Source apportionment of volatile organic compounds measured near a cold heavy oil production area

Yayne-abeba Aklilu, Sunny Cho, Qianyu Zhang, Emily Taylor

Government of Alberta, Alberta Environment and Parks, Edmonton T5J 1G4, Canada

1. Introduction

Deposits of heavy oil and oil sands are present in a number of areas around the world (Meyer et al., 2007). The production amount and method of extraction from these deposits vary depending on crude properties and ease of access (Chopra et al., 2010). The Peace River Oil Sands Area (PROSA) is one of the three major oil sands deposits in Alberta, Canada. Its area (~29,000 km²) comprises 21% of Alberta’s oil sands area and is located in northwest-central Alberta (Alberta oil sands industry, 2016; Alberta Energy, 2015). The Peace River area deposits occur at a depth of about 600–700 m below the surface (Chopra et al., 2010), too deep for bitumen extraction by open-pit mining. Approximately 81% of extraction and processing of heavy oil in the PROSA is accomplished using cold heavy oil production with sand (CHOPS), with the remainder being extracted by in-situ steam assisted gravity drainage (SAGD) and cyclic steam stimulation (CSS) thermal methods (Alberta Energy, 2002; Clearstone Engineering Ltd., 2014). CHOPS stocktanks in the region are approximately 7–10 m high, insulated with sprayed polyurethane foam and heated to 60–80 °C to facilitate separation of the produced slurry (Alberta Energy, 2002). The CHOPS extraction process, also used in other regions of the world, produces oil, gas, water and sand from the underground reservoir (Chopra et al., 2010). Until the onset of mitigation efforts with the revision of Alberta Energy Regulator Directive 060 (Alberta Energy Regulator, 2014a), the gas evolved from CHOPS stocktanks in PROSA was vented through a short stock on top of the stocktanks (Alberta Energy, 2002). Gas emissions associated with the CHOPS process include casing gas, tank top vent, and other fugitive emissions and can contain methane, volatile organic compounds (VOCs), reduced sulphur compounds (RSCs), and semivolatile organic compounds including polyaromatic hydrocarbons (PAHs) (Alberta Environment, 2008; Clearstone Engineering Ltd., 2014). The PROSA encompasses four extraction areas: Three Creeks, Reno, Seal Lake, and Walrus. While some of the extraction areas are in relatively remote locations, the extraction area in Three Creeks is located near a community. Concurrent with the growth in oil extraction activity, there has been an increase in the number of hydrocarbon odour complaints from...
residents in the community near Three Creeks. Identifying the sources of VOCs and their contributions are crucial for emission reduction strategies and understanding the effect of abatement measures (Simpson et al., 2016; Liggio et al., 2016; Li et al., 2017).

VOCs are of concern because of their potential to contribute to odours as well as their potential to impact human health and the ecosystem (Wu et al., 2014; Wang et al., 1996; Rumchev et al., 2004; Adgate et al., 2014). Furthermore, VOCs play important roles in the atmosphere as precursors to ground-level ozone and secondary organic aerosols (Johnson et al., 2006; Ban et al., 2011; Zhang et al., 2014; Hester and Harrison, 1995; Koppmann, 2007; Seinfeld and Pandis, 2006). Analysis tools such as receptor models have been successfully used to analyze ambient data sets and identify and quantify potential source contributions affecting a monitoring site (Paatero, 1997; Buzcu-Guven and Fraser, 2006; Brown et al., 2007; Bon et al., 2011; Gainmoz et al., 2011; Shim et al., 2007; McCarthy et al., 2013; Liu et al., 2017). This information can also provide an approach to evaluate emission inventories (Paatero and Tapper, 1994; Watson et al., 2001; Morino et al., 2011), develop emission reduction strategies and understand the effects of emissions abatement measures.

This study was initiated by local odour complaints and a lack of knowledge on the speciation and potential sources VOCs in the community near Three Creeks in the PROSA. The objective of this study is to better understand ambient hydrocarbon constituents and potential sources of VOCs in the community near Three Creeks. In order to determine potential sources, a receptor source apportionment technique was applied.

2. Methodology

2.1. Ambient air monitoring

Two monitoring stations, station 986 (longitude −116.941, latitude 56.376) and station 842 (longitude −116.982, latitude 56.2741), are located within the Three Creeks CHOPS operation and the nearby community (Fig. 1). The sites are separated by a distance of ~10 km. Both sites are located in a rural area with limited motor vehicle traffic. The oil production facilities are located at a higher elevation than the atmosphere as precursors to ground-level ozone and secondary organic aerosols (Johnson et al., 2006; Ran et al., 2011; Zhang et al., 2014; Bon et al., 2011; Gainmoz et al., 2011; Shim et al., 2007; McCarthy et al., 2013; Liu et al., 2017). The GC-FID method has a higher detection limit of 0.5 ppmv.

The GC–MS analysis was initiated by drawing and passing a volume of sample gas and a measured volume of standard gas through a pre-concentrator fitted with an extended cold trap dehydration system where water is removed by dehydration and the VOCs are trapped on to a Tenax trap. This is followed by back desorption of the trapped volatiles and cryogenic focusing onto a pre-column for rapid and split-less injection into a GC–MS. The mass spectrometer detector is operated by alternating between continuously scanning a wide range of mass to charge ratios and operating in selected ion monitoring (SIM) mode for the compounds on the target list. Target compound data review is performed from SIM spectra using relative retention times and relative abundances of two or more characteristic ions. Non-target compounds may be identified from scan spectra using Mass Hunter Mass Spectral libraries and detailed interpretation of the GC–MS data. The approximate concentration ranges of non-target compounds are determined using total ion profiles and response factors of the closest internal standards.

The samples were analyzed for fifty-four targeted hydrocarbons such as those containing one to four carbons (C1–C4; Tables S2 & S3), reduced sulphur compounds, toxic organic compounds and ozone precursors (US EPA, 1998 & 1999). Lists of compound name, chemical abstract service number (CAS), method detection limit (MDL) and percentage of samples that were above detection limit (> MDL) are summarized in Table S4. In addition to these target compounds, non-target compounds with varying match quality were identified. Concentrations reported for non-target compounds are considered to have higher level of uncertainty thus this information is used as an indication of the types of compounds present.

2.2. PMF and data input preparation

The Positive Matrix Factorization (PMF) used in this study is a receptor model developed by the US Environmental Protection Agency (USEPA) for source apportionment (EPA, 2008; Norris et al., 2008). The method is described in greater detail elsewhere (Paatero, 1997, 1999; Paatero and Tapper, 1994). PMF requires as an input both measured concentrations of a compound as well as the uncertainty associated with each concentration. The PMF output includes a chemical fingerprint of the resolved factors, which are then tested by the bootstrapping method for robustness. In this study, once a stable solution is identified, an individual factor is linked to potential origins using its chemical profile, a key chemical contributor and/or temporal variability.

Due to the proximity of the two stations and similarity of sources that could potentially impact the sites the samples collected at the two stations were appended when preparing inputs for PMF. Concentrations that were below the MDL or that were missing were replaced by three-quarters of the MDL or by the median concentration, respectively. Furthermore, only compounds with concentrations above the MDL in over 50% of samples were included in the analysis. The detection limit and uncertainty for each VOC species are listed in Table S2.

The uncertainties are used to prevent low confidence data from unduly influencing a solution. The uncertainty for a concentration was calculated as the sum of the sampling uncertainty and analytical concentrations of NMHC at the stations reached a set trigger. The trigger values for the study period ranged between 0.15 and 0.30 ppmv of NMHC. A total of 124 samples were triggered. Samples were integrated over 10–60 min. The VOC canister NMHC trigger set points and their adjustment dates are shown in Table S1. The samples were collected using fully lined SilcoCanTM or SiloniteTM canisters and sent for analysis. VOC analysis was conducted using gas chromatography and mass spectroscopy (GC–MS) for compounds C3 and greater. In addition to GC–MS analysis, the collected samples were also analyzed using gas chromatography with a flame ionization detector (GC-FID). This method was used primarily to identify compounds with less than four carbon atoms which could not be analyzed using GC–MS. The GC-FID method has a higher detection limit of 0.5 ppmv.

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uncertainty. The sampling uncertainty was set to one-tenth of the reported concentration while the analytical uncertainty was determined as the product of a laboratory reported uncertainty factor and reported concentrations. The uncertainty for values below the MDL was assigned as three-quarters of the MDL for the compound. The uncertainty associated with missing data was set to four times the median concentration to minimize their impact on the solution. The methods for replacing missing values and determining uncertainty are summarized in Table S1. Following the data quality processing, the resulting PMF input data included twenty-two VOCs and ninety-four samples including twenty-six winter samples, twenty spring samples, twenty-one summer samples and twenty-seven fall samples.

PMF looks for temporal covariation to apportion the input into factors. Compounds with insufficient variability due to low signal to noise ratio (S/N) are not likely to provide meaningful contributions to factor identification. Paatero and Hopke (2003) suggest removing any compound with a S/N ratio lower than 0.2 from the PMF analysis and assigning compounds with a S/N ratio between 0.2 and 2 as weak. Of the twenty-two VOCs included in the final PMF analysis, three compounds were categorized as weak due to S/N < 2. These three compounds were Freon-11, pentane and carbonyl sulphide. The non-target species were not included in the final PMF analysis. PMF triples the provided uncertainty for VOCs categorized as weak.

3. Results and discussion

3.1. Meteorology

At station 842 and 986, the predominant wind direction observed was from the SW and SE, respectively (Fig. S1). Also, low wind speeds (< 5 km hr⁻¹) were observed most frequently from easterly directions (ENE, E, ESE, SE and SSE) at station 842 and ESE and SE at station 986. Low wind speeds at both stations were more frequently measured at night (Fig. S2) from a relatively narrow range of wind directions (Figs. 2 and 3). The two monitoring stations are located on a slope with higher ground to the east of station 842 and southeast of station 986 (Fig. 1). These nocturnal calm winds are most likely due to downslope flow (Goulden et al., 2006), which can occur during clear, low-wind nights (Clements et al., 2002; Jiménez and Cuxart, 2014). During such conditions monitoring stations and nearby residences are downwind from a number of CHOPS facilities. Emission sources from CHOPS facilities are near the ground (7–10 m high), below the nocturnal boundary layer and heated to 60–80°C.
3.2. Total hydrocarbons

Fig. S3 (a, b) illustrates the hourly 2nd, 25th, 50th, 75th, and 95th percentiles for THC for station 842 and station 986, respectively. The most pronounced diurnal variability was observed for the 95th percentile concentrations which peaked in the morning hours. The 25th percentile concentrations were comparable to the annual global average methane concentration (1.8 ppmv), inferred from remote background sites (Dlugokencky et al., 2011). The diurnal profile of elevated concentrations supports the influence of downslope flow. One-hour average NMHC concentrations were found to be above the detection limit for < 1% of the samples, therefore box-and-whisker plots were used to display the NMHC data instead of diurnal averages. Fig. S3 (c, d) presents the 98th percentile and the maximum concentrations of NMHC for station 842 and station 986. The diurnal profile of NMHC concentration was comparable to that of THC.

The highest THC concentrations were observed for easterly winds with low speed (Figs. 2 and 3). In general, the higher THC

![Fig. 2. Wind roses at station 986 for various THC and NMHC concentration ranges.](image-url)
concentrations also occurred in the winter and the lower concentrations were observed in the summer (Fig. S4a). This seasonal variability was found to be statistically significant through the Kruskal-Wallis test (Theodorsson-Norheim, 1986) with $\alpha = 0.05$. The highest percentage of THC concentrations identified as elevated was observed during the winter and fall (Fig. S5a and d, respectively). The higher THC concentration during the colder months likely resulted from lower mixing height. The observed THC variability is driven by variability of CH$_4$, the dominant component of THC.

As a large fraction of the NMHC concentrations were below the detection limit, 98th percentile NMHC concentrations were used to examine seasonal variability (Fig. S4b). On average, the highest seasonal 98th percentile NMHC concentration at station 842 was observed during the summer months (0.07 ppmv). Concentrations were lower (0.01 ppmv) during the winter and below detection limit for the spring and fall (Fig. S4b). At station 986, which has operated for a longer period of time, the 98th percentile NMHC concentrations were above the detection limit for spring (0.05 ppmv), summer (0.05 ppmv), and

Fig. 3. Wind roses at station 842 for various THC and NMHC concentration ranges.
fall (0.06 ppmv). This seasonal variability differs from that observed for THC seasonal concentrations (Fig. S4a). Higher concentrations of NMHC during the summer may be due to increased evaporation during the warmer months and/or atmospheric chemistry.

Elevated THC and NMHC were most frequently associated with easterly winds with low speeds (Figs. S5 and S6). Over the study period, a decline in the percentage of hourly concentrations identified as elevated THC (> 2.5 ppmv) was observed (Fig. S6a). Oil production volume during this period increased in the study area (Alberta Energy Regulator, 2015) while reported venting volumes decreased (Fig. S7). Thus, the observed decrease is not due to changes in production volume. Furthermore, the number of odour complaint calls into Alberta Energy Regulator also decreased after 2012 (Fig. S6b).

The frequency of observed elevated concentrations increased between 2011 and 2012, followed by a decrease in the years that followed (Fig. S5). There were two exceptions to this. First, a continuous decreasing trend in the frequency of elevated concentrations was noted for samples collected when the wind was east north easterly (ENE). The second exception is that data collected during the winter with a wind direction of east-southeast (ESE) contained a notable fraction of elevated THC throughout the study period, with the exception of 2011 data.

Capturing and conservation of the casing and tank top gases became a requirement in March 2014 (Alberta Energy Regulator, 2014a). Reduction in the occurrence of elevated THC concentrations at the monitoring locations over time likely reflects the effects of fugitive emission mitigation implementation in the area (i.e. Alberta Energy Regulator Directive 060). Mitigation efforts by some operators in the area started well before the requirement to capture and conserve tank top and casing gases. It appears that production facilities (located ENE of monitoring site) began to mitigate fugitive emissions earlier than the Alberta Energy Regulator, 2015) while reported venting volumes decreased (Fig. S7).

Fig. 4. Alkanes contributed the greatest concentration in all seasons and during periods of elevated hydrocarbon concentrations. The average methane concentration during elevated hydrocarbon events was 5.5 ppmv, well above background. Ethane concentrations during elevated hydrocarbon events were above the 0.05 ppmv detection limit for a few samples (7 out of 124). The detected ethane mole concentrations ranged from 0.1 to 0.3 ppmv. Carbonyl sulphide and carbon disulphide were the most commonly detected sulphur compounds. Mole concentrations of these compounds during periods of elevated hydrocarbon concentrations ranged from 5.3 to 0.4 ppbv and 6.3 ppbv to below the detection limit (0.1 ppbv) respectively. Mercaptans (two samples) and thiophenes (nine samples) were also detected.

With the exception of methane and ethane, all other alkanes with less than four carbons had mole concentrations below the detection limit (0.05 ppmv using GC-FID) for air samples collected during periods of elevated hydrocarbon concentrations. The average methane concentration during elevated hydrocarbon events was 5.5 ppmv, well above background. Ethane concentrations during elevated hydrocarbon events were above the 0.05 ppmv detection limit for a few samples (7 out of 124). The detected ethane mole concentrations ranged from 0.1 to 0.3 ppmv. Carbonyl sulphide and carbon disulphide were the most commonly detected sulphur compounds. Mole concentrations of these compounds during periods of elevated hydrocarbon concentrations ranged from 5.3 to 0.4 ppbv and 6.3 ppbv to below the detection limit (0.1 ppbv) respectively. Mercaptans (two samples) and thiophenes (nine samples) were also detected.

Ninety-five of the 124 samples with clear sample start dates were used to test seasonal variability. Twenty-seven of these samples were collected in the winter, twenty in the spring, twenty-one in the summer and twenty-seven in the fall. The seasonal variability of VOCs measured during periods of elevated hydrocarbon concentrations is illustrated in Fig. S4. Alkanes contributed the greatest concentration in all seasons and the average mole concentrations for hydrocarbon event periods were relatively consistent throughout the seasons suggesting non-temperature dependent sources. Deygout (2011) also identified alkanes as the major contributor to VOCs emitted from heated bitumen storage tanks. Simpson et al. (2010) found notably enhanced C2–C9 alkane concentrations in oil sands plumes from open-pit mining processes in the Athabasca oil sands area as well. Butane, isobutane, pentane, and isopentane were the most abundant alkanes present in the samples collected during periods of elevated hydrocarbon concentrations in PROSA. Concentrations of ketones (primarily acetone), alcohols (mostly ethanol) and sulphur containing compounds were significantly higher in summer with $p$ values of 0.003, 0.05 and 0.0002, respectively. The significance of seasonal variations was tested using the Kruskal-Wallis test. The average acetone mole concentration for periods of elevated hydrocarbons was 14.0 ppbv and the average ethanol mole concentration was 1.8 ppbv. For samples collected during periods of elevated hydrocarbon concentrations, aromatic hydrocarbon concentrations were significantly higher in winter and summer ($p = 0.003$), compared to the fall and spring months. The most abundant aromatic hydrocarbons were toluene and benzene, with an average mole concentration of 3.5 ppbv and 1.4 ppbv respectively for samples collected during periods of elevated hydrocarbon concentrations. Halogenated hydrocarbons which included Freon 11, 113, 114 and 12 were on average higher in the spring.

3.3. Volatile organic compounds

On average 77% of the total canister VOC mole concentration was composed of target compounds. The identified non-target compounds varied from sample to sample. The most commonly identified non-target compounds were C8 alkyl cycloalkane and C8 oxygenated alkanes, compounds also identified in air monitoring associated with Athabasca Oil Sands Area (Simpson et al., 2010). While on average 23% of VOCs concentration was identified as being part of non-targeted compounds, the contribution of non-targeted compounds to total detected VOC mole concentration in general decreased over the study period (Fig. S8). Furthermore, some target compounds routinely detected in samples collected during periods of elevated hydrocarbon concentrations at the start of the study were below detection levels for similar samples at the end of the study period. The reduced detection of targeted and non-targeted VOCs may be due to the reduction of some fugitive emissions which may be related to changes in the oil production process. The notable presence of non-target compounds also illustrates the shortcomings of using target compounds designed for different objectives to analyze samples from heavy oil production areas.
3.4. Factors analysis using VOCs measured during periods of elevated hydrocarbon concentrations

Three to seven factor solutions were iteratively explored to identify the most robust PMF solution. Bootstrapping, consisting of 1000 total runs, was used to test the stability of solutions. A solution was deemed stable if at least 70% of the bootstrap results were mapped to the base run. A five-factor solution yielded results that were shown to be numerically stable. Fig. S9a illustrates the results of the iterative process. Three- and four-factor solutions resulted in unstable factors that resolved into two or more factors in a higher number of factor solution runs. Six- and seven-factor solutions resulted in one or more factors that did not meet the stable solution criteria. For the five-factor solution, four of the five factors were mapped to the base factor over 80% of the time. The remaining factor was mapped over 70% of the time. The five-factor profile shown in terms of the percent of VOC concentration attributed to a particular factor is illustrated in Fig. 5. The average relative contribution of each factor to the total reconstruction mass is presented in Fig. 6. Each of the identified factors was named based on the key contributing compound or potential origin.

Associated Local/Regional Air Mass had the highest mass concentration contribution, followed by Acetone and Oil Evaporative factor. The seasonal average concentrations are presented in Fig. 7A and annual average factor concentrations are presented in Fig. 7B. In general, PMF reconstructed concentrations were higher during the summer period. This is mainly due to increased contribution from the Acetone factor. The reconstructed concentration was higher in 2012 compared to the other years, also largely due to Acetone factor. The unassigned concentration was greater for samples collected in the spring and in 2013. Fig. S10 illustrates a correlation plot for the five-factor solution and shows good separation for most of the selected factors, however, some correlation between the Oil Evaporative factor and the Regional Air Mass factor indicates some overlap between these factors.

Fig. 5. Five-factor profiles shown in terms of the percent attributed to a particular factor for VOCs sampled during periods of elevated hydrocarbons. The five-factor profile includes VOCs that met data inclusion criteria for PMF analysis (Section 2.1).

Fig. 6. Average relative contribution of factors to the reconstructed concentrations for periods of elevated hydrocarbon concentrations.
3.4.1. Acetone factor

For the study period, the Acetone factor contributes 19% of the total reconstructed and unassigned concentration, but this value varies seasonally and by year. On average, 88% of acetone, 54% of carbonyl sulphide and 28% of benzene concentrations were apportioned to this factor. Atmospheric oxidation of alkanes such as propane, isobutane and isopentane and VOCs linked to biomass burning can be dominant sources of acetone (Singh et al., 1994; Jacob et al., 2002; Sahu and Saxena, 2015). Carbonyl sulphide can be directly emitted into the air or converted from carbon disulphide or dimethyl sulphide by atmospheric oxidation processes (Kettle et al., 2002). The source of benzene emissions could be linked to oil and gas wellheads or petroleum refineries in the region (US EPA, 1998). Benzene with possible atmospheric life time of about 9 days (Simpson et al., 2010) is also relatively stable and could have contributions from sources outside the study area. This factor had minimal contribution from larger (> C6) hydrocarbons. Such compounds have atmospheric lifetime < 2 days are not readily detected in the background boundary layer (Simpson et al., 2010). The average contribution of the Acetone factor is significantly (Kruskal-Wallis test \( \alpha = 0.05 \)) higher during the summer months. The Acetone factor most likely has its origin in atmospheric chemistry however contribution from regional forest fire smoke cannot be ruled out.

3.4.2. Assorted Local/Regional Air Mass factor

The Assorted Local/Regional Air Mass factor had the highest concentration and made up 30% of the total reconstructed and unassigned concentration. The key contributing compounds that identify the Assorted Local/Regional Air Mass factor are Freon-11, n-butane and isobutane. Factors containing Freon characterized as background air were also identified by Saew and Thepanondh (2015), albeit the relative contribution of such factor to total measured VOCs were lower. Freon has a long atmospheric lifetime. For example, Freon 11 is estimated to have an atmospheric lifetime of 55 years (Elkins et al., 1993). For this reason, these compounds are commonly identified as markers.
of a well-mixed regional air mass. N-butane and isobutane identified in evaporated gasoline also have relatively long atmospheric lifetimes of about 5-days (Watson et al., 2001; Cai et al., 2010).

The Assorted Local/Regional Air Mass factor is the least stable factor of the five factors. PMF uncertainty analysis matched 74% of the bootstrapped cast resultant factors to the original factor, the lowest of all the five factors. This is likely due to the contributions from many assorted local/regional sources to this factor and/or recirculated air masses. Furthermore, this factor has similarities to other resolved factors such as the Oil Evaporative factor. This factor may have the potential to resolve into two (or more) factors. However, for this study a stable solution was not obtained beyond five factors.

3.4.3. Benzene/Hexane factor

The Benzene/Hexane factor made up 7% of the reconstructed and unassigned concentration. As the name indicates, n-hexane and benzene were the key compounds to this factor, of which > 60% of n-hexane and benzene concentrations were apportioned to the factor. Hexane could be present in crude oil however, the presence of benzene in crude oil is much smaller (USEPA, 2014). Li et al. (2017) found the emission rate of benzene over the Athabasca oil sands area to be much lower than other aromatics. Previous studies have associated benzene to gasoline and diesel evaporation and/or combustion exhaust (McCarthy et al., 2013) and solvent use (Dumanoglu et al., 2014). However, the key contributing VOCs (i.e., toluene, m,p-xylene, o-xylene) associated with transportation emissions were not present in samples collected for this study. Buzcu-Guven and Fraser (2006) also identified an n-hexane factor in Houston that included aromatics, predominantly observed during the night and potentially associated with industrial emission or vehicle exhaust. The heavy oil extracted in the study area is less viscous than other oil sands deposits in Alberta (Alberta Energy Regulator, 2014b) however storage in heated Stoke tanks may result in release of fugitive VOCs from the tanks. This factor with its higher contribution during winter and spring is likely associated with emissions from crude oil production and may be linked to fugitives from heated storage tanks. Seasonal differences in fugitive emissions can occur due to differences in operation/heating of these storage tanks.

3.4.4. Toluene/Xylene factor

The Toluene/Xylene factor accounted for 5% of the reconstructed and unassigned concentration. On average 80% of xylene isomers and 65% of toluene were apportioned to this factor. This factor is one of the factors that resolved early in the PMF analysis (Fig. S9a) and 95% of the bootstrapped cast resultant factors were matched to the original factor. Emission monitoring at some of the CHOPS operations identified xylenes, butane, isobutane, and isopentane in the exhausts of combustion engines associated with tank heaters and compressors from select CHOPS sites (Cleartone Engineering Ltd., 2014). Li et al. (2017) also measured toluene above some oil sands operations in the Athabasca oil sands region where open pit mining is the practice. The OH atmospheric lifetime of m-xylene and p-xylene are of the order of hours and these compounds were not detected in background air samples in the Athabasca oil sands region (Simpson et al., 2010), thus their presence indicates local source. Fig. 8 compares VOCs identified in these exhausts to VOCs found in the Toluene/Xylene factor. Exhaust from Combustion #1 largely contained xylene isomers. Exhaust from Combustion #2, likely fueled by flue gas, contained a number of VOCs that were also identified in the Toluene/Xylene factor. With the exception of toluene, combined VOC contributions from the two combustion sources are comparable to the composition of the Toluene/Xylene factor. Toluene and xylene are substances that can be present in tank vapours that use demulsifiers, defoamers and corrosion inhibitors (Cleartone Engineering Ltd., 2014). Higher toluene contributions to the resolved factor could have arisen from demulsifiers, defoamers and corrosion inhibitors added to some heated tanks. The Toluene/Xylene factor has a higher average contribution in summer which may have resulted from increased evaporation. For samples collected during elevated hydrocarbon concentrations, annual average contribution from this factor increased throughout the study with the highest contribution measured in 2013 (Fig. 7B). The Toluene/Xylene factor likely represents multiple sources including combustion engines associated with tanks and compressors, natural gas, flue gas and/or tank vapours. The differences observed could be due to differing flue gas composition and/or engines used by the various facilities operating in PROSA.

3.4.5. Oil evaporative factor

The Oil Evaporative factor accounted for 15% of the total reconstructed and unassigned concentration. The factor mainly consists of alkanes containing 5 to 7 carbons (Fig. 5). Elevated C5–7 alkanes were also observed in another bitumen deposit area in Alberta (i.e., Athabasca oil sands region) (Simpson et al., 2010). With an OH atmospheric lifetime between 2 and 3 days, C5 alkanes were also detected in background air, albeit at much lower concentrations (Simpson et al., 2010). On average, > 70% of the concentration of 2,3-dimethylpentane, 2,3-dimethylbutane and cyclopentane was apportioned to this factor. The VOC profile of the Oil Evaporative factor highly resembles the VOC constituents of casing and solution gas venting, which was quantified using a factor-based approach (Cleartone Engineering Ltd., 2014). Fig. 9 compares the average mole fraction of VOCs estimated to be vented to the Oil Evaporative factors. The similarities observed indicate the Oil Evaporative factor is likely associated with storage tank evaporation (tank top gas vent), the loading and unloading of trucks, storage tank de-sanding processes and other storage fugitive emissions, but due to the contribution of C5 alkanes to the factor contribution from atmospheric chemistry cannot be ruled out. The seasonal variation observed for this factor was not significant. Contribution from the Oil Evaporative factor was higher during the latter portion of the study. Correlation between the Oil Evaporative factor and the Regional Air Mass factor (Fig. S10) indicates some overlap between these factors. Fig. S9 illustrates that this factor resolves into two factors when considering a seven-factor solution into a factor resembling the Oil Evaporative factor and a residual labeled Carryover.

3.5. Biogenic and transportation factors

A Biogenic factor was not resolved for the data collected in this study. Isoprene is widely used as a key VOC indicator of biogenic contribution (Dumanoglu et al., 2014; McCarthy et al., 2013; Buzcu-Guven and Fraser, 2006). The study area and surrounding region have abundant vegetation, containing both broadleaf and coniferous forests. However, isoprene was below the MDL in over 50% of these event-based samples and thus could not be included in the PMF analysis. Isoprene emissions are increased at higher temperatures and with the availability of sunlight (Fuentes et al., 2000). Sahu and Saxena (2015) observed that isoprene concentrations were higher during the warmer hours of the day and lower at night. Buzcu-Guven and Fraser (2006) for example were able to identify a biogenic factor for day time samples but were not able to resolve a biogenic factor using night time samples. Whole air canister samples used in this study were triggered during elevated hydrocarbon events and these events tended to occur in the early morning hours. Thus, the low isoprene concentration was likely due to samples being collected when isoprene emissions were expected to be low.

A transportation Emission factor was also not resolved for data collected at station 986 and 842. The key compounds associated with transportation factors in previous work (McCarthy et al., 2013; Yurdakul et al., 2013; Dumanoglu et al., 2014; Shao et al., 2016) include 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene and p-ethyltoluene for gasoline vehicle emissions and undecane, decane, dodecane, and nonane for diesel vehicle emissions. For samples collected as part of this study, these VOCs were below the MDL for > 50% of the samples.
and thus were not included in the PMF analysis. Low concentrations of VOCs associated with transportation emissions were likely due to the low motor vehicle traffic in the sample area especially during the early morning hours when most samples were collected. This indicates that transportation emissions may not be a significant contributor to VOC/THC at the monitoring locations, and therefore may not be responsible for the odour complaints in the area.

4. Conclusion

Analysis of THC and NMHC concentrations and meteorological data from the two stations in the Three Creeks area showed that elevated concentrations were most frequently observed in the morning hours and were associated with low wind speed. The CHOPS operations are located at a higher elevation than the monitoring stations and nearby community. The low easterly winds observed during the morning hours were likely promoted by nocturnal gravitational drainage flow. Such meteorological conditions placed the monitoring stations and nearby residents downwind of the CHOPS operations. Higher concentrations of THC were observed during the colder months, likely promoted by lower mixing height. Elevated NMHC and VOC concentrations, however, were more likely to be measured during the warmer months, when evaporation losses and contribution from atmospheric chemistry are more likely.

Using air samples collected during periods of elevated hydrocarbon concentrations, twenty-two VOCs were apportioned to five factors using the PMF receptor model. These factors were compared to emission inventories, real-world measurement data and previous monitoring in the Athabasca oil sands region. The resolved PMF factors imply that the hydrocarbons measured during periods of elevated hydrocarbon concentrations at the two stations are not only due to emissions associated with nearby crude oil extraction/production but are also likely the product of atmospheric chemistry and other local/regional sources (which could include oil and gas processing outside of the region). Three factors accounting for 27% of the apportioned concentration were likely significantly influenced by emissions from crude oil extraction activities. Emissions from the venting of solution gas, exhaust from combustion sources and evaporation of additives to the process are also likely contributors. On average, 73% of the VOC concentration measured during periods of elevated hydrocarbon concentrations could not be directly attributed to sources in the area, but instead were apportioned to factors likely associated with atmospheric chemistry and regional or local air masses or were unassigned. The Assorted Local/Regional Air Mass factor, with long-lived key chemical compounds such as Freon-11 may have contributions from many regional or local industrial sources or may be associated with recirculated air masses. In addition, the Assorted Local/Regional Air Mass factor has several key chemical components (e.g. butane, isobutane, pentane, isopentane, cyclohexane, methylecyclopentane) in common with venting emissions and the Oil Evaporative factor. Therefore, this Assorted Local/Regional Air Mass component almost certainly has contributions from CHOPS facilities inside and/or outside of the local area. VOC concentration was not apportioned to factors that could be associated with biogenic or transportation emissions. Although these sources were present in the study area, they are not expected to be significant contributors to VOC concentrations during periods of elevated hydrocarbon concentrations at the monitoring location or the odour complaints in the community near Three Creeks.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosres.2018.02.007.

References


