subset of samples, elevated NMHC concentrations were not sustained for the whole sample hour. In three of the five samples NMHC and CH₄ co-varied. On April 30, the CH₄ concentration remained elevated, while NMHC decreased and on July 12, the CH₄ concentration remained near the background level while NMHC levels increased for a brief period. Concentrations during the hour were variable indicating samples from a heterogeneous airmass, and possibly indicating a relatively nearby source(s).

Figure 7: One-minute average NMHC and CH₄ concentration during event samples.



VOC in Canister Air Samples

24-hour integrated samples

To determine the general constituents of VOCs in ambient air at the Bruderheim (I) station, 24-hour integrated samples were collected once every six days. The combined detected VOC concentration (Σ VOC) for samples collected in the current study varied. While more than half of the samples in the study have Σ VOC less than 160 ppbv, there were a number of samples with Σ VOC that are notably higher. Samples with Σ VOC greater than 160 ppbv were usually collected between the months of May and August (Table A-1 in Appendix). The one exception (Σ VOC=428.9 ppbv) was collected on December 21, 2017.

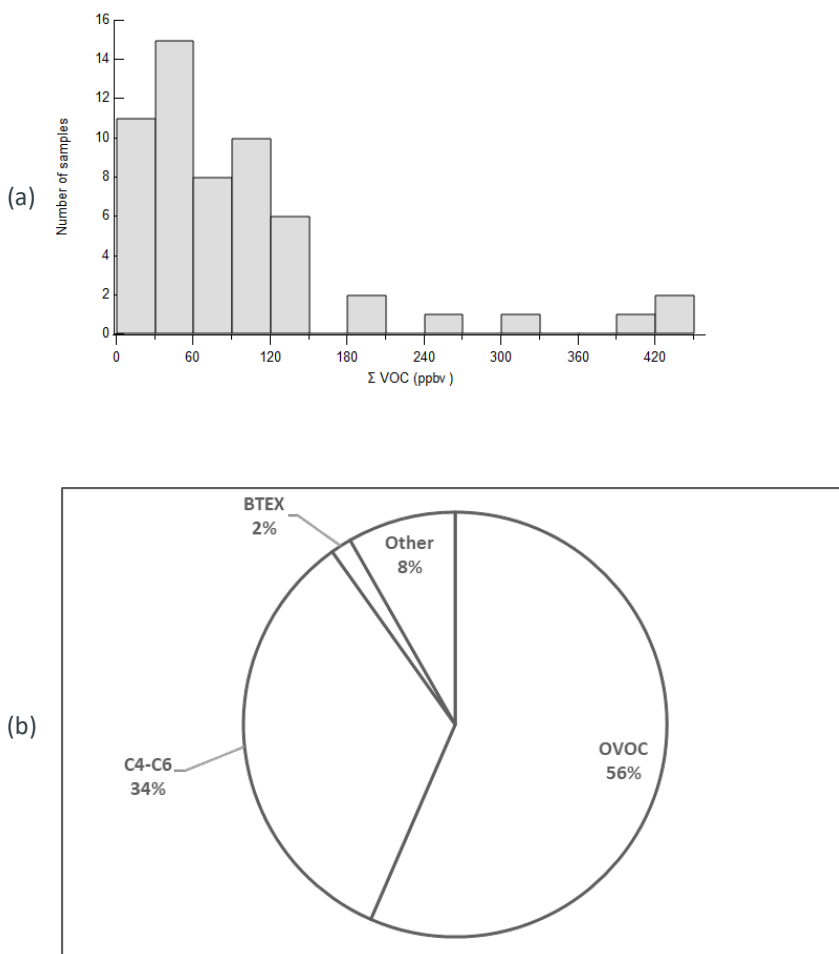
Figure 8 illustrates the relative contribution of VOC groups to Σ VOC. On average, oxygenated VOCs (OVOCs) formed more than half of the detected VOCs, C₄-C₆ branched and chain alkanes contributed 34% and BTEX (benzene, toluene, ethylbenzene and xylene) and other VOCs contributed 2% and 8%, respectively.

Sources of OVOCs are varied in addition to production through atmospheric processing. OVOCs emission sources include vegetation, biomass burning and use of solvents (Jacob et al., 2002; Simpson et al., 2010). Short branched and chain alkanes, as well as components of BTEX, have been associated with various industrial and urban activities.

The seasonal variability of VOCs analyzed in 24-hour integrated samples on average differs from the seasonal variability for 1-hour NMHC concentrations (Thermo 55i analyzer) at the Bruderheim (I) station, where higher concentrations were predominantly measured during the cooler months. The Thermo 55i analyzer, used for continuous measurement of NMHC at Bruderheim (I), determines NMHC concentration by detecting C₂-C₁₁ compounds, but the instrument is less sensitive to oxygenated hydrocarbons. In addition, the Thermo 55i analyzer detects ethane (C₂ alkanes) and propane (C₃ alkanes). These light alkanes could not be included in the canister analysis suite.

Ethane and propane, due to their various sources and relatively long atmospheric lifetime have a notable contribution to VOCs measured in many environments (Hakola et al., 2006; Schade and Roest, 2018; Swarthout et al., 2013). This is especially true during the cold months when the atmospheric mixing height and processing is low (Hakola et al., 2006). The absence of C₂ and C₃ alkanes analysis for canister samples, in addition to the low sensitivity of the Thermo 55i analyzer to oxygenated hydrocarbons, likely contributed to the observed difference between the seasonal variability of canister samples and NMHC as measured by the Thermo 55i analyzer. For example, the monthly average Σ VOC during the Fort Saskatchewan regional study that included propane but excluded oxygenated volatile organic compounds (OVOCs) such as acetone and ethanol, were higher during the winter months (Environment Canada, 2006).

Figure 8: (a) Frequency of observed total detected VOCs (Σ VOC) for 24-hour integrated samples. Five samples with concentrations greater than 450 ppbv are not included in the figure. (b) Study average relative contribution from oxygenated VOCs (OVOC), branched and chain alkanes (C₄-C₆), sum of benzene, toluene, ethylbenzene and xylene (BTEX) and other VOCs (other) to VOCs detected in 24-hour integrated air samples.



Notable VOC constituents in 24-hour integrated samples

A shortlist of VOCs was routinely detected in the 24-hour integrated samples. These routinely detected VOCs were generally most abundant in the warmer months; some were found in abundance while others had a concentration of a few ppbv. Summary statistics for these VOCs were calculated by replacing all concentrations below the detection limit with half the detection limit. All VOCs discussed were detected in more than 70% of the samples.

The OVOC fraction of the Σ VOC was predominantly composed of acetone and ethanol. Acetone was detected in every sample with concentrations higher in the summer (maximum of 148.4 ppbv detected in July). Concentration for samples collected in January and February were often less than 10 ppbv. Acetone has both anthropogenic and natural sources including vehicle emissions and wildfire smoke (Simpson et al., 2011). However, a major source of atmospheric acetone is the oxidation of C₃-C₅ isoalkanes (Jacob et al., 2002; Singh et al., 1994). Isopentane (C₅ isoalkane) and isobutane (C₄ isoalkane) were both found at relatively high concentrations in samples collected in this study and are likely precursor VOCs to acetone in the region.

Ethanol concentrations for this study were highly variable. A few samples had ethanol concentrations below or at detection limit. A maximum ethanol concentration of 2,800 ppbv was detected for a sample collected in July. The Σ VOC concentration for the same sample was 3,750 ppbv. The study average ethanol concentration of 79.7 ppbv was the highest of all VOCs. Common sources of ethanol include vegetation respiration, plant decay, biomass burning and vehicle exhaust from ethanol blended fuels (Kirstine and Galbally, 2012).

C₄-C₆ alkanes in 24-hour integrated samples were routinely composed of butane, pentane and hexane. Concentrations of n- and i-pentane were usually ($\geq 90\%$) above the detection limit. Study average concentrations of n- and i-pentane were 24.5 and 30.4 ppbv, respectively. The maximum concentrations for these VOCs were the highest measured for all non-oxygenated VOCs. Not all samples contained highly elevated concentrations of n- and i-pentane. The median concentration of 5.8 (n-pentane) and 4.0 (i-pentane) ppbv were notably lower. Half of the samples had concentrations below these values. Although detected in at least 70% of the samples, concentrations of n- and i-butane and n-hexane were an order of magnitude lower than those of n- and i-pentane. Study average concentration of n- and i-butane and n-hexane ranged between 2.0-3.3 ppbv. Enhanced concentrations of C₄-C₆ alkanes (butane, pentane and hexane) have previously been associated with petroleum production (Buzcu and Fraser, 2006) and oil and gas wells (Gilman et al., 2013; Petron et al., 2014).

Toluene and benzene were the most routinely detected BTEX compounds and were detected in about half the samples. The median concentration of these VOCs was at or below detection limit. The study average benzene concentration was 0.5 ppbv. The maximum benzene concentration was 2.1 ppbv. Some samples (n=7) contained an elevated concentration of toluene (ranging from 5.6 to 34.2 ppbv). Thus, the study average toluene concentration of 2.3 ppbv was higher than that for benzene. Benzene and toluene are typically associated with evaporative loss and/or spillage of gasoline (Srivastava et al., 2005) and vehicle emission (Gelencsér et al., 1997). However, there are a number of industrial sources in the region that emit benzene and toluene (Environment and Climate Change Canada, 2017).

In addition to the above noted VOCs, the alkene propylene was also detected regularly in 24-hour integrated samples. Propylene concentrations were above detection for 89% of the samples. The study average and maximum concentrations were 2.3 and 13.1 ppbv, respectively. Notable concentrations of atmospheric propylene have been measured downwind of industrial point sources (Washenfelder et al., 2010).

Comparison with previous studies

In addition to emission intensity, a number of factors such as meteorology, sampling and laboratory analysis methods can affect reported concentrations. Previous studies evaluating VOCs in the region had some differences in the suite of VOCs analyzed, location and time of monitoring, and laboratory conducting the analysis. As a result, only a general comparison is made between the results reported in those studies and this one.

The Fort Saskatchewan regional study collected air samples from various monitoring locations that included far downwind to fence line monitoring sites (Environment Canada, 2006). The emissions in the region may have changed since the time of the study; however, the study averages provide regional concentrations for the time.

In 2014, as part of an investigative study to understand elevated NMHC concentrations at the Bruderheim monitoring station, 13 samples were collected during the winter months. The averages for this short study are at best representative of concentrations during the colder months within the town of Bruderheim. If the sources influencing elevated NMHC concentrations at Bruderheim(l) are the same or similar, the results from the investigative study should be comparable to this study. The investigative study, because it included only winter samples, may show higher concentrations for some VOCs that are emitted during the colder months and are lost to atmospheric oxidation during the summer months. At the same time, the wintertime investigative study may show lower concentrations for VOCs that are produced through photo-oxidation and/or emitted via fugitive evaporation (i.e. those VOCs typically affected by warm weather conditions).

Table 3 lists the summary statistics for VOC studies in the region. A number of the VOCs detected within all or almost all of the samples in previous studies were not detected in as many of the samples collected during the current study. This difference is most likely due to the analysis method and higher reported method detection limit by the laboratory used in the current study. Propane with a study average concentration of 3.76 and 9.70 ppbv, was ubiquitous in both the regional and investigative study samples, respectively. Due to laboratory analysis limitations, propane was not included in the analysis suite for this study.

Concentrations below the detection limits in this study were replaced by half the detection limit to calculate summary statistics. This method is comparable to the summary statistic calculation method used in the earlier two studies. To avoid a high bias, the average and 90th percentile concentrations are only presented for compounds detected in at least 50% of the samples. The maximum concentration for all detected VOCs is presented here. For those VOCs below detection, the maximum concentration is indicated as less than the detection limit. Table 3 compares the study average concentrations measured for select VOCs during the current and previous studies within the Fort Air Partnership monitoring region.

Acetone and ethanol were routinely detected in both the investigative and this study albeit concentrations in the investigative study (conducted in the colder months) were notably lower. This study's wintertime (December to February) average concentration of 5.8 ppbv for ethanol was on the same order of magnitude as that of the previous investigative study. However, the wintertime average concentration of 20.3 ppbv for acetone was considerably higher. Acetone is also a notable contributor to event samples. Acetone and ethanol were not reported in the 2006 study.

Alkanes such as butane and pentane were detected in almost all samples for all three studies. The study average concentrations for butane and pentane were the lowest for the regional study. Study average i-butane concentrations for this study and the investigative and regional studies were 3.3, 2.50 and 1.14 ppbv, respectively. The study average concentration for n-butane was 3.3 ppbv for this study, 4.53 ppbv for the investigative study and 2.21 ppbv for the regional study.

Average concentrations of i- and n-pentane for this study of 24.8 and 30.1 ppbv, respectively, were an order of magnitude higher than previous studies. The 90th percentile and maximum concentrations for i- and n-pentane (331.1 and 406.6 ppbv, respectively) were several orders of magnitude higher than observed for the previous studies.

I-pentane is also a dominant contributor to event samples. Average, 90th percentile and maximum n-hexane and propylene concentrations calculated for this study are also markedly higher than both previous studies. Elevated concentrations for propylene and n-hexane were mainly measured outside of the winter months; this may in part explain the observed difference between the 2014 investigative study and this study.

Aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene were detected in about half or less (in the case of xylene and ethylbenzene) of the study samples. The study average benzene concentrations for both the 2014 investigate and 2006 regional study of ~0.2 ppbv were comparable to current observations (0.5 ppbv). This study's average toluene concentration was noticeably higher than the average for both the previous studies. Higher concentrations were measured for samples collected during the warmer months, and all but one of the samples collected between January and April had concentrations that were below the detection limit. This is in agreement with the investigative study average concentration of 0.20 ppbv collected during the winter months. M and p-xylene and ethylbenzene concentrations were largely below the detection limit of this study. Concentrations above detection were measured in the summer and maximum concentration measured were comparable to the maximum concentration measured during the 2006 regional study. Higher aromatic hydrocarbon concentrations during the warmer months could be attributed to contributions from fugitive emissions due to evaporation.

Most other VOCs summarized for the previous two studies were detected in less than 10% of this study's samples. The maximum concentration for most of the VOCs detected was comparable to those observed for the 2006 regional study. The exceptions are styrene and vinyl chloride which had lower concentrations in this study. A major vinyl chloride source in the area stopped operating in 2006. The maximum concentration for tetrachloroethylene and trichloroethylene were higher for this study albeit these VOCs were detected in two samples or less in the case of trichloroethylene and may have been associated with a very localized and sporadic source. Samples in this study were not analyzed for 2,2,4-trimethylpentane and dichloromethane.

Table 3: Summary statistics of selected VOCs (ppbv) from studies in the Fort Saskatchewan area. Bold indicates the highest average values for compounds included in all three studies.

Compound	2006 Fort Saskatchewan Study (365 samples from 5 sites)				2014 Investigative study (13 samples)				Current Study (83 samples)			
	Above detection	Ave	90 th Perc	Max.	Above detection	Ave	90 th Perc	Max.	Above detection	Ave	90 th Perc	Max.
Propane	100%	3.76	8.26	28.33	100%	9.70	18.91	24.90	N/A	N/A	N/A	N/A
Acetone	--	--	--	--	100%	1.52	2.66	2.88	100%	35.4	68.22	148.36
Ethanol	--	--	--	--	100%	2.22	3.31	4.07	94%	79.03	44.96	2800
n-Butane	100%	2.21	4.75	41.56	100%	4.53	9.97	14.85	84%	3.3	8.6	20.3
Isopentane	100%	0.94	2.20	17.08	100%	2.57	5.05	11.05	89%	24.8	65.7	331.1
Isobutane	100%	1.14	2.36	32.10	100%	2.50	5.97	6.86	69%	3.3	8.5	32.2
Toluene	100%	0.52	1.25	8.01	100%	0.20	0.32	0.40	54%	2.3	6.9	34.2
n-Pentane	99%	0.64	1.36	4.44	100%	2.03	4.24	8.81	96%	30.1	67.6	406.6
n-Hexane	99%	0.37	0.79	3.49	100%	0.67	1.62	2.89	70%	2.0	5.8	12.5
m,p-Xylene	99%	0.18	0.46	1.82	100%	0.08	0.18	0.21	19%	--	--	2.8
Benzene	100%	0.22	0.44	5.13	100%	0.21	0.38	0.44	53%	0.5	1.4	2.1
Propylene	100%	0.26	0.64	2.32	100%	0.24	0.41	0.41	88%	2.3	5.2	13.1
1,2-Dichloroethane	100%	0.10	0.15	5.31	100%	0.02	0.02	0.02	8%	--	--	4.8
2,2,4-Trimethylpentane	82%	0.06	0.15	0.54	77%	0.02	0.04	0.04	N/A	N/A	N/A	N/A
Dichloromethane	100%	0.08	0.14	1.58	100%	0.08	0.12	0.12	N/A	N/A	N/A	N/A
Ethylbenzene	99%	0.06	0.16	1.50	100%	0.03	0.07	0.07	10%	--	--	1.6
o-Xylene	99%	0.06	0.16	0.76	100%	0.03	0.07	0.07	10%	--	--	1.1
1,2,4-Trimethylbenzene	77%	0.04	0.10	1.00	85%	0.02	0.04	0.08	5%	--	--	0.9
Styrene	84%	0.04	0.07	3.31	69%	0.01	0.02	0.05	5%	--	--	0.5
Vinylchloride	37%	0.00	0.00	1.02	0%	--	--	--	0%	--	--	<0.3
Tetrachloroethylene	92%	0.01	0.03	0.13	100%	0.01	0.01	0.01	5%	--	--	0.6
Naphthalene	99%	0.01	0.02	0.10	100%	0.01	0.02	0.04	0%	--	--	<0.3
1,3-Butadiene	95%	0.02	0.05	0.27	100%	0.02	0.05	0.05	2%	--	--	0.4

Compound	2006 Fort Saskatchewan Study (365 samples from 5 sites)				2014 Investigative study (13 samples)				Current Study (83 samples)			
	Above detection	Ave	90 th Perc	Max.	Above detection	Ave	90 th Perc	Max.	Above detection	Ave	90 th Perc	Max.
1,2,3-Trimethylbenzene	47%	--	--	0.39	62%	0.01	0.00	0.02	2%	--	--	0.5
1,3,5-Trimethylbenzene	58%	0.01	0.02	0.18	69%	0.01	0.00	0.02	1%	--	--	0.4
Trichloroethylene	84%	0.01	0.02	0.11	23%	--	--	0.06	2%	--	--	4.6

Comparison with other Canadian monitoring sites

As part of the NAPS program (Government of Canada, 2019), 24-hour integrated air samples are collected once every six days at a number of Canadian monitoring sites for VOC analysis. The summary statistics for VOCs measured (2014-2016) at selected Canadian urban NAPS sites are listed in Table 4. The NAPS sites are classified as large or medium urban sites. Some of these urban sites are also classified as influenced by industrial activities.

For general comparison, the table also lists the average and median VOC concentrations measured during the current study. The average and median concentrations for most of the VOCs noted to be ubiquitous in 24-hour integrated samples were higher than concentrations reported for the selected NAPS urban sites. This difference is especially notable for i- and n-pentane and to a lesser extent i- and n-butane, propylene and n-hexane. Maximum 24-hour integrated concentrations for most VOCs were comparable or higher for this study. The exceptions were n-butane, benzene and toluene where concentrations at an urban site were higher.

Table 4: Summary statistics of selected VOCs detected in 24-hour integrated samples at Canadian urban and industrial sites compared to this study.

VOC	Current Study (ppbv)			Canadian Urban sites (2014-16) (ppbv)		
	Average	Median	Maximum	Average	Median	Maximum
Propylene	2.3	1.6	13.1	0.37	0.03	13.63
i-butane	3.3	1.2	32.2	0.81	0.03	15.05
n-Butane	3.3	1.8	20.3	1.54	0.06	42.04
i-pentane	24.8	6.2	331.1	0.91	0.03	13.90
n-Pentane	30.1	4.0	406.6	0.71	0.11	116.58
Ethanol	79.0	8.2	2800.0	N/A	N/A	N/A
2,2-Dimethylbutane	0.6	0.5	4.36	0.03	<0.01	0.37
Acetone	35.4	30.0	148.4	N/A	N/A	N/A
2-Methylpentane	0.8	0.3	7.9	0.16	0.01	3.63
n-Hexane	2.0	0.9	12.5	0.17	0.02	19.37
Methyl cyclopentane	0.7	0.4	4.0	0.09	<0.01	4.27
Methyl ethyl ketone	3.2	0.3	76.1	N/A	N/A	N/A
Benzene	0.5	0.3	2.1	0.23	0.01	6.58
Toluene	2.3	0.3	34.2	0.69	0.17	190.02

Canadian urban sites included: Toronto (Etobicoke south-2), Montreal (St. Jean Baptiste), Saint John (Forest Hills), Edmonton (Central), Burnaby (South), Winnipeg (Ellen) and Regina (Regina-2). Some sites were also classified as impacted by industrial emissions

Event samples

Periods of elevated NMHCs measured at the Bruderheim(I) station often lasted less than a day. Such events are likely not fully characterized by 24-hour integrated samples. To examine constituents of VOCs during these periods, one-hour integrated event samples were collected when NMHC concentrations reached a set trigger. With the exception of March 8, 2017 all event samples were collected after the NMHC trigger was changed from a 3-minute average at 3 ppm to a 10-minute average at 1 ppm, in January of 2018.

Table 5 lists the date and time, trigger criteria, meteorological conditions and the Σ VOCs concentration for the event samples selected for analysis. Due to the small sample size, the data only provides a preliminary characterization of the VOC constituent's profile of event samples.

Table 5: 1-hour event samples. Wind direction indicates most frequently observed wind direction. Wind speed is the average wind speed for the sample hour.

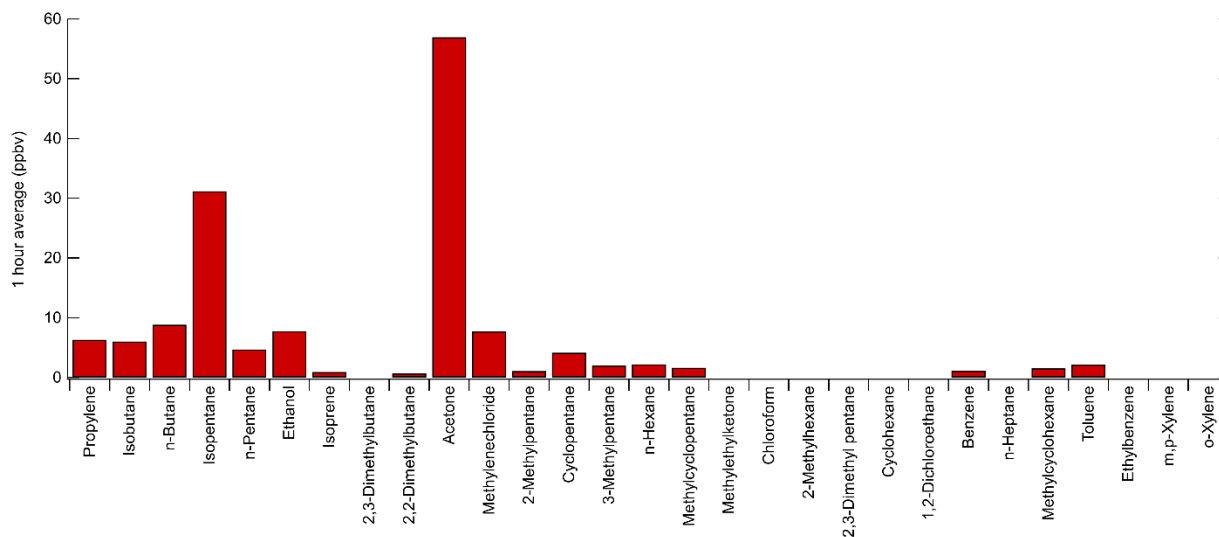
Date	Trigger Conc	Trigger Ave time	Start time	Wind direction (°)	Wind speed (km/hr)	Σ VOCs (ppbv)
Sept 7 th 2017	3ppm	3 min	07:13	292	2.5	94
Mar 8 th 2018	1ppm	10 min	03:56	81	3.4	53
April 30 th 2018	1ppm	10 min	04:44	191	2.1	288
July 12 2018*	1ppm	10 min	01:06	191	8.7	66
July 26 th 2018*	1ppm	10 min	04:40	360	2.3	6958

* These days do not appear to be notably impacted by forest fire smoke

NMHC concentrations were more frequently detected at higher concentrations under the nocturnal boundary layer. This is demonstrated by higher 95th percentile NMHC concentrations in samples collected at night. Consequently, most event samples were collected in the early morning hours and all samples were collected before 8:00 a.m. (Swarthout et al. 2013) attributes similar NMHC 24-hour variability to nocturnal ground base sources, vertical mixing and increase in photochemical processing during the day. None of the event samples were significantly influenced by wildfire smoke.

The Σ VOC concentration in event samples was highly variable and ranged from 53 to 6,498 ppbv. As a result, the median and not the average is used to summarize VOC concentrations. The median concentration for VOCs detected in at least three of the five event samples are presented in Figure 9. Much like 24-hour integrated samples, event samples had notable contributions from acetone, i-pentane and n-butane.

Figure 9: Median 1-hour concentration for VOCs detected in at least three of the five event samples.



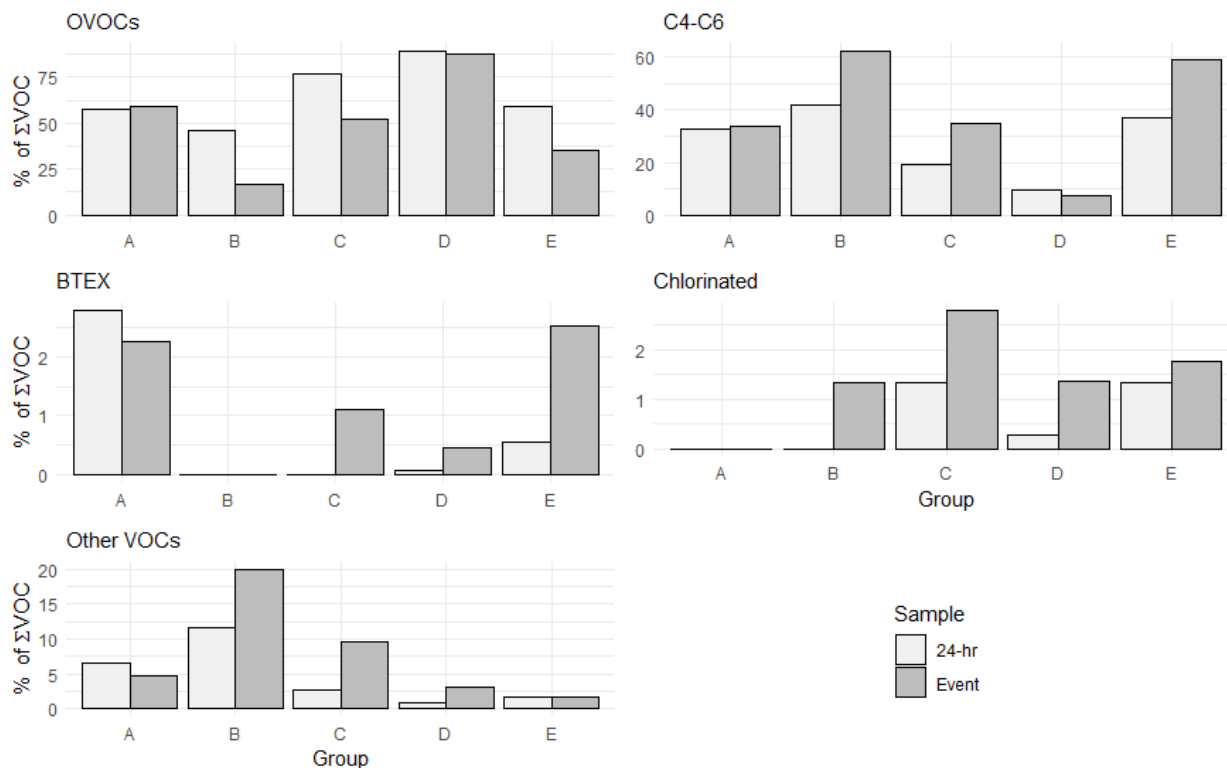
VOC species constituents and their relative contribution vary with time, therefore the event sample concentrations were compared with 24-hour integrated samples collected in the samples immediately preceding and after the triggered sample. The individual VOC concentration within each event and comparison 24-hour samples are listed in Table A-2 in the Appendix. VOCs were grouped to facilitate comparison. Concentrations of grouped VOCs in event and 24-hour samples are listed in Table 6.

Table 6: Grouped VOCs concentration (ppbv) in event and 24-hour samples. Individual VOCs concentrations are presented in Table A-2 in the Appendix.

Name	07-Sep	Sept 4 & 10	08-Mar	Mar 3 & 9	30-Apr	Apr 26 & May 3	12-Jul	Jul 7 & 13	26-Jul	25-Jul
	Event A	24-hr A	Event B	24-hr B	Event C	24-hr C	Event D	24-hr D	Event E	24-hr E
OVOCS	55.1	27.1	8.6	9.1	144.4	29	58	473.8	2421.4	233.2
C4-C6	31.8	15.3	32.8	8.3	96.7	7.3	4.8	51.6	4090.8	146.4
Other	4.4	3.1	10.5	2.3	26.5	1	2.1	4.3	110.8	6.2
BTEX	2.1	1.3	0	0	3.1	0	0.3	0.4	174.7	2.2
Chloro	0	0	0.7	0	7.8	0.5	0.9	1.5	122.5	5.2
ΣVOC	93.4	46.8	52.6	19.7	278.5	37.8	66.1	531.6	6920.2	393.2

The relative contribution of these groups to Σ VOC is illustrated in Figure 10.

Figure 10: Relative contribution of grouped VOCs in Event and 24-hour integrated samples. The groups relate to the dates indicated in Table 4.



For this comparison, and due to their relatively large contribution, chlorinated hydrocarbons have been separated from “other VOCs”. Chlorinated hydrocarbons are hydrocarbons that contain chlorine atom(s).

Acetone and/or ethanol constituted a large fraction of the Σ VOCs in a number of event samples. However, the relative contribution of both acetone and ethanol in event samples were similar to or lower than the relative contribution of these VOCs to 24-hour integrated samples. The presence of OVOCs such as acetone in event samples collected in the early morning hours could be due to a significant contribution from atmospheric oxidation during the day coupled with a relatively long atmospheric life time (>days) (Borbon et al., 2004; Simpson et al., 2010).

The relative contribution of C_4 – C_6 alkanes to event samples was comparable to or higher than 24-hour integrated samples. In event samples, this group of alkanes had contributions from n- and i- pentane, n- and i- butane, propylene, and n-hexane. These VOCs were detected in 70% or more of the 24-hour integrated samples collected in this study. With the exception of the event sample collected on July 12th (Group D), C_4 – C_6 alkanes contributed to >50% Σ VOCs. Enhanced concentrations of C_4 – C_6 alkanes (butane, pentane and hexane) have previously been associated with petroleum production (Buzcu and Fraser, 2006) and oil and gas wells (Gilman et al., 2013; Petron et al., 2014).

The relative contribution of BTEX and chlorinated hydrocarbons to Σ VOC in both event and 24-hour integrated samples was under 5%. That being said, the contribution from these VOCs to event samples was marginally higher than that of 24-hour integrated samples. This is especially evident for the July 26 sample, where BTEX and Chlorinated hydrocarbons are two orders of magnitude higher in the event samples.

Other VOCs includes propylene, larger alkanes ($>C_6$) and cycloalkanes with propylene and cycloalkanes being the larger contributors. Propylene was a notable contributor to the VOC composition of both event and 24-hour samples. Cyclic alkanes such as methylcyclohexane with a study average of 0.6 ppbv was detected in 42% of the 24-hour samples. The concentration of methylcyclohexane within event samples ranged from below detection to 30.9 ppbv. Cyclic alkanes such as methylcyclohexane have been associated with oil and gas production (Swarthout et al., 2013; Warneke and Gouw, 2001).

The highest combined VOC concentrations were observed for the event sample collected on July 26. In addition to the enhanced VOCs observed in the other events samples, the event sample on July 26 also included enhanced concentrations of cyclic hydrocarbons such as cyclopentane, cyclohexane, aromatic compounds such as benzene, toluene, xylene and ethylbenzene, chlorinated hydrocarbons such as methylenechloride, 1,2 dichloroethane, tetrachloroethylene and n-decane. One hour average event sample concentrations for these VOCs were greater than 5 ppbv, whereas a large number of these VOCs were below or close to the detection limit of 0.3 ppbv in the duplicate 24-hour integrated sample collected on July 25. Cyclic hydrocarbons, aromatics and n-decane have been associated with various sources including vehicular emissions, gasoline vapours, petrochemical production, storage tanks and oil and gas activities (Aklilu et al., 2018; Chambers et al., 2008; Hendler and Nunn, 2009; Kansal, 2009; Petron et al., 2014).

The analysis of event samples collected on July 12 resulted in unexpectedly low VOC concentrations (Table A-2, Appendix A). The combined VOC concentration is predominantly composed of acetone. NMHC concentrations during this sample period were the highest observed, with a maximum 1-min average concentration of 24 ppm. A NMHC concentration above detection was observed for a quarter of the period (~15 min).

CH₄ concentrations remained at the regional background concentration of ~2 ppm throughout the sample period. Although collected in the early morning hours, the wind speed of 8.7 km/hr was relatively high for an event sample. Higher wind speeds are generally more favorable to emission dispersion. Most of the VOC concentrations reported for this event sample were much lower than the 24-hour integrated sample. Elevated NMHC during this event may have resulted from smaller hydrocarbons such as ethane and propane ($< C_4$ alkanes). These VOCs can dominate ambient samples influenced by petrogenic fugitive emissions (Gilman et al., 2013; Swarthout et al., 2013).

In general, the VOC constituents of event samples collected in this study were comparable to 24-hour integrated samples, albeit with higher contributions from C₄-C₆, propylene, cycloalkanes and to a lesser extent BTEX and chlorinated hydrocarbons. However, the July 12 and 26 event samples illustrate that during certain conditions elevated hydrocarbons may have a contribution from a complex mixture of VOCs or may largely be composed of light alkanes ($< C_4$), implying observed elevated concentrations are likely associated with multiple source types.

Comparison of measured concentrations to benchmarks

In addition to identifying the components of summative NMHCs and meteorological conditions conducive to the periodic elevated concentrations of NMHC, concentrations were also compared to ambient air benchmarks. Alberta does not have objectives in place for summative NMHCs but has ambient air quality objectives (AAQOs) for selected VOC species. The established objectives include:

- 1-hour objectives for eight VOCs: acetone, isopropyl alcohol, carbon disulfide, n-hexane, benzene, toluene, ethylbenzene and styrene.
- 24-hour objective for n-hexane and toluene.

In the absence of AAQOs, concentrations were compared to Texas Air Monitoring Comparison Values (AMCVs). The AMCVs are used to assess the potential for effects to occur as a result of exposure to concentrations (Texas Commission on Environmental Quality, n.d.). Short-term AMCVs are based on acute health, vegetation effects or odour potential. Long-term AMCVs are based on chronic health and vegetation effects.

The maximum measured VOCs concentrations from the 1-hour event samples were compared to 1-hour objectives or short term AMCV in the absence of AAQOs. Maximum measured VOCs concentrations from 24-hour integrated samples were compared to the 24-hour objective. Study average concentrations were compared to long-term AMCVs.

Tables A-3 to A-5 (in Appendix) present the measured concentration and related benchmarks. The measured concentrations were lower than AAQOs nor AMCVs, where those values were available.

Summary

This study was initiated, in part, to address monitoring objectives for the area: to characterize emerging issues. As such, the VOC study at the Bruderheim(I) station was initiated to investigate periodically measured elevated NMHC concentrations. This study follows two other VOCs studies conducted in the region: a regional VOC study which included a number of monitoring sites and conducted over multiple years starting in 2001 and a short investigate study when air samples were collected at the initial Bruderheim station between October 2014 and March 2015.

Using data collected between 2017 and 2018, this study identifies the components of summative NMHCs and meteorological conditions conducive to the periodic elevated concentrations of NMHC. The measured VOCs concentrations were also compared to ambient air benchmarks. VOCs measured during the study did not exceed established AAQOs nor the published AMCVs. This being said, summative NMHC concentration at Bruderheim (I) station should continue to be measured and evaluated to examine trends and changes in the atmospheric concentration of NMHC going forward.

On average for this study, oxygenated VOCs (OVOCs) formed more than half of the detected VOCs for 24-hour integrated samples. Sources of these VOCs include atmospheric oxidation of other VOCs such as branched and chain alkanes, wildfire smoke and to a lesser extent vehicle emissions. The OVOC fraction of the Σ VOC was predominantly composed of acetone and ethanol. Atmospheric processing is known contributor to OVOCs. These VOCs were more abundant for the summer months, a period conducive to photochemical processing.

Branched and chain alkanes (C_4 - C_6) contributed on average 34% of the measured VOCs. Branched and chain alkanes have previously been associated with fugitive emissions from activities related to the production and storage of petroleum-based products. The branched and chain alkanes fraction in 24-hour integrated samples were routinely composed of butane, pentane and hexane, with pentane as the most notable contributor.

Average concentrations of i- and n-pentane for this study of 24.8 and 30.1 ppbv, respectively were an order of magnitude higher than previous studies in the area. Higher concentrations of butane were measured for samples collected during the investigative study conducted during the colder months. The current study average concentrations of hexane were higher than that of the investigative or regional study. This observation indicates that these alkanes at the study site were higher than a regional average concentration suggesting impact from a nearby source.

BTEX and other VOCs contributed on average 2% and 8% of the detected VOCs, respectively. Benzene and toluene were detected in about half of the 24-hour integrated samples. This study's average benzene concentration of 0.5 ppbv was close to the analysis detection limit and comparable to averages for both the investigative and regional studies. The study average concentration for toluene of 2.3 ppbv was higher than that for benzene. Some samples contained an elevated concentration of toluene ranging from 5.6 to 34.2 ppbv. Toluene is emitted by industrial activities in the study area (Environment and Climate Change Canada, 2017). Some samples collected at the study sites were likely influenced by such nearby industrial activities.

The average concentration for most of the VOCs noted to be ubiquitous in 24-hour integrated samples collected in the current study were higher than average concentrations reported for selected Canadian urban sites. This difference is especially notable for i- and n-pentane and to a lesser extent i- and n-butane, propylene and n-hexane. Implying that elevated NMHC concentrations at the Bruderheim(I) monitoring site is not solely due to urban emissions.

On average NMHC concentrations at the Bruderheim(I) station are higher than measured at a downwind regional site and a nearby urban site while being comparable those measured near industrial operations. Typically, NMHC concentrations were higher in the colder months, in the early morning hours and were more frequently observed during low east-southeast winds, indicating a possible nearby nocturnal source. NMHC concentrations positively correlated with CH_4 ($r = 0.55$), implying some association between these two gases. The correlation coefficient between NMHC and other co-monitored gases and particulate matter was notably lower ($r < 0.25$). CH_4 and NMHC concentrations during event samples were highly variable over the short sample period, indicating samples from a heterogeneous airmass and supporting a relatively nearby source(s). Event air samples were collected during periods of elevated NMHC at Bruderheim(I) to examine contributing constituents VOCs.

Event samples triggered during elevated NMHC concentrations were also mostly collected during the early morning hours. The Σ VOC concentration in these samples ranged from 53 to 6498 ppbv. On average VOC constituents of event samples were comparable to 24-hour integrated samples. However, relative to the 24-hour integrated samples, almost all samples had enhanced concentrations of n- and i-pentane, n- and i-butane, propylene, n-hexane and methylcyclohexane.

One event sample contained a complex mixture of VOCs at concentrations higher than typically observed for an event or 24-hour integrated samples, while analyzed VOCs concentrations within another were unexpectedly low. These observations indicate that in general, elevated VOCs within event samples were also found at higher concentration in the 24-hour integrated samples, albeit the relative contribution of these VOCs in event samples were markedly higher. In addition, event samples can also contain complex mixtures of VOCs, or at times are likely to be largely composed of small (<C₄) hydrocarbons. The observed variability in these event samples supports multiple source types.

Continued evaluation of summative NMHC concentrations at the Bruderheim station can be used to examine trends and changes in the atmospheric concentrations of NMHC going forward. In addition, future studies should optimize the sampling to increase the number of samples collected to better characterize the VOC constituents of samples collected during periods of elevated NMHC.

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Appendix

Table A-1: Total detected VOC (ppbv) for 24-hour integrated canister air samples.

Σ VOC -sum of all detected VOC concentration

OVOC - acetone, ethanol and ketones (including methyl ethyl ketone (MEK))

C₄-C₆ - branched and chain alkanes with less than seven and more than three carbons

BTEX - benzene, toluene, ethylbenzene and xylenes

BDL – Below method detection limit

Date	Σ VOC	OVOC	C ₄ -C ₆	BTEX	Other
2017-07-24	44.8	37.4	1.1	1.4	4.9
2017-07-30	733.4	507.6	133.5	38.3	53.9
2017-08-05	269.4	174.0	58.7	10.8	25.9
2017-08-11	187.0	78.6	70.6	3.9	33.9
2017-08-17	68.7	50.1	10.8	1.3	6.5
2017-08-23	108.0	73.9	21.6	2.5	10.0
2017-08-29	110.1	31.0	57.5	2.1	19.5
2017-09-04	52.2	24.0	21.7	0.9	5.5
2017-09-10	48.5	32.7	10.9	1.0	3.9
2017-09-16	49.3	25.7	21.5	1.0	1.1
2017-09-22	82.0	23.0	58.0	0.5	0.5
2017-09-28	139.3	55.8	69.1	0.3	14.2
2017-10-04	128.7	51.9	73.5	0.5	2.7
2017-10-10	138.1	54.3	79.6	1.8	2.4
2017-10-16	99.7	56.8	20.7	5.4	16.8
2017-10-22	136.5	72.8	23.4	10.9	29.3
2017-10-28	60.3	53.5	5.3	0.7	0.8
2017-11-03	75.1	38.9	22.1	2.0	12.1
2017-11-09	45.4	27.7	9.0	0.5	8.2
2017-11-15	33.2	26.9	3.6	1.1	1.5
2017-11-21	33.5	14.9	16.0	BDL	2.6
2017-11-27	74.1	55.0	6.8	3.0	9.3
2017-12-03	71.8	53.8	BDL	1.6	16.4
2017-12-09	77.3	53.7	14.4	1.9	7.4
2017-12-15	111.7	63.0	17.3	19.3	12.1
2017-12-21	428.9	40.4	382.0	2.2	4.3
2017-12-27	13.5	10.2	2.5	BDL	0.8
2018-01-02	56.9	44.6	9.3	0.5	2.5
2018-01-08	49.1	25.2	21.3	BDL	2.6
2018-01-14	25.7	12.3	12.0	BDL	1.5
2018-01-20	19.5	10.9	7.0	BDL	1.7
2018-01-26	28.8	22.0	5.3	0.5	1.0
2018-02-01	16.5	11.7	3.9	BDL	1.0
2018-02-07	96.9	8.5	81.8	BDL	6.5
2018-02-13	49.7	25.6	20.3	0.6	3.2

Date	Σ VOC	OVOC	C ₄ -C ₆	BTEX	Other
2018-02-19	8.4	5.7	2.1	BDL	0.6
2018-02-25	15.7	7.4	8.3	BDL	BDL
2018-03-03	13.6	9.5	2.0	BDL	2.2
2018-03-09	19.4	8.4	8.5	BDL	2.6
2018-03-15	136.8	85.1	43.6	0.5	7.5
2018-03-21	112.3	41.0	58.1	BDL	13.2
2018-03-27	14.3	9.4	4.1	BDL	0.8
2018-04-02	43.9	23.8	15.6	BDL	4.5
2018-04-08	13.6	9.8	2.8	BDL	1.0
2018-04-14	48.5	33.1	7.2	BDL	8.2
2018-04-20	40.3	29.8	8.4	BDL	2.1
2018-04-26	50.8	32.2	10.7	BDL	7.9
2018-05-02	30.1	25.8	3.7	BDL	0.7
2018-05-08	538.6	134.5	396.8	0.9	6.4
2018-05-14	667.8	101.5	555.7	1.3	9.4
2018-05-20	75.2	43.5	14.4	BDL	17.3
2018-05-26	316.2	107.0	187.1	10.8	11.4
2018-06-01	91.3	42.9	39.4	1.7	7.3
2018-06-07	93.4	47.1	32.1	3.3	10.8
2018-06-13	432.9	127.9	285.5	15.4	4.2
2018-06-19	119.9	60.3	50.2	1.1	8.4
2018-06-25	96.0	72.1	16.2	BDL	7.7
2018-07-01	3639.6	2982.5	601.3	17.9	38.0
2018-07-07	1109.3	883.4	202.6	7.0	16.3
2018-07-13	135.0	92.0	32.5	1.5	9.1
2018-07-19	180.7	78.0	90.8	2.6	9.3
2018-07-25	397.6	233.1	146.6	3.1	14.8

Table A-2: Comparison of event samples to 24-hour integrated samples.

VOC	Sept 7	Sept 4 & 10	Mar 8	Mar 3 & 9	Apr 30	Apr 26 & May 3	Jul 12	Jul 7 & 13	Jul 26	Jul 25
	Event	24-hr	Event	24-hr	Event	24-hr	Event	24-hr	Event	24-hr
	A	A	B	B	C	C	D	D	E	E
Acetone	47.4	22.3	8.3	5.9	103.0	23.6	56.9	50.4	1700.0	88.3
Isopentane	7.6	3.5	10.4	4.0	47.6	3.8	< 0.3	< 0.3	1490.0	55.1
Ethanol	7.7	4.8	0.3	3.2	41.2	5.4	1.1	423.4	721.4	144.9
n-Butane	8.8	3.9	11.0	2.1	22.5	0.6	1.7	3.0	6.6	1.8
n-Hexane	2.2	1.1	1.2	< 0.3	8.7	< 0.3	0.5	1.6	14.8	1.2
2-Methylhexane	< 0.3	< 0.3	< 0.3	< 0.3	8.7	< 0.3	< 0.3	< 0.3	5.8	0.3
Isobutane	6.0	2.5	4.1	< 0.3	8.6	0.5	0.8	5.0	127.9	6.4
n-Pentane	3.6	2.1	4.7	2.2	8.4	2.2	0.7	40.2	2440.0	81.0
Methylenechloride	< 0.3	< 0.3	< 0.3	< 0.3	7.8	0.5	0.9	1.5	8.7	0.4
Propylene	1.1	1.0	8.3	2.3	7.8	1.0	1.2	2.7	6.3	2.6
Cyclopentane	< 0.3	< 0.3	0.5	< 0.3	4.2	< 0.3	< 0.3	< 0.3	31.2	1.2
Methylcyclopentane	0.6	0.9	0.7	< 0.3	2.6	< 0.3	< 0.3	< 0.3	6.7	0.7
Toluene	0.7	0.5	< 0.3	< 0.3	2.3	< 0.3	< 0.3	< 0.3	149.4	2.2
Methylcyclohexane	0.9	0.6	0.7	< 0.3	2.0	< 0.3	< 0.3	< 0.3	30.9	0.9
Benzene	1.4	0.8	< 0.3	< 0.3	0.8	< 0.3	0.3	0.4	< 0.3	< 0.3
n-Heptane	< 0.3	< 0.3	< 0.3	< 0.3	0.6	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
3-Methylhexane	< 0.3	< 0.3	0.3	< 0.3	0.6	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
2,2-Dimethylbutane	0.6	1.1	< 0.3	< 0.3	0.5	0.2	0.3	1.3	11.5	0.9
2,3-Dimethylbutane	< 0.3	< 0.3	< 0.3	< 0.3	0.4	< 0.3	0.8	0.5	< 0.3	< 0.3
Methylethylketone	< 0.3	< 0.3	< 0.3	< 0.3	0.2	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Isoprene	0.9	0.6	< 0.3	< 0.3	< 0.3	< 0.3	0.9	1.6	< 0.3	< 0.3
2-Methylpentane	0.7	0.5	1.1	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
3-Methylpentane	2.3	0.6	0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
cis-1,2-dichloroethene	< 0.3	< 0.3	0.7	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3

VOC	Sept 7	Sept 4 & 10	Mar 8	Mar 3 & 9	Apr 30	Apr 26 & May 3	Jul 12	Jul 7 & 13	Jul 26	Jul 25
	Event	24-hr	Event	24-hr	Event	24-hr	Event	24-hr	Event	24-hr
	A	A	B	B	C	C	D	D	E	E
Carbendisulfide	0.9	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
1,2-Dichloroethane	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	87.5	3.7
Tetrachloroethylene	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	20.8	0.5
m,p-Xylene	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	11.1	0.0
Cyclohexane	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	9.3	0.5
Ethylbenzene	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	7.9	0.0
Isopropylbenzene	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	7.5	0.0
Styrene	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	6.7	0.0
n-Decane	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	6.4	0.0
o-Xylene	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	6.3	0.0
Chloroform	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	5.5	0.6
∑ VOC	93.5	46.8	52.7	19.6	278.4	37.8	66.4	531.5	6920.1	393.0

Table A-3: Comparison of maximum 1-hour concentrations with 1-hr AAAQOs and short term AMCVs.

VOC	CAS#	Event Sample Maximum 1-hr (ppbv)	AAAQO 1-hr (ppbv)	AMCVs Short Term (ppbv)
Isobutane	75-28-5	127.85	NA	33000
Vinyl chloride	75-01-4	BDL	NA	27000
n-Butane	106-97-8	24.67	NA	92000
1,3-Butadiene	106-99-0	BDL	NA	1700
Isopentane	78-78-4	1490.00	NA	68000
n-Pentane	109-66-0	2440.00	NA	68000
Ethanol	64-17-5	721.45	NA	NA
Isoprene	78-79-5	1.40	NA	1400
2,3-Dimethylbutane	79-29-8	3.28	NA	5400
2,2-Dimethylbutane	75-83-2	11.46	NA	5400
Acetone	67-64-1	1700.00	2400	--
Isopropylalcohol	67-63-0	BDL	3190	--
Carbondisulfide	75-15-0	0.91	10	--
Methylenechloride	75-09-2	8.75	NA	3400
2-Methylpentane	107-83-5	4.03	NA	5400
Cyclopentane	287-92-3	31.17	NA	5900
Methyltertbutylether	1634-04-4	BDL	NA	500
3-Methylpentane	96-14-0	2.33	NA	5400
1-Hexene	592-41-6	BDL	NA	500
n-Hexane	110-54-3	14.83	5960	--
1,1-Dichloroethane	75-34-3	BDL	NA	1000
2,4-Dimethylpentane	108-08-7	2.08	NA	8300
Methylcyclopentane	96-37-7	6.65	NA	750
Methylethylketone	78-93-3	BDL	NA	20000
Ethylacetate	141-78-6	BDL	NA	4000
Chloroform	67-66-3	5.48	NA	20
2-Methylhexane	591-76-4	9.15	NA	8300
1,1,1-Trichloroethane	71-55-6	BDL	NA	1700
2,3-Dimethyl pentane	565-59-3	1.97	NA	8300
Cyclohexane	110-82-7	9.29	NA	1000
3-Methylhexane	589-34-4	3.72	NA	8300
1,2-Dichloroethane	107-06-2	87.53	NA	540
Benzene	71-43-2	1.48	9	--
Isooctane	540-84-1	0.88	NA	4100
n-Heptane	142-82-5	4.08	NA	8300
Trichloroethylene	79-01-6	BDL	NA	100
Methylcyclohexane	108-87-2	30.85	NA	4000
2,3,4-Trimethylpentane	565-75-3	BDL	NA	4100
2-Methylheptane	592-27-8	1.05	NA	4100
3-Methylheptane	589-81-1	BDL	NA	4100
Methylbutylketone	591-78-6	BDL	NA	10

VOC	CAS#	Event Sample Maximum 1-hr (ppbv)	AAAQO 1-hr (ppbv)	AMCVs Short Term (ppbv)
Toluene	108-88-3	149.44	499	--
n-Octane	111-65-9	4.05	NA	4100
1,1,2-Trichloroethane	79-00-5	0.44	NA	100
Tetrachloroethylene	127-18-4	20.76	NA	1000
Methylisobutylketone	108-10-1	BDL	NA	200
Chlorobenzene	108-90-7	BDL	NA	100
Ethylbenzene	100-41-4	7.92	460	--
n-Nonane	111-84-2	0.60	NA	3000
m,p-Xylene	108-38-3 106-42-3	11.09	530	--
o-Xylene	95-47-6	6.32	530	--
Styrene	100-42-5	6.66	52	--
Isopropylbenzene	98-82-8	7.46	NA	510
1,1,2,2-Tetrachloroethane	79-34-5	BDL	NA	10
Propylbenzene	103-65-1	BDL	NA	510
m,p-Ethyltoluene	620-14-4 622-96-8	1.27	NA	250
n-Decane	124-18-5	6.43	NA	1000
1,3,5-Trimethylbenzene	108-67-8	0.58	NA	3000
o-Ethyltoluene	611-14-3	BDL	NA	250
1,2,4-Trimethylbenzene	95-63-6	3.26	NA	3000
1,2,3-Trimethylbenzene	526-73-8	1.12	NA	3000
m-Diethylbenzene	141-93-5	BDL	NA	450
Undecane	1120-21-4	0.44	NA	550
Naphthalene	91-20-3	BDL	NA	95

Table A-4: Comparison of maximum 24-hour study average with 24-hour AAAQOs and short term AMCVs.

VOC	CAS#	24-hr integrated Study Max (ppbv)	AAAQOs 24-hr (ppbv)
n-Hexane	110-54-3	12.45	1990
Toluene	108-88-3	34.21	106
m,p-Xylene	108-38-3 106-42-3	2.82	161
o-Xylene	95-47-6	1.13	161

Table A-5: Comparison of study average concentration with long-term AMCVs

VOC	CAS#	Study Average (ppbv)	Long Term (ppbv)
Isobutane	75-28-5	3.29	10000
Vinyl chloride	75-01-4	BDL	0.47
n-Butane	106-97-8	3.30	10000
1,3-Butadiene	106-99-0	0.16	9
Isopentane	78-78-4	24.78	8100
n-Pentane	109-66-0	30.08	8100
Isoprene	78-79-5	0.60	140
2,3-Dimethylbutane	79-29-8	3.17	190
2,2-Dimethylbutane	75-83-2	0.59	190
Acetone	67-64-1	35.42	6700
Methylenechloride	75-09-2	1.11	100
2-Methylpentane	107-83-5	0.78	190
Cyclopentane	287-92-3	0.55	590
Methyltertbutylether	1634-04-4	BDL	50
3-Methylpentane	96-14-0	0.54	190
1-Hexene	592-41-6	0.16	50
n-Hexane	110-54-3	1.99	190
1,1-Dichloroethane	75-34-3	BDL	100
2,4-Dimethylpentane	108-08-7	0.16	2200
Methylcyclopentane	96-37-7	0.74	75
Methylethylketone	78-93-3	3.16	3000
Ethylacetate	141-78-6	0.21	400
Chloroform	67-66-3	0.21	2
2-Methylhexane	591-76-4	0.73	2200
1,1,1-Trichloroethane	71-55-6	BDL	930
2,3-Dimethyl pentane	565-59-3	0.37	2200
Cyclohexane	110-82-7	0.38	100
3-Methylhexane	589-34-4	1.04	2200
1,2-Dichloroethane	107-06-2	0.31	0.72
Benzene	71-43-2	0.52	1.4
Isooctane	540-84-1	0.16	380
n-Heptane	142-82-5	0.57	2200
Trichloroethylene	79-01-6	0.22	10
Methylcyclohexane	108-87-2	0.61	400
2,3,4-Trimethylpentane	565-75-3	0.16	380
2-Methylheptane	592-27-8	0.16	380
3-Methylheptane	589-81-1	BDL	380
Methylbutylketone	591-78-6	0.16	1
Toluene	108-88-3	2.26	1100
n-Octane	111-65-9	0.17	380
1,1,2-Trichloroethane	79-00-5	BDL	10
Tetrachloroethylene	127-18-4	0.16	3.8
Methylisobutylketone	108-10-1	0.29	20

Chlorobenzene	108-90-7	BDL	10
Ethylbenzene	100-41-4	0.21	440
n-Nonane	111-84-2	0.16	280
m,p-Xylene	108-38-3 106-42-3	0.30	140
o-Xylene	95-47-6	0.21	140
Styrene	100-42-5	0.16	110
Isopropylbenzene	98-82-8	0.16	51
1,1,2,2-Tetrachloroethane	79-34-5	BDL	1
Propylbenzene	103-65-1	BDL	51
m,p-Ethyltoluene	620-14-4 622-96-8	0.15	25
n-Decane	124-18-5	0.17	190
1,3,5-Trimethylbenzene	108-67-8	0.15	37
o-Ethyltoluene	611-14-3	BDL	25
1,2,4-Trimethylbenzene	95-63-6	0.17	37
1,2,3-Trimethylbenzene	526-73-8	0.16	37
m-Diethylbenzene	141-93-5	0.15	45
Undecane	1120-21-4	0.16	55
Naphthalene	91-20-3	BDL	9.5

