THESIS

IMPACTS OF OIL AND NATURAL GAS DEVELOPMENT AND OTHER SOURCES ON VOLATILE ORGANIC

COMPOUND CONCENTRATIONS IN BROOMFIELD, COLORADO

Submitted by

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ABSTRACT

IMPACTS OF OIL AND NATURAL GAS DEVELOPMENT AND OTHER SOURCES ON VOLATILE ORGANIC

COMPOUND CONCENTRATIONS IN BROOMFIELD, COLORADO

In 2017 substantial new oil and natural gas (ONG) extraction was approved by the City and County of Broomfield (CCOB). A monitoring program was established by CCOB to determine how new ONG extraction impacted local air quality. Multiple instruments were utilized to monitor air quality in the county including weekly volatile organic carbon (VOC) sampling canisters deployed across CCOB by Colorado State University and Ajax Analytics and hourly VOC, methane, and criteria pollutant measurements taken by the Colorado Air Monitoring Mobile Lab (CAMML) deployed near an ONG well-pad by the Colorado Department of Public Health and Environment (CDPHE). Weekly samples, collected from October 2018 through December 2020 were analyzed for 52 VOCs using a 5-channel gas chromatograph. The CAMML reported 20 VOCs, methane, PM2.5, PM10, nitrogen oxides (NO_x), and ozone. Positive Matrix Factorization (PMF) was applied to both datasets to characterize key air pollution sources and their impacts in space and time.

Six factors were found to describe the weekly data best: Background (biogenic), Combustion, Light Alkane, Complex Alkane, a Drilling factor, and an Ethyne factor. Contributions of the ONG-related PMF factors increased most strongly near well-pads during particular ONG pre-production activities. The Light Alkane factor was most active during production and coiled tubing operations, and flowback at one or more of the new well-pads. The Complex Alkane factor

was strongly associated with drilling and coiled tubing operations and flowback at one of two well-pads. The Drilling factor contained a VOC profile that closely matched volatiles released from a drilling mud (lubricant for the drill bit) used at two of the three sites. The Ethyne profile represents an unknown and previously undocumented source composition originating from a well-pad. This ethyne and benzene-rich emission was independently observed in other CCOB air monitoring efforts.

Five factors best explained the hourly CAMML data; these factors resembled those derived from PMF analysis of the weekly data set. Three factors, Combustion, Ozone background, and Particulate Matter, were not found to be related to local ONG extraction while the profiles containing many of the alkane species (Light Alkane factor and Complex Alkane factor) showed correlation with pad activities. Wind direction analysis suggests emissions associated with these factors were transported from the pad.

Benzene was a particular focus of the study given its potential health effects at modest concentration levels. On average, the source factors contributing most to benzene were combustion (38%), longer-lived alkanes from ONG production (22%), and shorter-lived alkanes from ONG production (16%). ONG activities contributed more strongly to benzene levels during pre-production and production phases.

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INTRODUCTION

1.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are carbon containing compounds that are found predominately in the gas phase under typical ambient atmospheric temperatures and pressures. These compounds – which have both anthropogenic and biogenic sources – play an important role in the chemistry of the atmosphere and some may cause adverse health effects (Technical Overview of Volatile Organic Compounds, 2021). Biogenic VOCs are emitted from soils, oceans, vegetation, and wildfires. Terrestrial vegetation accounts for about 90% of total biogenic emissions (Sindelarova et al., 2014). Of these emissions, isoprene and monoterpenes are the most abundant compounds (Sindelarova et al., 2014). Anthropogenic VOC sources include fossil fuel combustion and storage, solvent utilization and evaporation, chemical manufacturing, oil and natural gas (ONG) operations, industrial processes, and consumer products (Gu et al., 2019, Abeleira et al., 2017). On a global scale, biogenic emissions dominate the organic carbon budget with anthropogenic emissions contributing < 15%. However, VOC emission sources can vary across regions with anthropogenic emissions sometimes dominating urban areas (Abeleira et al., 2017). Many VOCs are classified by the EPA as hazardous air pollutants (HAPs) and are regulated due to known adverse health effects (Hazardous Air Pollutants, 2021). Oil and natural gas processes and operations typically contain 5 different HAPs: benzene, toluene, ethyl benzene, mixed xylenes (BTEX), and n-hexane (Oil and Natural Gas Production Facilities: National Emission Standards for Hazardous Air Pollutants (NESHAP), 2021).

Some key chemical classes of VOCs include alkanes (single-bonded saturated hydrocarbons), alkenes (double-bonded, unsaturated hydrocarbons), alkynes (triple-bonded, unsaturated hydrocarbons) and aromatic hydrocarbons (cyclic hydrocarbons containing a benzene ring) (Akimoto, 2016). These compounds are oxidized in the atmosphere by reacting with the hydroxyl radical (OH), ozone (O_3), and

nitrate ($NO_3^{\cdot}$) radical (Hodan & Barnard, 2004). Reaction timescales vary widely, from minutes to years, depending on compound structure and oxidant availability. The oxidation of VOCs in the atmosphere can lead to organic products with a vapor pressure lower than their starting reactants. These products can condense and produce secondary organic aerosols (SOAs), either by nucleation or by condensation onto existing particles, with subsequent growth though additional condensation and/or coagulation (Zhang et al., 2012).

1.2 Oil and Gas

1.2.1 Unconventional Techniques

The oil and natural gas (ONG) industry is the largest industrial source of VOCs in the United States (Basic Information about Oil and Natural Gas Air Pollution Standards, 2021). The industry targets fossil fuels, which are a mixture of hydrocarbons located in reservoirs or tiny spaces within sedimentary rocks and near the earth's surface in tar or oil sands (Oil and Petroleum Products Explained, 2021), defined by OSHA as a subsurface, porous, permeable, or a naturally fractured rock body in which oil or gas are stored (OSHA glossary of terms). The variety of hydrocarbons in reservoirs means a single well may produce crude oil, raw natural gas, condensate, and/or water depending on the reservoir (Gilman et al., 2013). A well is classified as either an oil or natural gas well based on a gas-oil ratio (GOR) of 6,000 cubic feet (cf) of natural gas to 1 barrel (b) of oil (cf/b) for each year's production. If the GOR is equal to or less than 6,000 cf/b, then it is classified as an oil well (EIA Oil and Gas Wells by Production Rate). With recent improvements to unconventional extraction methods, including hydraulic fracturing (commonly known as "fracking") and directional drilling, previously uneconomical reserves have become commercially viable options (The Process of Unconventional Oil and Natural Gas Production, 2021). Unconventional ONG is an umbrella term for development and extraction that does not meet conventional production criteria (Field et al., 2014).

During conventional ONG extraction, wells are drilled vertically into porous rock formations made up of sands or carbonates. The free-flowing nature of these formations yields high amounts of oil with little extra effort. These formations are targeted specifically due to this free-flowing characteristic. Up until the early 2000s, other types of less permeable rocks, which include tight gas sandstones, oil or tar sands, shale rock, and other low-permeable tight formations (Zee Ma, 2016), were not highly recoverable and therefore not economically viable. With the invention of horizontal drilling, allowing both vertical and horizontal drilling, and improvements to hydraulic fracturing techniques, these less permeable rock formations could now be used to produce profitable amounts of ONG. These 'unconventional' techniques utilize mechanical stimulation to create permeability and mimic the conventional free-flowing nature. Wells are drilled vertically until the rock formation deviates and becomes horizontal. At this point, the direction of drilling shifts horizontally to match the target rock formation. Fissures are initiated along the well bore and then a mixture of fluid and sand is injected into the low permeable rock, fracturing the formation, allowing the oil and gas to be released with less resistance. The sand acts as a proppant to help keep cracks open when the water is removed. The injected fluid is mainly water based and is hydraulically pressurized before being injected into the well (Georgevich, 2020).

1.2.2 Phases of ONG Extraction

Most of the information in the following section can be found in the report by the EPA: *Management of Exploration, Development and Production Wastes: Factors Informing a Decision on the Need for Regulatory Action* which provides an overview of recent developments in unconventional techniques. This document reviews information surrounding generation, management, and disposal of wastes, assesses any adverse effects to health or the environment and their likelihood, and investigates if current regulations should change based on findings.

The first step in ONG extraction is exploration and assessment of a potential site using field surveys and seismic data. Exploratory wells may be drilled to further assess geological data, fluid

properties, initial reservoir pressure, and reservoir productivity. Well installation then begins. A drilling

pad is the first thing constructed at the site to support a drilling rig and any additional personnel or

equipment such as trucks. An access road as well as any pits or tanks to manage waste are also built

(Management of Exploration, Development and Production Wastes, 2019).

Once the basic well layouts are done, drilling can begin. Rotary drill rigs with an attached drill bit

are typically used to create a wellbore which is a hole drilled by the bit. These drill rigs can be diesel,

natural gas, hybrid diesel/natural gas, or electric powered. As drilling occurs, drill pipe segments are added

in sections until a designated depth when steel casing is added to prevent the collapse of surrounding

rock into the wellbore, prevent intrusion of formation fluids into the wellbore during construction, and to

avoid mixing hydrocarbons and other contaminants with overlying aquifers during production. The first

interval of steel casing, called the conductor casing, only extends a relatively short depth of fifty to several

hundred feet as to prevent initial collapse. Once in place, drilling is advanced just below where the

"surface casing" will be installed. This casing is smaller in diameter and extends anywhere from fifty to

one hundred feet below the lowest aquifer of potential use depending on state regulations. Intermediate

casings are then installed as needed to reach the target formation. A well may be drilled vertical or

horizontal, known as a deviated well, depending on the formation. The deviated section of the well is

drilled using a hydraulic motor that spins the drill bit but not the drill pipe (Management of Exploration,

Development and Production Wastes, 2019).

Fluid known as the drilling mud or drilling fluid is injected down the drill pipe and out the nozzles

of the drill bit to lubricate the bit, control the pressure within the wellbore, seal drilled formations to

prevent fluid loss, and transport excess debris to the surface. A variety of drilling mud compositions are

in common use. The excess drilling fluid and debris flows up to the surface through the space between

the drill pipe and the wellbore. This returned fluid contains fragments of soil, rock, and other ground

materials that were dislodged during drilling, called drill cuttings. Cuttings are mechanically removed from

the drilling mud and the drilling fluids are reused until they are either too contaminated to recycle, the formation requires another type of drilling mud, or the drilling process is complete. The used fluid is then sent to a reserve pit or tank as waste (Management of Exploration, Development and Production Wastes, 2019).

After drilling is completed, the remaining drilling mud is replaced with a dense fluid to rid the well of excess solids that could react with the targeted formations or plug the production zone. This fluid generally contains dissolved inorganic salts such as chloride and bromide. To allow oil and gas to flow into the wellbore, a perforated gun with explosives shaped to pinpoint charges is lowered into the production zone and fired remotely creating holes in the casing and cement. At this point, well stimulation techniques, like hydraulic fracturing can occur. Common fracking fluids are water or a mixture of water and entrained gas like nitrogen or carbon dioxide. Proppants like sand or ceramic beads are injected into the well to prevent newly formed fractures, which are under immense pressure, from resealing (Management of Exploration, Development and Production Wastes, 2019).

These injected proppants may impede production by blocking the flow of oil and/or natural gas. Coiled tubing operations circulate fluids through a jet nozzle which carries the fluid and debris back to the surface. Typical fluids used include water and brine (Varhaung, 2014). Production casing is the final tubing installed and typically runs the full depth of the well and isolates the production zone from the outer formations.

A well is in flowback when the wastewater primarily contains hydraulic fracturing fluids that have returned to the surface. As time progresses, this wastewater may alter to a mixture of hydraulic fracturing fluids and fluid that originated within the formation. Water returned from the well is collectively referred to as produced water and is separated from any salable hydrocarbons at the surface (Management of Exploration, Development and Production Wastes, 2019). Wells that undergo hydraulic fracturing result in a higher rate of flowback due to fluids and proppants previously injected into the well. In the past this

flowback mixture has typically been kept in an open pit or tank to vent or flare the volatile components of the liquids into the atmosphere. Reduced Emission Completions or "green completions" are often implemented to reduce emissions during this period. A common green completion utilizes a portable vessel to store and separate the produced water and hydrocarbon mixture (Green Completions, 2014). In recent years some operators have employed closed loop systems to carry these materials offsite rather than accumulating them on the pad itself. Additional information can be found in the EPA's report *Management of Exploration, Development and Production Wastes: Factors Informing a Decision of the Need for Regulatory Action* (*Management of Exploration, Development and Production Wastes*, 2019)*.

1.2.2.1 Waste Management

Substantial quantities of waste are produced during ONG exploration and production. A general estimation from 2016 by the EPA suggests that 97.7% of the waste is produced water with a mass of 4,452 million metric tons. Wastewater treatment residuals are the second largest contributor at 1.7% and 77 million metric tons (*Management of Exploration, Development and Production Wastes*, 2019). These values represent a general overview of all ONG production in the US, and it should be noted that the volume of waste generated by a given well depends on the type of hydrocarbon produced, the geographic location, and the extraction and production methods. There are several waste-management options to manage wastes before disposal. These waste management options include pits, tanks, and offsite disposal (see Phases of ONG Extraction (Green Completions, 2014)). The type of disposal can highly influence air emissions (Management of Exploration, Development and Production Wastes, 2019).

Pits are typically excavated areas of land where waste is placed for temporary storage or disposal and are sized depending on the volume of waste generated. They can be constructed with compacted soils or lined with materials such as concrete, compacted clay or high-density polyethylene. They are open to air and can be hazardous to birds and other wildlife. Many states require or recommend a barrier to prevent any intruders. State regulations have specifications for the types of pits based on factors such as

the duration of time the pit is in use, the stage of operation, and the type of waste that will be stored in the pit (Management of Exploration, Development and Production Wastes, 2019).

Tanks are structures that are used to store both waste prior to disposal and separate waste from product. They can be installed above-ground or below the surface and typically hold between 100 to 1,000 barrels of volume. Some tanks are open to the atmosphere while others may be enclosed, with pressure-relief vents or floating lids to reduce evaporative emissions. Tanks designed to collect flowback fluids or produced water are generally emptied periodically into trucks that takes fluid wastes offsite for treatment and/or disposal. The method of connection to the truck can influence whether significant volatile emissions are removed during this process or mostly contained. Systems like closed-loop drilling utilize tanks for waste storage. In a closed-loop system a series of tanks are put in succession to separate drilling fluid from drill cuttings and other solids. This process optimizes the amount of fluid recycled back into the drilling process and results in less fluid waste. Closed-loop drilling is often considered a best management practice. Other offsite disposal methods include landfills, treatment, and disposal facilities, including injection wells. As of 2019, Colorado was one of eight states that had a dedicated network of offsite disposal facilities overseen by a state regulatory agency (Management of Exploration, Development and Production Wastes, 2019). Closed-loop drilling refers to eliminating the use of drilling pits which tend to be open to the air. Flowback fluids and produced water are recycled for reuse in additional wells using special on-site equipment (Kroepsch et al., 2014)

1.2.2.2 US and Colorado ONG Wells

The United States surpassed Russia in 2011 to become the world's largest producer of natural gas and surpassed Saudi Arabia in 2018 to become the world's largest producer of petroleum, which includes crude oil (Brown Kahan, 2019). The first year that production of natural gas in the US exceeded its consumption was 2017. Production outgrew consumption by 0.2 trillion cubic feet (Tcf). In 2019, this differential increased to 2.87 Tcf (Natural Gas Explained: Where Our Natural Gas Comes From, 2021).

In 2019 Colorado was the 7th largest natural gas producing state (Natural Gas Explained: Where Our Natural Gas Comes From, 2021) accounting for 5% of the total natural gas in the US (Dakota, 2021) and producing 1,846 billion cubic feet (Natural Gas Explained: Where Our Natural Gas Comes From, 2021). The state also accounts for almost 4% of the United States economically recoverable crude oil reserves (EIA state analysis CO). Mainly due to horizontal drilling and fracking, ONG production in Colorado has quadrupled since 2010 and increased by 40% since 2016 (Dakota, 2021).

There are two main oil and gas fields in Colorado, the Wattenberg field located in Northeast Colorado, and the Piceance Basin located in the Western Rockies (Dakota, 2021). The Wattenberg field is found in the Denver-Julesburg (D-J) Basin which covers over 180,000 square km (Weber, 2018). The D-J Basin is located primarily in Northeastern Colorado but stretches into Southeast Wyoming, Western Nebraska, Northwest Kansas, and the Southwest-most tip of South Dakota (Weber, 2018). Within the D-J Basin, the Wattenberg field spans Weld County, the City and County of Broomfield (CCOB), Adams County, and Denver County. The Wattenberg field is stratified into multiple reservoirs. The targeted reservoirs within the field are from the Cretaceous era and include the Dakota, J, and Codell sandstones, Niobrara shale/Greenhorn shale and Limestone, and the Sussex and Shannon formations. The J sandstone and Dakota produce primarily gas, the Codell and Niobrara produce both oil and gas, and the Sussex and Shannon produces mainly oil (EnCana, n.d.). Much of Colorado's production in the Piceance Basin is in Garfield County and comes primarily as natural gas.
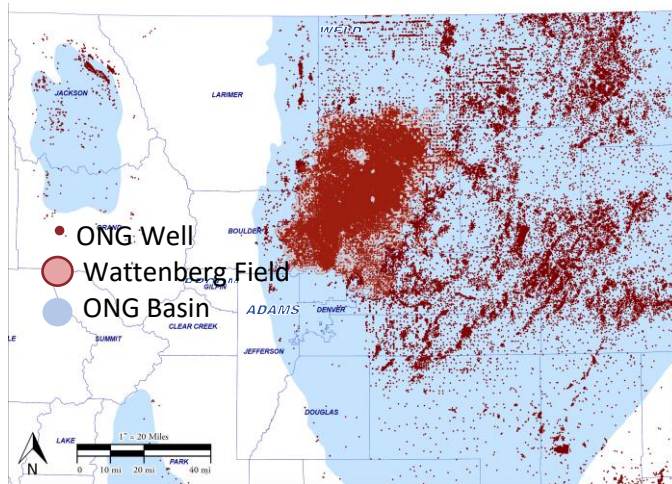
Figure 1-1: Colorado ONG basins and wells. Basins are highlighted in light blue while wells are stippled red. The Wattenberg field is outlined in red encompassing most of Weld, Broomfield, and Adams County. https://cogccmap.state.co.us/cogcc_gis_online/

1.3 Emissions

There can be several thousand unique hydrocarbon molecules in each crude oil reservoir (Whitson, 1983) and depending on what type of material is being extracted – wet natural gas, dry natural gas, or crude oil – emission spectra may vary. Dry gas is predominately methane while wet gas is defined as natural gas containing less than 85% methane (Field et al., 2014). Wet gas contains a larger proportion of complex hydrocarbons and non-hydrocarbon gases including CO_2, H_2S, SO_2, and others (Gilman et al., 2013). Crude oil generally contains hydrocarbon chains from 5 to 40 carbon atoms per molecule. Typically, hydrocarbons with a greater number of carbon atoms exhibit lower volatility and are less likely to be emitted into the atmosphere (Field et al., 2014). Emissions from the well can occur at any point during exploration or production by way of venting, flashing, flaring, or fugitive/nonpermitted emissions. During the ONG extraction process, there may also be other point sources of emissions including trucks, industrial equipment, and waste (Gilman et al., 2013).

A full emission spectrum can be difficult to quantify because emission sources can be spread over multiple acres (Field et al., 2014). Hecobian et. al. (2019) reported emission rates of 46 VOCs during five

different site operation categories in the Piceance Basin and D-J Basin. Measurements were made between 2013 and 2016 and mostly involved green completions, but not the closed loop systems that send fluids offsite as increasingly used in some populated areas of the DJ Basin. Large differences were seen across operation types, across facilities conducting the same operation types, and over time during a single operation at a singular facility. Of the five operations – drilling, fracking, flowback, liquids load out, and production operations – emissions were typically greatest during flowback. This was true for benzene, a key air toxic, as well as many other compounds. Holder et al. (2019) utilized activity-specific emission rates reported by Hecobian et al. (2019), coupled with dispersion modeling, to evaluate risk of exposure to benzene and other air toxics for those living and working near Colorado oil and gas operations. Exceedances of compound health guideline levels were predicted to be more common for acute than chronic exposure and observed at distances up to at least 2000 feet from operations.

The extraction and use of ONG has been linked with several primary and secondary pollutants. Primary pollutants are compounds and particles emitted directly from a source. Methane can be emitted directly from ONG wells and is a potent greenhouse gas (GHG) which can trap heat in the atmosphere resulting in a warming climate (Weinhold, 2012, EPA global GHG emissions data). Hazardous air pollutant (HAP) emissions have also been correlated with the extraction process (Weinhold, 2012). HAPs are classified by the EPA as compounds that are known or suspected to cause cancer or other serious health effects (Hazardous Air Pollutants, 2021). HAPs that are known to be associated with the ONG extraction process include hydrogen sulfide, n-hexane, 2,2,4-trimethylpentane, benzene, toluene, ethylbenzene, and xylenes (BTEX) (Weinhold, 2012).

Secondary pollutants, or particles and compounds produced *in situ* from primary emissions, associated with ONG emissions include particulate matter less than 2.5 microns ($PM_{2.5}$) and ground level ozone (O_3). Particulate matter (PM) and O_3 are regulated by the EPA as criteria pollutants (Hazardous Air Pollutants, 2021). PM is segmented by particle size diameter. Coarser PM is classified by having an

aerodynamic diameter less than 10 μm (PM10) and is typically a primary pollutant, while fine PM has an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) and is often a secondary pollutant. Secondary fine particles related to ONG emissions can include ammonium nitrate, formed by the reaction of gaseous nitric acid (produced from emitted nitrogen oxides) and ammonia (Li et al., 2014; Evanoski-Cole et al., 2017), and SOA formed by the condensation of low volatility products of the photooxidation of hydrocarbons (Pandis, 1998, Ylisirnio et al., 2020). SOA forms from a complex cascade of gas-phase oxidation and multi-phase aging reactions, and the physical properties of SOA are dictated by the initial VOC emissions and the oxidative conditions (Ylisirnio et al., 2020). SOA is most abundant during summer and is mainly produced in the day forming particle sizes in the $PM_{2.5}$ category (Fine et al., 2008).

Once emitted, VOCs can also be oxidized in the presence of nitrogen oxides (NO_x: NO + NO_2) and sunlight to produce tropospheric ozone. Areas of the Northern Front Range in Colorado have repeatedly exceeded the National Ambient Air Quality Standard for O_3 during the past decade (Abeleira et al., 2017). Ozone production can be limited by either NO_x or VOC concentrations. Urban O_3 is driven to a large extent by the reaction of shorter-lived VOCs with the OH radical where NO_x catalyzes the reaction. In the remote troposphere, VOCs with long atmospheric lifetimes – like CO and CH_4 – drive ozone formation through a reaction with OH. NO_x and VOCs compete to react with the OH radical creating a complex entanglement of ozone producing reactions. This is a sensitive balance where an increase in NO_x concentrations for given [VOC:NO_x] ratio may lead to an increase in ozone production, while conversely, for a lower than optimum ratio, an increase in NO_x concentrations may lead to a decrease in ozone productions (Seinfeld & Pandis, 2006). Colorado, in comparison to other oil and gas producing states like Texas and Pennsylvania, has significantly lower biogenic VOC emissions and is therefore considered to be more often in the VOC-sensitive regime (an increase in VOCs can lead to more O_3 production). Therefore, ozone production may be relatively more sensitive to increases in VOCs from local ONG emissions (Cheadle et al., 2017) than in other ONG producing regions.

Many additional sources of emissions are present during the ONG extraction process. Diesel trucks, transport equipment, and hydraulic pump engines can all emit criteria pollutants. Volatile compounds in fracking fluid and drilling mud can be released during flowback and drilling, respectively. Drilling mud can also entrain VOCs and methane while in the subsurface that can later be emitted into the atmosphere (Lange et al., 2014). In a literature review by the EPA, significant concentrations of BTEX were found in drilling solids with increased concentrations found in horizontal wells (*Management of Exploration, Development and Production Wastes*, 2019). Steps can be taken by ONG operators to minimize atmospheric impacts by targeting to reduce emissions from ONG activities that have been shown to have greater emissions. Flowback, for example, is shown to have some of the highest emissions during the extraction process (Hecobian et al. 2019). To mitigate direct impacts, operators can use alternative 'green' methods, including utilization of closed loop flowback and production systems to carry fluids offsite explained further in section 1.2.2.1 Waste Management.
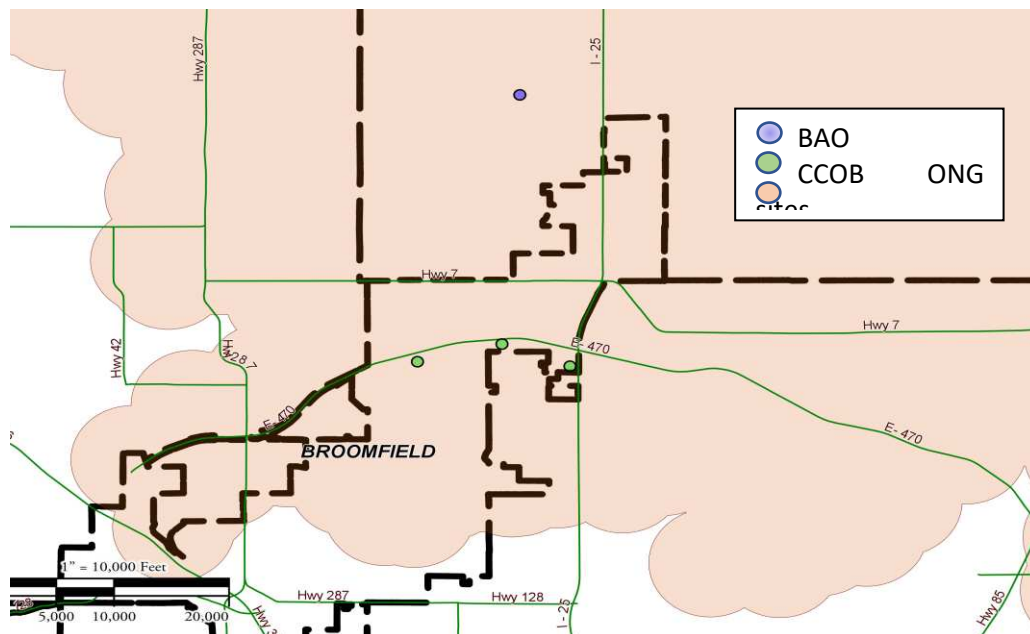

Figure 1-2:Wattenberg Field in relationship to the CCOB. Locations of active ONG sites during this study are highlighted in green and BAO, an observational location of previous studies is highlighted in blue.
https://cogccmap.state.co.us/cogcc_gis_online/

1.3.1.1 DJ-Basin Emissions

Due to a high number of extraction sites near residential areas and several non-attainment tropospheric ozone locations, the D-J Basin and surrounding areas have been the subject of multiple ONG studies (Abeleira et al., 2017, Gilman et al., 2013, Hecobian & Collett, 2019, Swarthout et al., 2013, Halliday et al., 2016, Pollack et al., 2021, Weber, 2018). Some of these studies have focused on direct comparisons of VOC emissions to ONG extraction timelines (Hecobian & Collett, 2019) while others have sampled ambient air to determine the influence of ONG extraction in the D-J Basin's neighboring regions (Abeleira et al., 2017, Gilman et al., 2013, Swarthout et al., 2013, Halliday et al., 2016, Weber, 2018, Pollack et al., 2021). The Boulder Atmospheric Observatory (BAO), located in the southwest corner of the Wattenberg field, for example, was found to be substantially influenced by long- and short-lived ONG emissions (Gilman et al. 2013, Swarthout et al. 2013, Abeleira et al. 2017). Propane, a well characterized ONG tracer, was found to exceed the ratios observed at 28 other U.S. cities (Gilman et al., 2013). Higher than average mixing ratios of C_2-C_7 alkanes and C_5 and C_6 cycloalkanes and were observed and correlated with propane (coefficients of determination exceeding 0.90) (Gilman et al., 2013). Similarly, in 2021 around 80% of C_2–C_5 alkanes in the Colorado Northern Front Range (CNFR) were attributed to ONG emissions (Pollack et al., 2021). Some of these elevated concentrations matched the natural gas production and extraction timeline of the Wattenberg field located northeast of BAO (Swarthout et al., 2013).

A low ratio of isopentane to n-pentane (i/n pentane) has been extensively used as a signature for ONG activity. Higher i/n pentane ratios are typically attributed to gasoline evaporation and/or combustion because isopentane is more prevalent in gasoline than n-pentane. ONG i/n pentane ratios typically range from 0.82-0.89 and vary somewhat for different ONG reservoirs (Gilman et al., 2013). For the Wattenberg field, an i/n pentane ratio of 0.86 ± 0.02 has been suggested (Gilman et al., 2013). This ratio is largely independent of photochemistry, air mass mixing, and dilution since both compounds are similarly affected by these processes. Air masses influenced by nearby Wattenberg field extraction sites were found to have

statistically similar i/n pentane ratios (Abeleira et al., 2017, Gilman et al., 2013). Overall average i/n pentane mixing ratios at BAO and Fort Collins/Timnath Colorado were found to have an average ratio around 1.0 and 1-2.4, respectively, suggesting a mix of combustion and ONG activity (Swarthout, 2011; Weber, 2018). Mean i/n pentane ratios in other regions around the US tended to be approximately 1.5-4 times larger due to a greater influence from gasoline evaporation and combustion (Swarthout et al., 2013).

1.4 Positive Matrix Factorization

Studies around Colorado have applied Positive Matrix Factorization (PMF) to better characterize VOC source profiles impacting the area (Pollack et al 2021, Hecobian & Collett, 2019, Abeleria et al 2017) with some focusing directly on the CNFR (e.g., Pollack et al 2021, Abeleira et al 2017). Pollack et al. (2021) analyzed over 10,000 samples and reported concentrations of 12 VOCs measured at the Boulder Reservoir between April 2017 and December 2019. Samples were split into a winter and summer season to determine seasonal factors. Five factors were determined in winter and six in summer -- with the addition of a biogenic factor dominated by isoprene. The other five factors included: shorter-lived ONG, longer-lived ONG, traffic, shorter-lived alkenes, and a regional anthropogenic Background factor. Results indicated that around 80% of C_2-C_5 alkanes were attributed to ONG activities indicating a strong regional ONG influence (Pollack et al., 2021).

Hecobian & Collett (2019) focused on local natural gas production activity in Garfield County between 2008 and 2019. Five PMF factors were identified: Natural gas, Combustion (fresh gasoline exhaust), Combustion (diesel exhaust), Biogenic emissions mixed with aged vehicular exhaust, and Oil and gas processing/industrial emissions. Sites closer to local ONG operations showed higher VOC contributions from oil and gas processing/industrial emissions while those further away were dominated by combustion and biogenic sources.

Abeleira et al (2017) conducted a study at the Boulder Atmospheric Observatory, by measuring 46 VOCs hourly between March 20th and May 17th, 2015. PMF analysis of this dataset identified six VOC factors: Long-Lived ONG, Short-Lived ONG, Traffic, Background, Secondary Chemical Production, and a Summer Biogenic factor. The long-lived ONG related factor accounted for 36% - 100% of the observed C_2 − C_6 mixing ratios while the shorter-lived ONG was dominated by larger C_7 and C_8 alkanes split by atmospheric lifetime. This area was found to be dominated by ONG-related VOC rather than traffic emissions despite its location NW of the Denver metro area (Abeleira et al., 2017).

1.5 The City and County of Broomfield (CCOB)

The City and County of Broomfield (CCOB) is a populous area north of the Denver metro area with a growing population of 66,529 as of Nov 2020 (*About Broomfield*, n.d.) and located in the west section of the D-J Basin and southwest section of the Wattenberg field. In 2017 and in the face of considerable public concern, CCOB approved the exploration, development, production, and marketing of natural gas, oil, and natural gas liquids. To help ensure the health and safety of its residents, the CCOB put together Broomfield's Comprehensive Plan (CP) outlining recommended goals and policies to mitigate emissions using best practices and to monitor impacts of ONG activities through air quality sampling. The CP sets guidelines for minimizing the impact of ONG operations on the greater community. It requires ONG operators to design and operate facilities in Broomfield under specific conditions that include but are not limited to increased setback distances from neighborhoods, operating a closed loop system, using electric drill rigs that use utility grid electric power and pit-less drilling, ensuring completion and production systems operate without permanent on-site storage tanks, implementing an Enhanced Leak Detection and Repair (ELDR) program, and ongoing maintenance checks of all equipment to minimize the potential for leaks. The full list of guidelines can be found at (Byers et al., n.d.).

Broomfield's CP lays out goals and policies to protect the public health, safety, welfare, and environment of the citizens of Broomfield (Byers et al., n.d.). These guidelines aim to regulate the

development of oil and gas to the necessary extent to reach these goals. Air quality is a focus within this vision. Policy OG.1 aims to "Anticipate and mitigate potential risks associated with air emissions related to oil and gas development, particularly in and around populated areas". To reach this policy, nine action steps are outlined, the first of which includes the implementation of a site-specific air quality monitoring plan to monitor emissions.

Operations were limited to six pad sites with a well cap of 84 total wells that were allocated as follows: 19 new wells on the Livingston Pad, 8 new wells on the Northwest A Pad, 8 new wells on the Northwest B Pad, 16 new wells on the United pad, 16 new wells on the Interchange A pad, and 17 new wells on the Interchange B Pad. Following the guidelines outlined in the Extraction Oil and Gas Operator Agreement, the ONG operator provided a summary of planned operations and an operational timeline to the city. The phases were outlined to fit into one of four categories: construction phase, drilling phase, completion phase, and production phase. Categories labeled as construction included work done to install drilling pads, visual mitigation measures, roads, pipeline, and building construction. Any onsite activities that included the use of a drill rig or the installation of well casings were labeled as drilling phase. Hydraulic fracturing, coiling, workover, installation of tubing and flowback fell under the completion phase. The production phase included the period in which one or more wells could produce hydrocarbons into a pipeline system. The operator was mandated to operate under a closed loop pit-less system for the contaminated or recycled drilling fluids and had to take waste offsite after a maximum of 30 days (Resolution No. 2017-186, 2017).

From the CP the CCOB developed the Broomfield Air Quality Monitoring Program (AQMP) (Broomfield Air Quality Monitoring Program (AQM), n.d.). The AQMP is a network of air quality monitoring locations around the greater CCOB. Sites near OG well pads were selected to capture emissions prior to significant dispersion, while sites further away in residential areas were set to monitor neighborhood impacts of ONG emissions or determine regional background conditions. The monitoring program, which

has evolved over time, consisted of multiple approaches, both online and offline, to monitor VOCs. Time integrated weekly VOC canister samples were taken at up to 18 different sites from late 2018 through December 2020 and beyond. Additional monitoring included photoionization detector (PID) sensors, a proton transfer reaction mass spectrometer (PTRMS), and periodic sampling from the Colorado Department of Public Health and Energy's (CDPHE) Colorado Air Monitoring Mobile Lab (CAMML). A mobile plume tracking unit was also deployed to capture geospatial variations in methane, acetylene, BTEX, and other VOC concentrations.

As of 2020 there were a total of 84 active or constructed wells across six pad sites: Interchange A and B, Livingston, Northwest Parkway A and B, and United (Broomfield Air Quality Monitoring Program (AQM), n.d.). This plan included weekly samples collected at 19 different sites around the county. Long term sampling began in November 2018 and the first well construction at Interchange began in January 2019. The construction timeline of each pad site provided by the ONG operator changed over time due to the SARS-CoV-2 outbreak in 2020 and bankruptcy of the operator.

This thesis focuses on observations taken from the Broomfield air monitoring program to better understand air quality impacts of local ONG extraction. Impacting sources were determined though PMF analysis using two datasets: a spatially resolved weekly dataset including VOC measurements across 18 sites and a high temporal resolution dataset provided from CDPHE CAMML deployments. Source categories are identified, and their impacts analyzed both close to well-pads and in surrounding neighborhoods.

METHODS

1.6 CCOB Data

The City and County of Broomfield (CCOB) approved ONG extraction in 2017. In 2018 CCOB contracted with Ajax Analytics and Colorado State University's Atmospheric Science Department to jointly establish an air monitoring program. The program launched in Fall 2018 prior to the start of drilling on new ONG well-pads. This program included fixed monitoring sites close to and further from planned well-pads as well as mobile measurements during select periods. These measurements were complemented by select periods of deployment of the CDPHE CAMML air monitoring system, to examine air quality impacts during select ONG pre-production and production activities. In 2020 the program was expanded to include spatially distributed, continuous monitoring of total VOCs by photoionization detectors capable of triggering 1-minute VOC canister samples upon detection of high concentration VOC plumes as well as more sophisticated air monitoring trailers at two locations operated by Boulder AIR (one including a PTR-MS system operated by CSU). As this study represents a very large experimental effort, many members of the Ajax and CSU teams were involved in collection and laboratory analysis of VOC samples. Please see the Acknowledgments section for details.

1.6.1 Sampling Sites

At the start of the air monitoring program, eighteen locations were chosen as weekly sampling sites, eight of which were located close to an ONG pad and ten in the surrounding CCOB area. There were four proposed ONG well-pad sites near the CCOB sampling locations: Livingston, Interchange, Northwest Parkway, and United. Three of these four ONG pads were active during the sampling period discussed here, 10/10/2018 to 12/28/2020, and due to the COVID-19 outbreak and bankruptcy proceedings, only two reached the production phase within the observed time. Active ONG sites included Livingston, Interchange, and Nwpkwy. The United pad will henceforth be labeled as an IMPACT site in this study. Livingston and Interchange reached production phase while Nwpkwy completed processes through drilling.
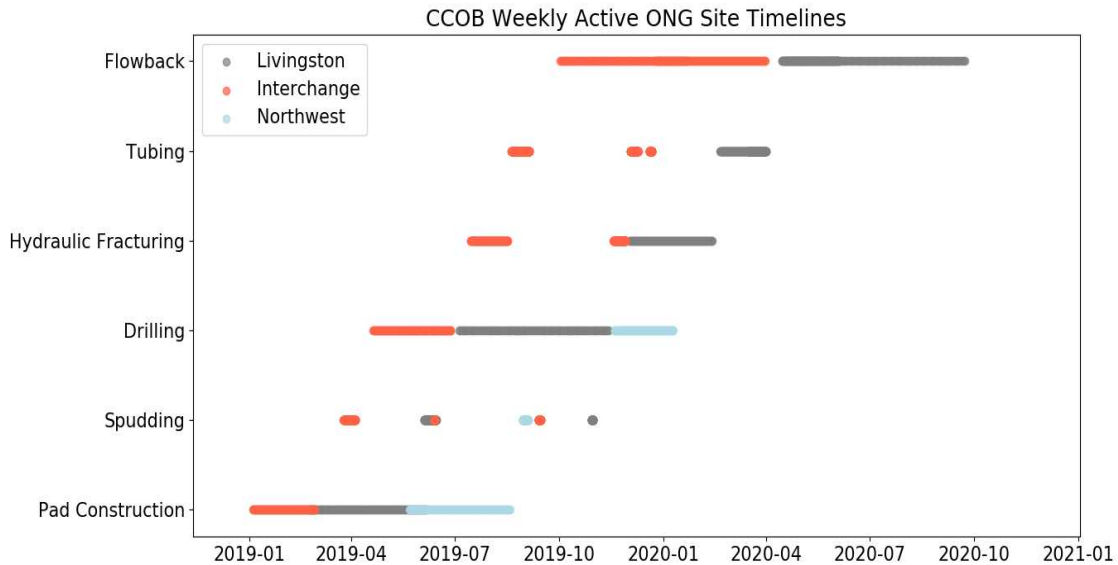

Figure 0-1: CCOB weekly activity timeline for the three active ONG sites. Colors are associated with an active pad and activities are shown on the y axis.

1.6.2   Weekly VOC Sampling

Sampling began before ONG development in CCOB. Sites around Broomfield were chosen to
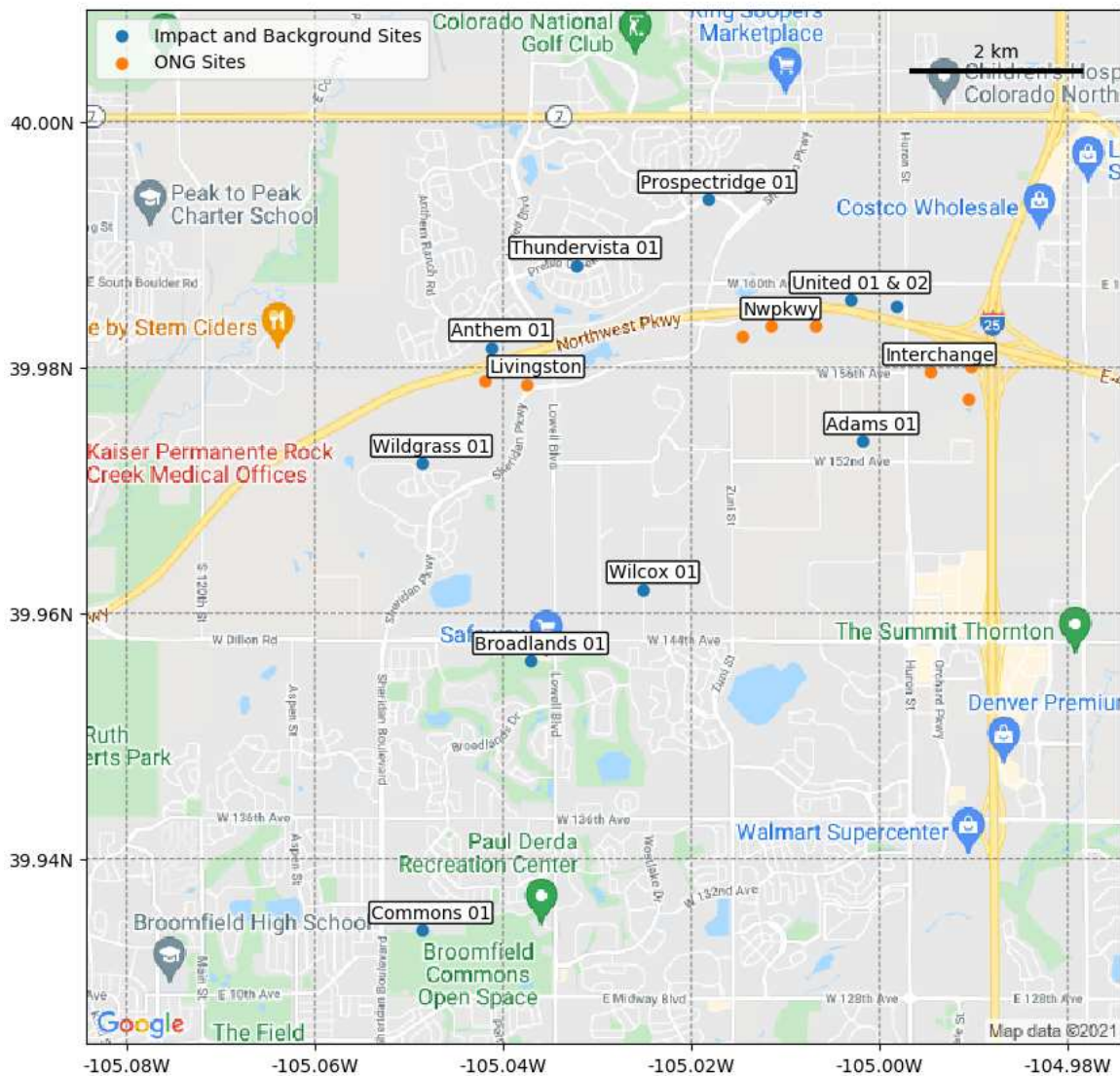

Figure 0-2: Sampling sites across the CCOB region. Orange dots represent stations located close to ONG sites and blue dots signify neighborhood impact and background sites. The United pad was not active during this sampling time and therefore proximate sites are classified as impact locations.

better understand the spatial gradient of atmospheric gases related to ONG activities. Each location

included a raised metal box in which a 6 L canister was placed during the sampling period. Samples were

changed on Thursdays. The exact sample change time was recorded and kept on record. Sample flow was

controlled into the canister to nearly fill a previously evacuated canister in one week. The starting and

final pressure were recorded to ensure the sample was taken over the entire week at the expected rate.

Air monitoring locations are labeled according to their proximity to an ONG extraction site. Sites located on or near a pad are labeled OG for oil and gas and other sites located around the greater CCOB are labeled IMPACT. There were eight ONG sites: Interchange 1, 2, and 3, Livingston 1 and 2, Northwest Parkway (Nwpkwy) 1, 2, and 3, and ten IMPACT or background sites: Anthem, Prospect Ridge, Thundervista, Adams, Wilcox, Wildgrass, Broadlands, United 01, United 02, and Commons. Commons was selected as a regional background site given its location south of the other sites further from ONG operations. Of the ten ONG sites, 8 were active during the sampling period with no active extraction occurring at the United pad. Samples included in this analysis were taken between October 10th, 2018, and December 28th, 2020, and henceforth will be referred to as the sampling period for the CCOB weekly data.

Three to eighteen sites were sampled each week. Periods of sampling are shown in Figure 0-3. Some core study sites sampled every week, other sets of sites were sampled less frequently to analyze spatial gradients across CCOB, and some site frequencies increased during select periods of nearby ONG operations. Anthem 01 and Commons 01 were sampled the most with 116 samples, with all but two weeks observed. Broadlands 01 was sampled the least with 21 observations.
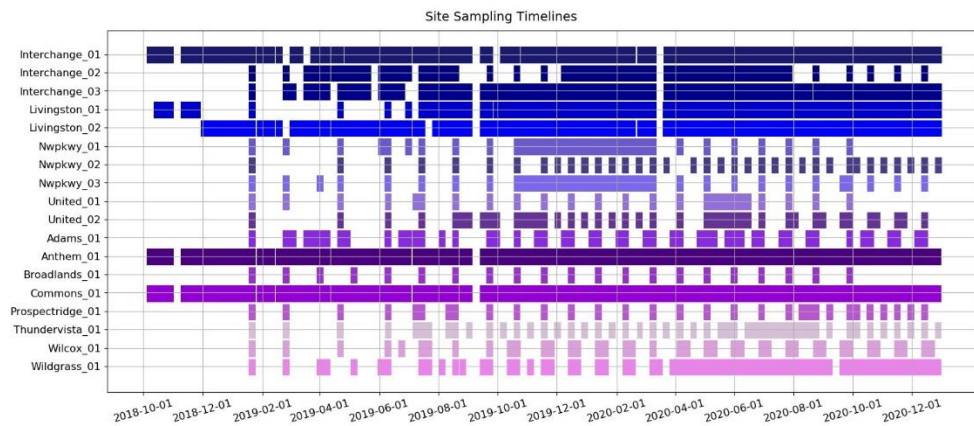

Figure 0-3: Weekly sampling dates for all 18 CCOB observational sites. Anthem 01 and Commons 01 were consistently sampling with the two unsampled weeks shown as gaps in the timeline.

1.6.3 Instrumentation

1.6.3.1 Time Integrated Canisters

Samples were collected using Entech Instruments 6L Stainless Steel Canisters with internal Silonite® coating (Entech Instruments Inc., Simi Valley, CA, USA). Silonite is a ceramic coating which provides an extremely inert surface that eliminates exposure of the sample to possible interactions with the stainless-steel canister interior (*ENTECHinstruments*, 2021). The 6L canister has a total outer diameter of 9 inches and inner diameter of 6.5 inches. It stands at 12.45 inches tall and features a TrueSeal™ Valve for leak free operation (*Canisters 2016*, 2016).

Using this sampling technique, VOCs have been shown to be stable and accurate within the canister for up to 30 days (LeBouf et al., 2012). Canisters were analyzed within a week of the one-week sampling period and unused canisters were cleaned again after three weeks of no use.

1.6.3.2 Flow Controller and Calibration

A CS1200E Entech Flow Controller was attached to the 6L Canister to fill canisters at a constant rate over the week-long sample. The flow controller features a large diaphragm and a control nozzle to control the pressure differential and ensure consistent flow. The inlets and filters are lined with Silonite to reduce any bias in sampling from sample reactions with the steel (*CS1200E Flow Controller*, 2021). Flow controllers were calibrated for an 87% final fill volume which for a 6L canister over a one-week sampling period equates to a flow rate of 0.52 cubic centimeters per minute (*CS1200E Flow Controller Operation and Care Guide*, 2017).

1.6.3.3 Gas Chromatograph and Post-Processing

Concentrations of 52 VOCs were analyzed using a 5-channel gas chromatograph (GC) with 3 Flame Ionization Detectors (FID), an Electron Capture Detector (ECD), and a quadrupole mass spectrometer (MS). Canisters were hooked up to a 30 cm long stainless-steel cryogenic pre-concentration loop filled with glass beads to enhance condensation of volatile compounds (Weber, 2018). The system is controlled

by valves that redirect air flow. Once the sample is trapped in the sample loop and is isolated, the trap is rapidly heated to 80 degrees C and a splitter box is moved from "trap" to "inject" which triggers the analysis (Sive et al., 2005).

The GC produces a chromatogram where peak area corresponds to compound concentration and peak identity is based on compound retention time and/or MS spectra. A standard gas mixture was run prior to, and following sample runs and used for a calibration curve to ensure consistent analysis. Samples were corrected for volume within ±0.2 torr. Analyses were completed and chromatograms were integrated by Dr. Yong Zhou.

1.6.4 CCOB Handling of Data

1.6.4.1 Limit of Detection

To determine the limit of detection (LOD) of the compounds analyzed using the GC, a highly diluted standard was run. The goal was to create a small, but quantifiable peak above the background noise. A small amount of standard, 50 torr, was mixed with zero air, 350 torr, which was analyzed three times. The LOD was calculated using equation 0-1.

0-1
$$x_{min} = ts_b\sqrt{\frac{N_1 + N_2}{N_1 N_2}}$$

where x_{min} is the minimum detectable quantity, t is the t-value for 2 degrees of freedom, s_b is the small sample standard deviation, N_1 = 1 sample analysis and N_2 = 3 replicate dilute standard analyses. Concentrations are quantified in ppb for all compounds except for halogenated compounds C_2HCl_3 and C_2Cl_4 for which x_{min} is computed in ppt. Concentrations that were found to be below the LOD within the data were replaced with half the LOD and the uncertainty was replaced with 5/6 of the LOD according to Polissar et al. (1998).

1.6.4.2 CCOB Uncertainties

Uncertainties in concentrations were influenced by the instrument and integration techniques. Chromatograms were integrated by a single person, Dr. Yong Zhou, to ensure human errors were consistent throughout the long set of observations. To quantify measurement precision VOC concentrations in a large canister sample taken in CCOB were quantified eight times using the GC. From these data the relative standard deviation (RSD) of each compound was calculated and plotted against the compound's mean concentration (Figure 0-4).

Analytical precision typically varies with analyte concentration, degrading as concentrations approach the LOD. As shown in Figure 0-4, RSD values for a broad range of VOCs exhibit a common variation with concentration. A power curve was fit to the data and used to calculate measurement precision using the equation, $unc = 0.022c^{-0.411}$. where unc is the uncertainty, and c is the concentration. This curve fit the data with an $R^2 = 0.53$, shown in Figure 0-4. The data were then handled according to Polissar et al. (1998) where precision estimates associated with determined concentrations had LOD/3 added to represent their uncertainty. A separate power curve was used for the chlorinated compounds as they are found at ppt levels. Data points below LOD were replaced with LOD/2 and uncertainties for these points were reported as LOD/3 + LOD/2, or 5/6 LOD which follows the methods of Polissar et al.

(1998). This method has been widely implemented in the use of PMF and is based on what provides useful

results rather than statistical findings (Hopke, 2016).

1.6.5   CCOB Data Pre-processing for PMF Analysis

A total of 52 VOCs were quantified by GC. The sample start and stop dates were averaged to

create the sample's mid-date which was reported as the sample date for PMF analysis. During the

chromatogram integration process, if concentration peaks were not visible, they were labeled as 'BL' for

below limit. If a peak was unquantifiable due to merging with other peaks, the concentration was labeled

'ND' for not detected. To determine what percentage of the data was useable for analysis, the percent of
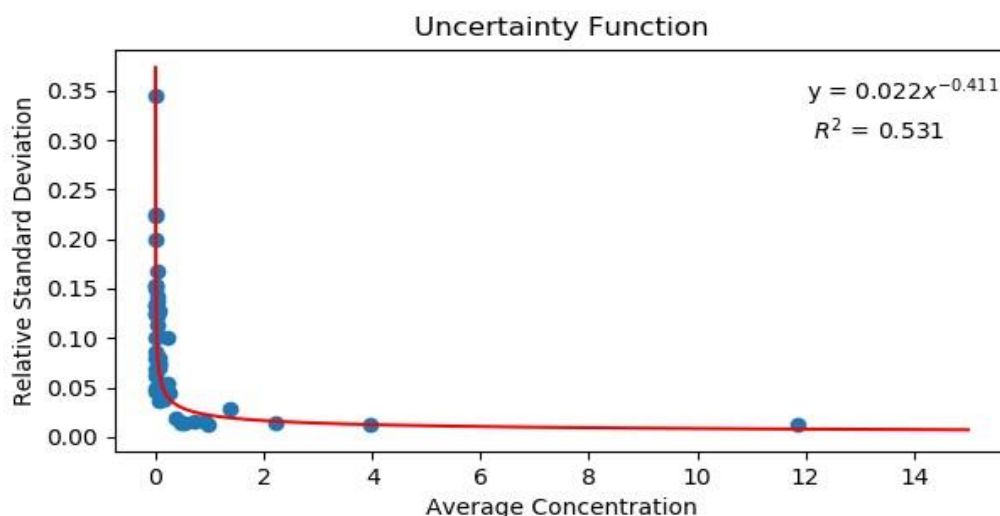

Figure 0-4: Uncertainty function fit to all observed VOCs within the large CCOB sample. The RSD of 8 GC runs was calculated for compounds (blue dots) not including chlorinated compounds.

ND and BL concentrations were calculated for each compound. Data for compounds with less than 40%

of quantifiable observations were dropped. These included: c-2-butene, t-2-pentene, 1-pentene, c-2-

pentene, 2,3,4-trimethylpentane, styrene, n-propylbenzene, 4-ethyltoluene, 1,3,5-trimethylbenzene, 2-

ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethlbenzene, 1,3-diethylbenzene, and 1,4-

diethylbenzene. ND concentrations in the remaining compounds were replaced with the compound's

median mixing ratio and BL concentrations were replaced with $\frac{LOD}{2}$.

25

Compounds were further filtered by the PMF signal to noise (S/N) ratio which was handled in PMF according to the suggestions in the PMF 5.0 User Guide (Norris et al., 2014). The S/N ratio as computed within PMF only accounts for values that exceed the uncertainty. The S/N ratio is calculated as the difference between the concentration (x_{ij}) and the uncertainty (s_{ij}) for all points within the given data that are above the uncertainty. The S/N ratio is then reported as the average signal greater than noise across the compound (Equation 2-2). Compounds with concentrations always below their uncertainties are given a ratio of 0 and those with concentrations double their uncertainty values are given a value of 1 (Norris et al., 2014). Compounds with a S/N ratio below 0.5 were labeled "bad" and values were not taken into account, while those 0.5 to 1 were labeled "weak" and the associated uncertainties were tripled. Two compounds were labeled "bad" and included C_2HCl_3 and C_2Cl_4 which had a S/N ratio of zero. 2,4-dimethylpentane was labeled "weak" with a S/N ratio equal to 0.9.

0-2

$$d_{ij} = \left(\frac{x_{ij} - s_{ij}}{s_{ij}} \right) \text{if } x_{ij} > s_{ij}$$

$$d_{ij} = 0 \text{ if } x_{ij} \leq s_{ij}$$

$$\left(\frac{S}{N} \right)_j = \frac{1}{n} \sum_{i=1}^{n} d_{ij}$$

Methane, although having a large S/N ratio was labeled as "bad" to remove it from the weekly canister PMF analysis. This choice was made since PMF factors that included methane were not robust enough to be analyzed. This may be due to low variation across the weekly time-integrated samples that reflected the high atmospheric background concentration of methane.

A total of 33 VOCs (Table 3-1) were included in PMF analysis of the weekly canister data after removing other analyzed compounds as outlined above. The average concentrations and spread of the data are further explored in Table 3-1 which depicts compound mean values, standard deviation, median, minimum, and maximum mixing ratios.

Six PMF factors were determined to fit the data best. The information gained from 5 to 6 factors was greater than the information from 6 to 7 as shown in the elbow plot in. One-hundred bootstraps were run on the six factors. The Drilling factor had the most factor swaps with 35 of 100 being mapped onto the Light Alkane factor. This mapping was deemed reasonable due to the methods by which the bootstrapping is performed (see Positive Matrix Factorization methods section) and the relatively short period of high concentrations that make up the Drilling factor. Uncertainties in the following analysis represent the 25th and 75th percentiles determined by the 100 bootstraps.
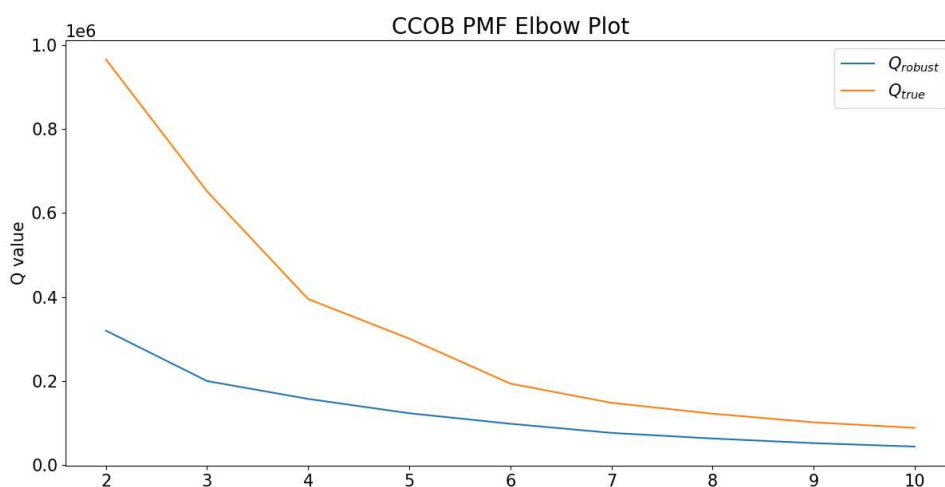

Figure 2-5: Elbow plot for weekly COOB PMF factors. A clear elbow is shown at 6 factors showing a large increase in information gained from 5 to 6 factors and less so from 6 to 7 factors.

Table 0-1: Compounds used in the CCOB PMF analysis.

Compounds	Mean (ppbv)	1σ SD (ppbv)	Median (ppbv)	Min (ppbv)	Max (ppbv)
ethane	12.55	7.72	9.98	3.31	61.55
propane	6.3	4.16	4.93	1.3	34.08
i-butane	1.12	0.75	0.88	0.23	6.32
n-butane	2.97	2.01	2.3	0.61	17.12
i-pentane	0.99	0.58	0.83	0.28	6.73
n-pentane	0.97	0.67	0.78	0.25	7.61
n-hexane	0.41	0.35	0.3	0.08	4.7
n-heptane	0.16	0.19	0.1	0.03	2.56

n-octane	0.11	0.15	0.06	0.01	1.73
n-nonane	0.09	0.19	0.04	0.01	2.04
n-decane	0.11	0.31	0.03	0.01	3.48
cyclopentane	0.08	0.05	0.06	0.02	0.62
2,2,4-trimethylpentane	0.06	0.04	0.05	0.01	0.48
2,3-dimethylpentane	0.08	0.08	0.06	0.02	1.14
2,4-dimethylpentane	0.02	0.02	0.01	0.01	0.24
cyclohexane	0.14	0.15	0.09	0.02	2.03
2-methylhexane	0.04	0.03	0.03	0.0	0.33
3-methylhexane	0.09	0.1	0.06	0.01	1.3
methylcyclohexane	0.17	0.25	0.09	0.02	3.86
2-methylheptane	0.04	0.07	0.01	0.01	0.97
3-methylheptane	0.03	0.05	0.02	0.0	0.52
ethene	0.93	0.58	0.76	0.21	5.6
propene	0.15	0.07	0.14	0.05	0.69
t-2-butene	0.01	0.02	0.01	0.0	0.28
1-butene	0.03	0.02	0.02	0.01	0.44
benzene	0.18	0.08	0.16	0.03	0.8
toluene	0.32	0.31	0.27	0.01	7.79
ethylbenzene	0.04	0.02	0.03	0.0	0.25
m+p-xylene	0.14	0.1	0.11	0.02	1.17
o-xylene	0.04	0.03	0.04	0.01	0.33
3-ethyltoluene	0.02	0.03	0.01	0.0	0.37
ethyne	0.85	1.03	0.62	0.1	18.03
isoprene	0.03	0.05	0.01	0.0	0.45

1.7 Colorado Air Monitoring Mobile Lab Data (CAMML)

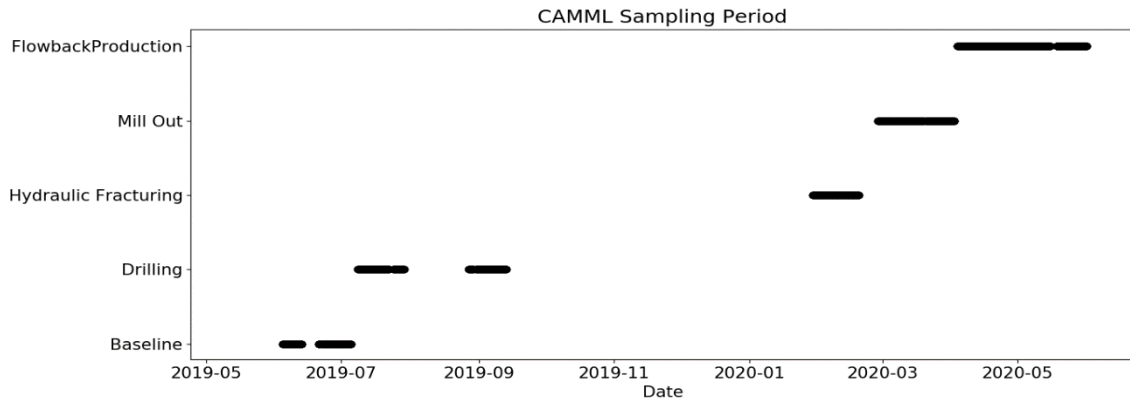### 1.7.1 CAMML Sampling

Figure 0-6: CAMML sampling periods. Activities are shown on the y-axis and periods of associated sampling are plotted horizontally on the time axis.

The CDPHE Colorado Air Monitoring Mobile Lab (CAMML) was deployed adjacent to the Livingston pad in Broomfield, Colorado during several periods. Samples were taken during five stages within the ONG development process at Livingston: baseline, drilling, hydraulic fracturing, mill-out, and flowback production. Periods of sampling are shown in Figure 2-6. Twenty-five VOCs were quantified hourly by a gas chromatograph (GC). Additional compounds analyzed – referred to as other data – were methane, Particulate Matter (PM) with an aerodynamic diameter less than 10 micrometers (PM_{10}) and 2.5 micrometers ($PM_{2.5}$), nitrogen oxide (NO), nitrogen dioxide (NO_2), NO_x (NO + NO_2), and ozone (O_3). These were quantified every minute.

1.7.2 CAMML Instrumentation

The Colorado Air Monitoring Mobile Lab (CAMML) was deployed by Dr. Daniel Bon of the Colorado Department of Public Health and Environment (CDPHE). A 15-foot heated mast collected VOC samples for 45 minutes per hour followed by the analysis cycle. VOC concentrations were determined using a two column GC flame ionization detector (FID) system. To ensure consistent quantification, a daily single point calibration check was run. If the concentration was outside of 10% of the known check standard benzene

and propane mixing ratios, a full six-point calibration with a required $R^2 = 0.99$ was performed. LODs were quantified annually or after a major system change.

Methane (CH_4) concentrations were quantified by a Los Gatos 4 gas analyzer. Nitrogen dioxide (NO_2) and nitric oxide (NO) – collectively known as NO_x -- $PM_{2.5}$, PM_{10}, and ozone (O_3) were monitored by standard instruments as described in the CDPHE Technical Services Program (Air Pollution Division Technical Services Program Quality Assurance Project Plan, 2015).

1.7.3   CAMML Data Pre-processing

VOC mixing ratios and other data, including methane, all nitrogen containing compounds, particulate matter, and ozone, were reported separately by the CDPHE. The VOC data, which were reported hourly, included flags alongside concentrations indicating if a data point was not detected (1), detected but failed calibration quality control (2), detected but failed continuing calibration verification (3), or detected but less than the LOD (4). Only seven compounds raised flags (2) or (3) during the observational period. Flags (2) and (3) were treated the same while flags (1) and (4) were treated the same. Ethane contained 135 (2) or (3) flags during baseline sampling, n-pentane contained 180 during baseline, both 2-methylpentane and 3-methylpentane each had 1262 during flowback production, n-undecane had 45 during baseline, n-dodecane had 219 during baseline, and a-pinene had 1262 during flowback production and 741 during mill out. Due to a high percentage of failed quality or calibration data, 2-methylpentane, 3-methylpentane, and a-pinene were dropped from the analyzed data set. The remaining (2) and (3) flags were treated the same as the ND data in the CCOB weekly data and replaced with the median mixing ratio value. P-ethyl-toluene, 1,2,4-trimethyl-benzene, and p-diethyl-benzene were dropped due to having greater than 85% of values raise a (1) or (4) flag. In the remaining data, concentrations that were associated with a (1) or (4) flag were treated as below the LOD and replaced with LOD/2.

The other (non-VOC) pollutant data were averaged over the VOC sampling time and merged to create a single data set. All LODs were provided by the CDPHE. Uncertainties for both the VOC and other data were either 5% of the determined value or 0.05 ppb, whichever value was found to be larger (Bon et al., 2011). Due to the high atmospheric background of methane, the minimum observed CH_4 value was subtracted to emphasize anomalies (CH_4 anomalies).

Compounds were analyzed for their signal to noise ratio within the PMF interface. Compounds with S/N below 0.5 were dropped and those between 0.5 and 1 were marked weak (excluding isoprene 0.4 S/N which was marked weak). VOCs labeled "strong" included: ethane, propane, isobutane, n-butane, isopentane, n-pentane, 2-methyl-pentane, 3-methyl-pentane, n-hexane, methyl-cyclopentane, benzene, and toluene. VOC compounds marked weak were cyclopentane, isoprene, n-octane, m+p-xylene, n-nonane and n-decane. VOC compounds marked "bad" were ethylbenzene, o-xylene, p-ethyl-toluene, 1,2,4-trimethyl-benzene, p-diethyl-benzene, n-undecane, and n-dodecane. Methane anomalies were found to produce more physically relevant factors and therefore the lowest concentration of observed methane was subtracted from the entire methane data set. Five of the seven other non-VOC compounds were labeled strong and used in analysis, including: O_3, $PM_{2.5}$, PM_{10}, CH_4 anomalies ($CH_4 anom$), and NO_x, while NO and NO_2 were dropped. Compounds used in the CAMML PMF analysis are shown in Table 0-2.

Table 0-2: Compounds used in the CAMML PMF analysis

	Mean	1σ SD	Median	Min	Max
Ethane (ppb)	8.04	18.05	4.95	0.03	789.55
Propane (ppb)	4.66	12.04	2.53	0.06	486.6
Isobutane (ppb)	0.8	2.05	0.41	0.01	81.21
n-butane (ppb)	2.1	5.6	1.02	0.02	211.35
Cyclopentane (ppb)	0.07	0.18	0.04	0.02	6.01
Isopentane (ppb)	0.79	2.18	0.43	0.02	88.2
n-pentane (ppb)	0.83	2.64	0.38	0.01	92.0
Isoprene (ppb)	0.05	0.09	0.01	0.01	1.39
n-hexane (ppb)	0.39	1.34	0.18	0.01	41.19
methyl-cyclopentane (ppb)	0.17	0.65	0.07	0.01	21.04
Benzene (ppb)	0.12	0.23	0.08	0.01	7.44

Toluene (ppb)	0.23	0.6	0.13	0.01	21.09
n-octane (ppb)	0.09	0.59	0.01	0.01	23.38
ethylbenzene (ppb)	0.02	0.07	0.01	0.01	2.53
M+p-xylene (ppb)	0.09	0.42	0.03	0.01	16.53
o-xylene (ppb)	0.03	0.11	0.01	0.01	4.09
n-nonane (ppb)	0.12	1.08	0.01	0.01	46.1
n-decane (ppb)	0.18	1.73	0.01	0.01	74.67
n-undecane (ppb)	0.11	0.89	0.02	0.02	38.28
n-dodecane (ppb)	0.09	0.58	0.04	0.04	25.76
PM2.5 ($\mu g/m^3$)	5.13	4.78	3.67	0.02	83.87
PM10 ($\mu g/m^3$)	10.35	11.44	8.08	0.02	464.74
NO_x (ppb)	7.18	7.2	4.93	0.02	90.61
O_3 (ppb)	37.92	17.65	39.86	0.02	280.71
CH4 anom (ppm)	0.13	0.15	0.1	0.0	3.69

1.8

1.9 Positive Matrix Factorization

The goal of source apportionment is to take an observational data series (x_{ij}) and determine how a set number of sources, or factors (p), influence it. The apportionment model determines the makeup of the factors (f_{kj}) and the factor contribution (g_{ik}) to each observational sample series. This chemical mass balance (CMB) equation is shown in equation 0-3.

0-3

$$x_{ij} = \Sigma_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

where e_{ij} is the residual error for each species and sample. This CMB can be solved using various models, one of which is Positive Matrix Factorization (PMF). The Environmental Protection Agency's (EPA's) PMF version 5.0.14 was utilized in this study; this model version implements the second version of the multilinear engine and provides a non-negativity constraint, iteratively solving the PMF equation (Norris et al., 2014).

0-4

$$Q = \Sigma_{i=1}^{n} \Sigma_{j=1}^{m} \left[\frac{x_{ij} - \Sigma_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2$$

PMF works by determining two matrices, factor contributions (G_{ixk}) and factor profiles (F_{kxj}). The resulting matrices, F and G, are constrained to only contain positive contributions in the resulting factor profiles. Input concentrations are accompanied by an uncertainty matrix that helps to account for the confidence in the measurement. To determine factor profiles, the objective function Q (equation 0-4) is minimized, where Q is optimized based on the summed square of the ratio of the compound's residual and uncertainties over the entire data set. The PMF interface reports two Q values, Q true which considers all input samples, and Q robust that is calculated using predicted samples with a residual less than 4 units (units reported in Table 2-1 and Table 2-2) -- meaning compounds in which the difference between the observational and the predicted concentrations greater than 4 were not considered. The best solution within the PMF interface is suggested as the lowest value of Q robust (Norris et al., 2014).

The robustness of the solution can be determined using three different built-in methods, bootstrapping (BS), displacement (DISP), and BS-DISP which is a hybrid of the two methods. BS detects if a portion of the observations disproportionally affects the outcome. Observations are randomly sampled in blocks until the resampled data is the same size as the original dataset and is then processed through the PMF algorithm. Each of the output BS factors are then compared to the base or original factors. If the BS factors correlate with a base factor above a user-specified threshold, automatically set to 60%, they are then mapped to that base factor. If the BS factor does not fit into a base factor category, it is labeled as unmapped. The results are summarized in a table output by the PMF user interface (Norris et al., 2014).

DISP explores the range of other potential factors within a given change of Q (dQ) to determine the rotational ambiguity of the PMF solution. Each value in the source profile is adjusted and then the others are secondarily computed to again minimize the Q value. If a factor has a large rotational ambiguity, it will be shown to swap factors in the DISP analysis. A factor swap is indicative of instability as the factor originally associated with a certain source is mapped to another factor. If this swap occurs at low dQ values, the factor should not be considered robust enough to analyze. DISP outputs the largest change in

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Q associated with dQ and whether a swap had occurred during analysis. Factors in this study were tested for their robustness using the built-in displacement error estimation (DISP) and bootstrap (BS) methods. Additional information can be found in the *EPA Positive Matrix Factorization (PMF) 5.0 Fundamentals and User Guide* (Norris et al., 2014).

1.10 CCOB Weekly VOC Observations

1.10.1 ONG timeline

Three Broomfield ONG sites were active during the sampling period between October 4th, 2018, and December 31st, 2020: Livingston, Interchange B, and Northwest Parkway A (Nwpkwy). Livingston and Interchange had 18 and 12 wells, respectively, fully in production by the end of 2020. Nwpkwy was still in the pre-production phase with 8 wells drilled. Operators reported activities including pad construction, spudding, drilling, hydraulic fracturing, coiled tubing, production tubing installation, flowback, and production (Table 0-1).

Table 0-1: Construction timeline for the three active ONG pads in CCOB during the sampling period.

Pad	Activity	Start Date	Stop Date
Interchange B	Pad Construction	1/4/2019	2/28/2019
Interchange B	Drilling	4/20/2019	6/28/2019
Interchange B	Hydraulic Fracturing	7/15/2019	8/17/2019
Interchange B	Coiled Tubing (plug milling)	8/20/2019	8/30/2019
Interchange B	Production Tubing Installation	8/30/2019	9/5/2019
Interchange B	Flowback (1st – 10 wells)	10/2/2019	1/22/2020
Interchange B	Flowback (2nd – 2 wells)	12/26/2019	3/31/2020
Livingston	Pad Construction	2/23/2019	6/6/2019
Livingston	Drilling	7/5/2019	11/14/2019
Livingston	Hydraulic Fracturing	12/2/2019	2/13/2020
Livingston	Coiled Tubing (plug milling)	2/20/2020	3/27/2020
Livingston	Production Tubing Installation	3/16/2020	4/1/2020
Livingston	Flowback	4/15/2020	7/31/2020
Northwest A	Pad Construction	5/22/2019	8/19/2019
Northwest A	Drilling	11/19/2019	1/10/2020
Northwest A	Hydraulic Fracturing	Not yet completed	
Northwest A	Coiled Tubing (plug milling)	Not yet completed	
Northwest A	Production Tubing Installation	Not yet completed	

1.10.2 VOC Trends

Just over two years of data were collected with a total of 1131 weekly samples across 18 sites (Figure 2-3). To better understand VOC influence in the CCOB, all samples were pooled and VOC species were grouped into eight subcategories: light alkanes (C_2-C_4), medium + heavy alkanes (C_5-C_{10}), branched alkanes, cyclic alkanes, alkenes + alkynes, aromatics, biogenic VOCs (isoprene), and chlorinated VOCs. Light alkanes concentrations dominated the abundance of total VOCs during all seasons, showing the largest contributions in fall and winter (Figure 0-1). Most emitted VOCs tend to follow this seasonal trend due to more stagnant conditions with shallower mixed layers and reduced dispersion during fall and winter (Hecobian and Collett, 2019).
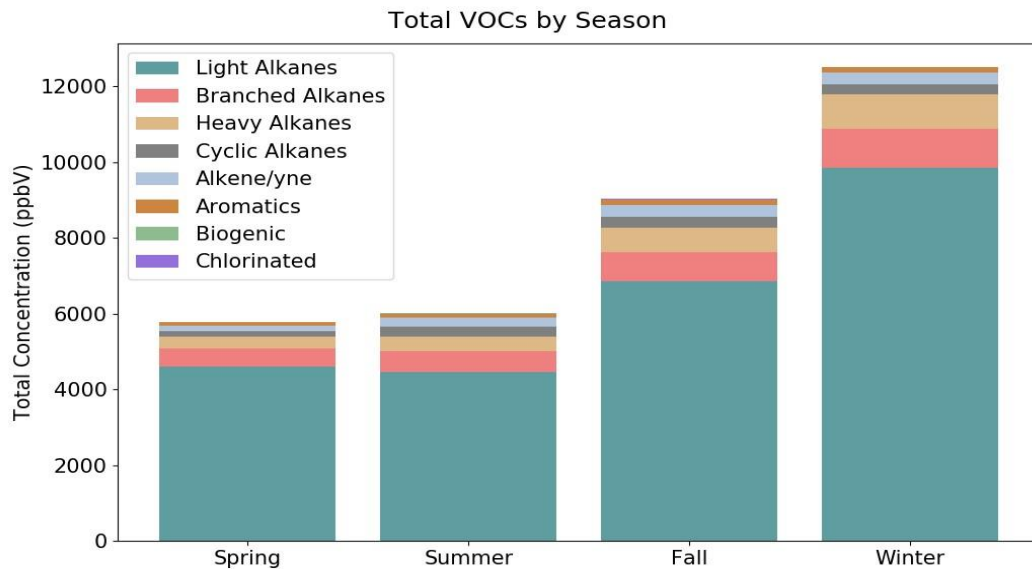
Figure 0-1: Depicts average VOC concentrations across all sites over the entire CCOB weekly sampling period for Spring (MAM), Summer (JJA), Fall (SON) and Winter (DJF).

Total sample VOC concentrations (TVOC) were calculated as the sum of all measured VOC concentrations at one site during a single week. Observations made in 2018 before the active ONG period showed sites across the CCOB had similar TVOC concentrations – seen prior to the construction period in Figure 0-2 -- suggesting all sites were influenced by similar, more regional, sources. TVOC measurements across CCOB began to diverge in spring of 2019 shortly after ONG activities began. This divergence suggests sites across the CCOB no longer experienced the same or similar source influences with greater influence from new, local emissions. An increase in the spatial divergence of TVOC concentrations corresponds with the onset of drilling at Interchange in April 2019 (Table 0-1).
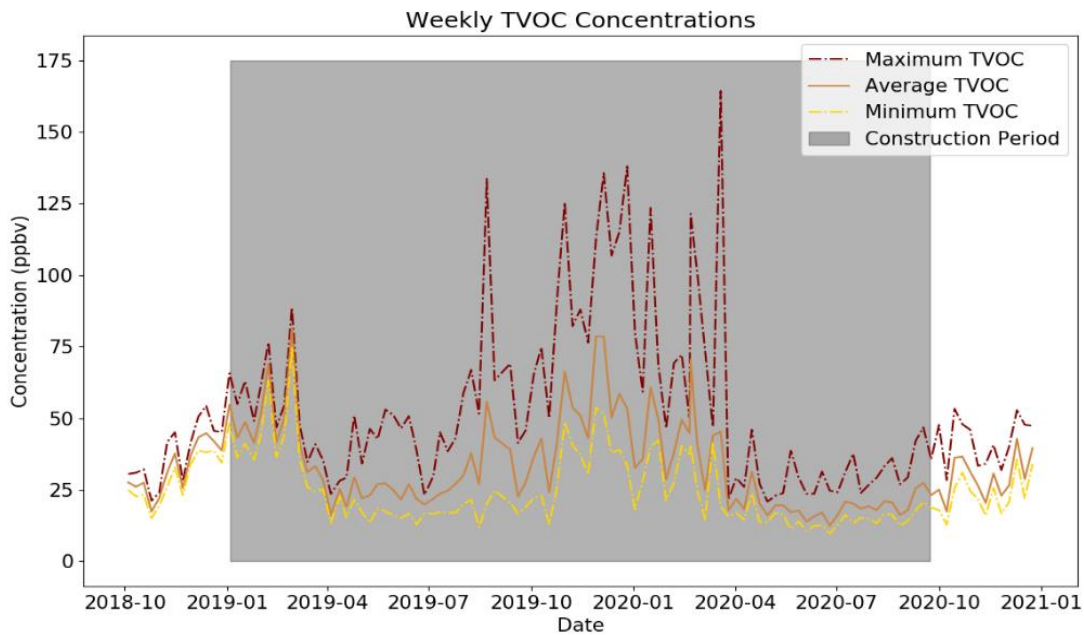
Figure 0-2: Plots show the highest, lowest, and average TVOC concentrations observed at 18 sites with weekly observations.

The ratio of isopentane to n-pentane (i/n pentane) is commonly used to indicate the influence of oil and gas emissions on measured VOCs (Pollack et al., 2021, Halliday et al., 2016, Gilman et al., 2013, Abeleira et al., 2017). Ratios of i/n pentane greater than 2 indicate strong influence by combustion while values less than 1 typically reflect a strong oil and gas signature. The average i/n pentane ratio over the sampling period, across all sites, was 1.02, reflecting a mixture of substantial ONG emissions with other VOC sources including traffic/combustion.
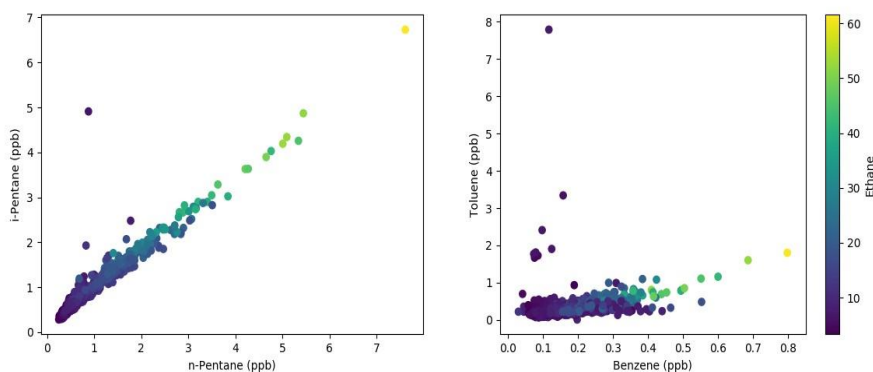
Figure 0-3: Isopentane and n-pentane and toluene to benzene concentrations were correlated over the sampling period. Higher mixing ratios of these key tracers were positively correlated with ethane mixing ratios.

The ratio of toluene to benzene (t/b) has similar utility, although the ratios are less well constrained. Two linear trends can be seen in the t/b ratio portion of Figure 0-3, one with high toluene and low benzene concentrations not associated with high ethane concentrations; these points suggest increased influence from combustion emissions. Another trend with relatively similar toluene and benzene concentrations, where higher concentrations of both species are associated with high ethane concentrations, is typical of ONG emissions. The average t/b ratio over the entire sampling period was 1.79.

1.10.3 CCOB PMF

The goal of PMF analysis was to identify and quantify contributions from various emission sources impacting air quality in CCOB. PMF was applied to weekly VOC data for all sites with more than 20 observations between October 4th, 2019, and December 31st, 2020. Observations from 18 sites were pooled into a singular data set and input into PMF with the sample mid-time as the sampling date. Six factors optimized the predicted time series residuals without over-fitting the data determined through an elbow method plot shown in Figure 0-4. Both Q_{robust} and Q_{true} are plotted. There is a clear "elbow" or bend in the function at 6 factors indicating a large amount of additional information was explained moving from 5 to 6 factors while less was gained from 6 to 7 factors. Once these six factors were identified, temporal variability of the PMF factors were analyzed for any correspondence with documented activities at the three active ONG sites. Factors were further analyzed for their spatial impacts across CCOB to help identify possible source emission locations.
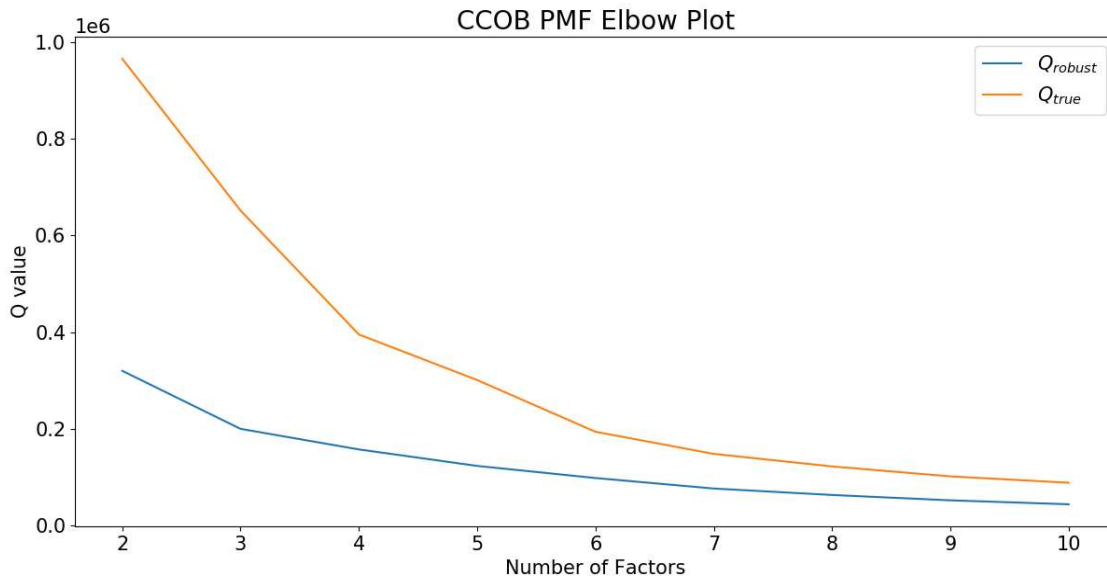
Figure 0-4: Elbow plot method used to help determine the number of factors.

The six factors chosen for the CCOB weekly data were labeled as: Background, Light Alkanes, Complex Alkanes, Combustion, Ethyne, and Drilling. Six was found to be the best solution because it

maximized the decrease in Q (Figure 0-4) while all factors made physical sense. A five factor solution lacked the Drilling factor, while seven factors split the alkanes into three, instead of two factors – further split by atmospheric lifetimes, as also seen elsewhere (Pollack et al., 2021).

Factors were tested for their robustness using the built-in displacement error estimation (DISP) and bootstrap (BS) methods as explained in section 1.8 The largest change of Q associated with the DISP analysis was -3.239 and no dQ values were associated with a factor swap. Given the drop in Q during the DISP analysis was much less than 1% of Q_{robust} and no factor swaps occurred, the chosen factors were determined to be rotationally robust. Factors labels were selected according to similarity to known source emissions composition as reflected by compound abundances in the profile including values of select compound ratios. A brief overview of factors is given below with a more detailed analysis in the following sections.

The Background factor contained 95% of the isoprene, a well-known biogenic VOC emission. This factor also contained low concentrations of BTEX with trace amounts of complex aromatics. Hecobian & Collett (2019) in their study of VOC concentration data in the Piceance Basin in Garfield County, Colorado, identified a Background factor mixed with vehicular exhaust which contained large percentages of complex aromatics, complex alkanes and complex alkenes, somewhat resembling the presence of these compounds in this study's Background factor. This profile had the largest contributions during the summer months reflecting greater biogenic emissions, increased prevalence of longer-range transport and enhanced photochemistry.

The Combustion factor was dominated by alkenes, aromatic compounds, and some larger alkanes which is consistent with tailpipe emissions (Abeleira et al. 2017). Alkenes are emitted from incomplete combustion and butene isomers are shown to be emitted from the exhaust of vehicles. Seventeen percent of the total ethyne concentration, which is a common combustion marker (Hecobian and Collett, 2019), is associated with this factor. Factor contributions were larger in winter than in summer which may reflect

both a shallower boundary layer trapping local combustion emissions and a decrease in the hydroxyl

radical concentrations that drive oxidation of exhaust emission. The i/n pentane ratio of the factor was

2.23. Literature values for i/n pentane ratios range from 2.3 from the combustion of liquid gasoline to 3.8

for the evaporation of liquid gasoline (Gilman et al., 2013). The factor's t/b ratio is 1.96 and although this

ratio is less strictly constrained than the i/n ratio, more toluene (higher t/b ratio) is typically associated

with some type of combustion (Hecobian & Collett, 2019).

The Light Alkane factor is mainly compromised of $C_2 - C_5$ alkanes and contains 63% of the total

ethane concentration, 74% of propane, 67% and 66% of i- and n- butane respectively, and 46% and 53%

of i- and n- pentane, respectively. Forty-four percent of cyclopentane was allocated to this factor;
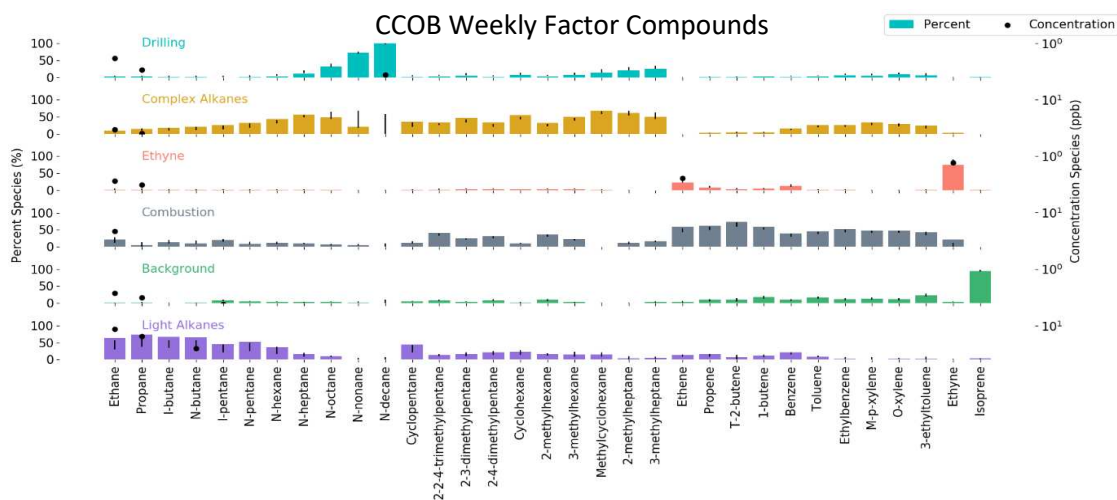
Figure 0-5: Compound concentrations and percent of species allocated to each CCOB weekly PMF factor. Uncertainties are given for the percent of the species as the 25th and 75th percentile from 100 bootstraps.

cyclopentane is associated with raw and unprocessed natural gas (Gilman et al., 2013). Gilman et al.

proposed an i/n pentane ratio for ONG emissions from the Greater Wattenberg Area of the D-J Basin to

be 0.86 ± 0.02. The i/n pentane ratio for this factor was 0.89 very similar to this proposed value. Previous

studies have found similar profiles pertaining to natural gas emissions (Hecobian & Collett, 2019, Abeleira

et al., 2017., McCarthy et al., 2013). Propane has an atmospheric lifetime of 3-4 days in the summer in

Colorado (Pollack et al., 2021) and has been shown to be emitted from liquid petroleum gas (Montero-

Montoya 2018). Propane, along with ethane, are key natural gas emission species (McCarthy et al., 2013).

This Light Alkane factor is believed to represent a regional long-lived ONG emissions profile with smaller

bouts of local emissions. Factors in PMF have been suggested to be split by atmospheric lifetime (Abeleira

et al., 2017, Pollack et al., 2021). The Light Alkane factor shows a seasonal cycle with a buildup of

concentrations in the winter. Similar, to the combustion profile, these higher concentrations may be

associated with emissions trapping within a shallower boundary layer and/or decreased concentrations

of the hydroxyl radical and increases in compound lifetime. The t/b ratio for this factor is 0.71, with the

prevalence of benzene over toluene also consistent with a non-combustion ONG source.
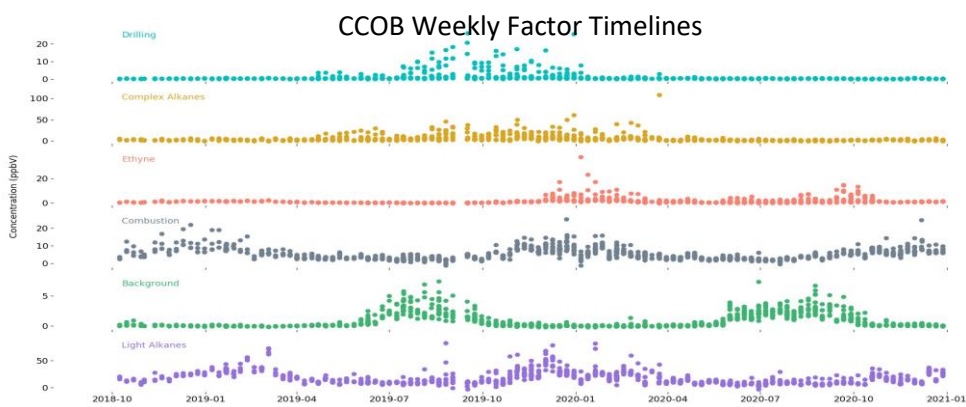
Figure 0-6: Time series associated with each CCOB weekly PMF factor

Medium, cyclic, and more complex alkanes contribute to the Complex Alkane factor. Compounds

with 50% or more of their total concentrations associated with this factor are n-heptane (57%),

cyclohexane (55%), 3-methylhexane (51%), methylcyclohexane (68%), 2-methylheptane (62%), and 3-

methylheptane (50%). Gilman et al. (2013) found C_2-C_7 alkanes and C_5-C_6 cyclic-alkanes to be tightly

correlated with propane which is an ONG tracer. This suggests the complex alkane profile is also

associated with ONG emissions. Similar factors have been labeled 'short-lived' ONG in the literature

(Abeleira et al., 2017, Pollack et al., 2021). The tracer ratios of this profile are 0.81 for i/n pentane and

2.70 for t/b. The i/n pentane ratio is slightly lower than previously proposed for the Greater Wattenberg

Area while the t/b ratio shows a relatively large contribution of toluene compared to benzene. Toluene

has a shorter lifetime (2 days) compared to benzene (2 weeks) and as PMF splits compounds by

atmospheric lifetime, most of the ONG benzene is associated with the longer-lived ONG factor. Previous studies with multiple factors associated with an ONG source have combined individual source factor i/n pentane ratios to reconstruct an overall ONG i/n pentane ratio by averaging the ratios across the factors (Abeleira et al 2017). Combining the Light and Complex Alkane factors, the i/n pentane ratio was 0.85 and the t/b ratio was 1.71.

The Drilling factor accounted for most of the heavy alkane concentrations with 100% of n-decane, 72% of n-nonane, and 31% of n-octane concentrations allocated to the factor. Heavy alkanes have previously been shown to be associated with diesel truck emissions (Hecobian & Collett, 2019) or gasoline (McCarthy et al., 2013), however, the compound profile observed here closely matches headspace analysis of VOCs observed from one of the drilling muds used at two of the pads and therefore this factor is referred to here as a Drilling factor. During the sampling period, three active ONG pads, Northwest-Parkway (Nwpkwy), Livingston and Interchange underwent drilling: Nwpkwy and Livingston used Neoflow drilling mud while Interchange used Gibson drilling mud. The headspace VOC composition measured for the Neoflow mud (see further discussion below) was similar to the Drilling factor composition suggesting this factor could be largely influenced by the type of drilling mud used.

Ethyne was the most abundant compound in the sixth factor contributing 74% of the total observed concentration followed by 23% of ethene, and 12% of benzene. The factor has an i/n pentane ratio of 1.05, close to the average in the full weekly VOC dataset and suggesting a mix between ONG and combustion emissions. The t/b ratio is very low at 0.20 which may imply a strong association with ONG or other non-combustion sources. Interestingly, ethyne and ethene are often considered combustion markers while smaller t/b ratios may suggest non-combustion ONG influence (Hecobian & Collett, 2019). This factor, therefore, by traditional considerations, could represent a mixture of two profiles; however, similar emission signatures were noted in other higher time resolution measurements during the sampling period as discussed below.

1.10.3.1 Spatial Pattern Analysis

For each factor, a spatial figure was constructed to help visually determine if the factor was associated with specific local ONG activities. Factor contributions were split into the sites at which the observations were taken, and site timelines were further split into periods of ONG activity (e.g., drilling, hydraulic fracturing, etc…) as determined by Table 0-1. All 18 sites were considered during this analysis. If a sample's mid-time fell within a week prior to the beginning of an activity or a week following an activity, it was labeled as observed during that activity. All three active ONG timelines were calculated separately. Site averages were then calculated and reported as the mean concentration during that activity and plotted in the spatial pattern figures. Average activity concentrations were overlaid on a map of the CCOB sampling locations with the plotted color corresponding to the concentration value. Color bars were set to have the factor's 85th percentile as a maximum and its 15th percentile as a minimum. Five activities (pad construction, drilling, hydraulic fracturing, tubing, and flowback) plus a background period were analyzed for Livingston and Interchange. Two types of tubing operation were reported by CCOB and if a factor was shown to correlate with this activity category, further analysis was performed. Nwpkwy was only broken down into three activities: background, pad construction, and drilling. Activities that showed correlations with increased concentrations are presented in the text; the entire analysis can be found in Appendix A.

1.10.3.2 Drilling factor
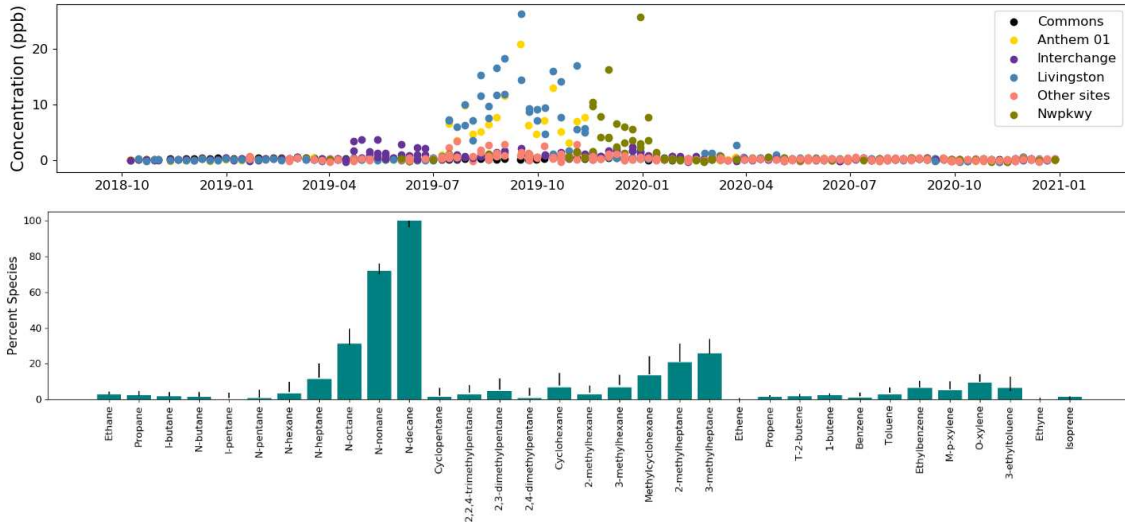
Figure 0-7: Concentrations of the Drilling factor split by active ONG sites and other sites. The percent of each of the VOCs associated with this factor is shown in the lower panel. All 18 sites are included in the timeline figure. Sites labeled in the legend correspond to the ONG sites, the background site at Commons, and any other increased concentration sites. Other sites include the remaining 14 sites.
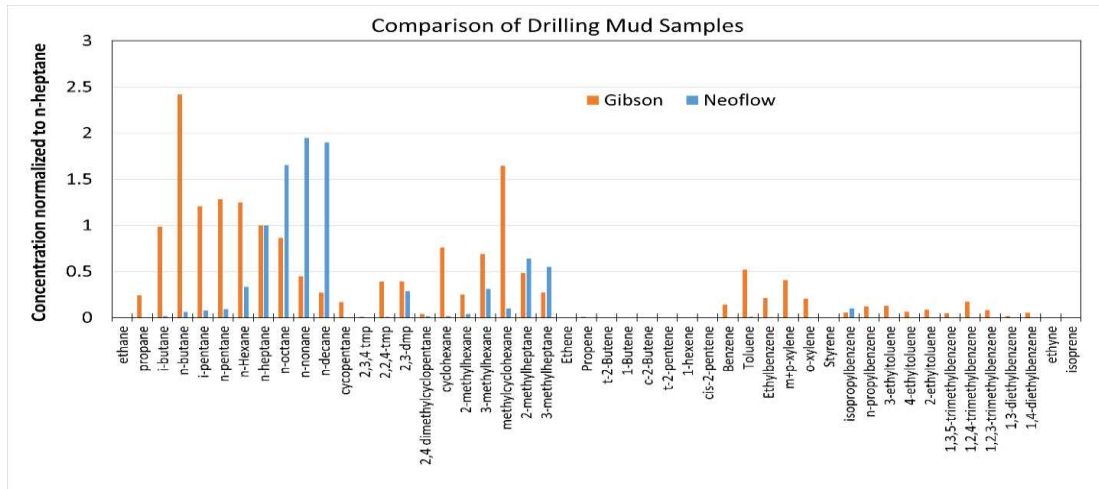

Figure 0-8: Headspace composition of Gibson and Neoflow drilling muds (normalized to n-heptane).

The Drilling factor had a large spike in concentration during a fairly narrow window of time (Figure 3-7). This high spike in concentration occurred mainly during drilling operations at Livingston and Nwpkwy. Livingston drilling began 7/5/2019 and ended 11/14/2019 while Nwpkwy drilling began 11/19/2019 and ended 1/10/2020 (a smaller contribution from this factor is shown in spring 2019 during drilling at Interchange). From Figure 0-7, many of the high factor concentrations were associated with either near-

pad sites at Livingston or Nwpkwy, or Anthem 01, a neighborhood impact site near the Livingston pad. During the study period, two different types of drilling mud were used. Gibson mud was used at Interchange until residents complained about odor. The mud was switched to Neoflow for drilling at Livingston and Nwpkwy. Both muds were sampled for their headspace vapor mixing ratios. The results are shown in Figure 3-8.
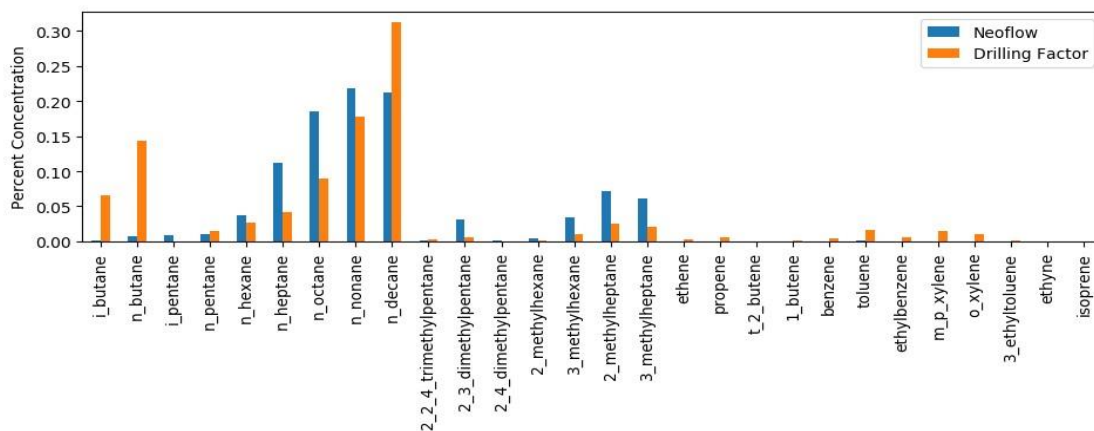
Figure 0-9: Percent contributions of the Drilling factor compound profile and the analyzed Neoflow sample.

The Neoflow drilling mud headspace analysis showed high contributions of heavy alkanes. The Drilling factor was so named due to its similarity to the Neoflow volatiles composition (Figure 0-) and its occurrence during drilling operations at Livingston and NWPKWY. The compounds most abundant in Neoflow volatiles, which ranged from 5-23 ppb within the headspace sample, were n-nonane, n-decane, n-octane, n-heptane, 2-methylheptane, and 3-methylheptane. Similarly, compounds that were the most heavily allocated to the Drilling factor (20% or more) were n-octane, n-nonane, n-decane, and 3-methylheptane with 2-methylheptane contributing 19% of its total concentration.

PMF splits each observed sample into contributions from the six chosen factors, effectively reducing the number of dimensions in each sample to six. Sites with samples containing the largest contributions from a single factor are considered the most influenced by that factor. Since the Neoflow mud was used for drilling at Livingston and Nwpkwy, it is expected that sites nearest these pads should be most heavily influenced by the Drilling factor.
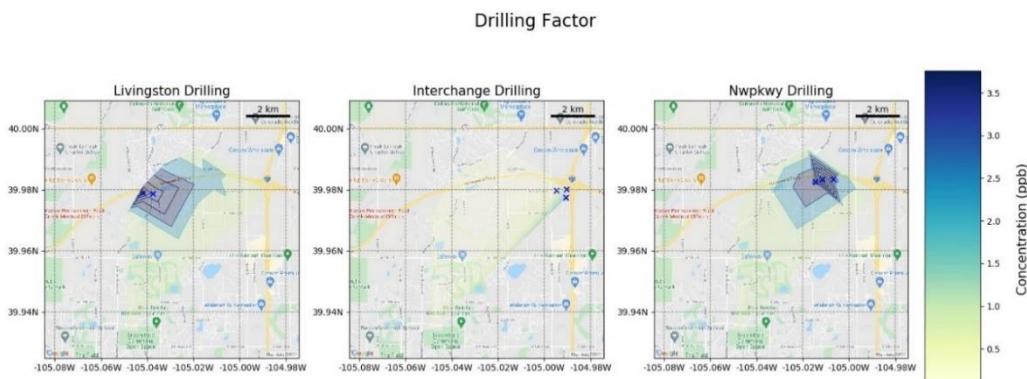

Figure 0-10: Pads of the activity in question are labeled with a blue x. The Drilling factor shows a strong correlation with the Livingston and Nwpkwy drilling periods showing high mixing ratios near the site and dissipating with distance.

Figure 3-10 confirms the association of this factor with the drilling periods at both Livingston and Nwpkwy with the largest average concentrations associated with near-pad sites and concentrations dropping off with distance. From this analysis, the origins of this factor are almost certainly activities on the Livingston and Nwpkwy pad during their respective drilling periods at these locations.

High concentrations of the Drilling factor are associated with individual pad sites during their drilling period and the factor profile resembles the Neoflow drilling mud VOC profile. Therefore, it is most likely that this factor is highly influenced by the emissions of this particular drilling mud. However, this factor makes only a minor appearance during drilling at Interchange where Gibson mud, with its different VOC profile, was used (Figure 0-7). Heavy alkanes such as hexane, heptane, octane, 2,3-methylpentanes, and 2,2,4-trimethylpentane may suggest ONG in the pre-production phase which includes drilling (Wilde et al., 2020).
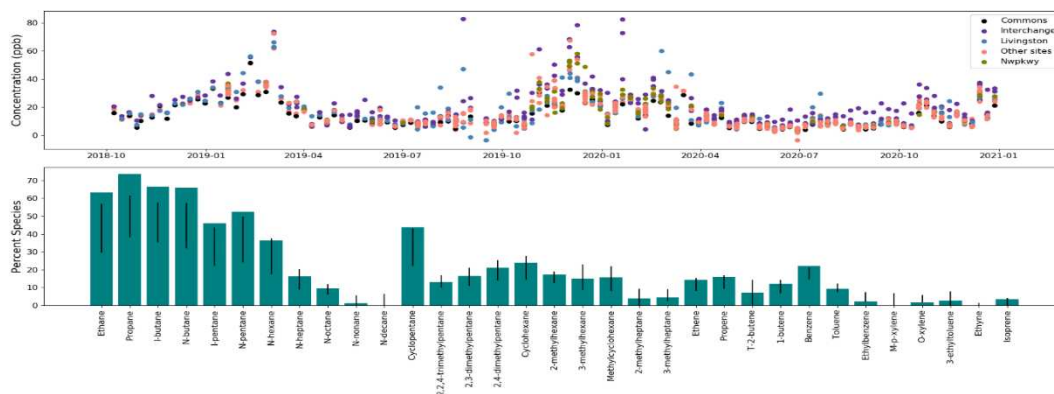
1.10.3.3 Light Alkane factor

Figure 0-11: Light Alkane factor timeline and compound makeup.

Twenty percent or more of twelve observed compounds were allocated to the Light Alkane factor. These included propane (78%), i-butane (71%), n-butane (70%), ethane (67%), n-pentane (56%), i-pentane (50%), cyclopentane (48%), n-hexane (39%), tetrachloroethylene (41%), cyclohexane (26%), 2,4-dimethylpentane (23%), and benzene (23%). This factor had the largest overall concentrations during the sampling period, and of all the samples over all compounds this factor accounted for 61% of the total measured concentrations. This factor had an i/n pentane ratio of 0.89. Gilman et al, (2013) observed a typical i/n pentane ratio of 0.86± 0.02 for the Wattenberg basin raw natural gas emission profile which suggests this factor may be of ONG origin.

Light alkanes with 2 to 6 carbon chains have been shown to be associated with ONG emissions (Hecobian et al. 2019; Abeleira et al. 2017; Pollock et al, 2021). Abeleira et al (2017) analyzed samples in the Northern Front Range of Colorado, finding a similar ONG-Long Lived factor with significant contributions of ethane, propane, i-butane, n-butane, c-2-pentane, cyclopentane, i-pentane, n-pentane, n-hexane, and cyclohexane. The factor timeline shows a seasonal cycle with higher concentrations in winter, suggesting that there may be a strong regional influence on the factor.

The spatial distribution of the average factor concentration over the sampling period was plotted to understand possible spatial correlations (Figure 0-12). The patterns suggests that this factor may also be partly associated with the active ONG sites, since higher average concentrations are spatially associated with CCOB ONG sites. However, recognizing the large seasonal cycle associated with this factor (Figure 0-11), when concentrations are broken down by time of year, local patterns are more difficult to determine. Concentrations associated with activity periods are many times spatially uniform as shown in Figure 0-13.
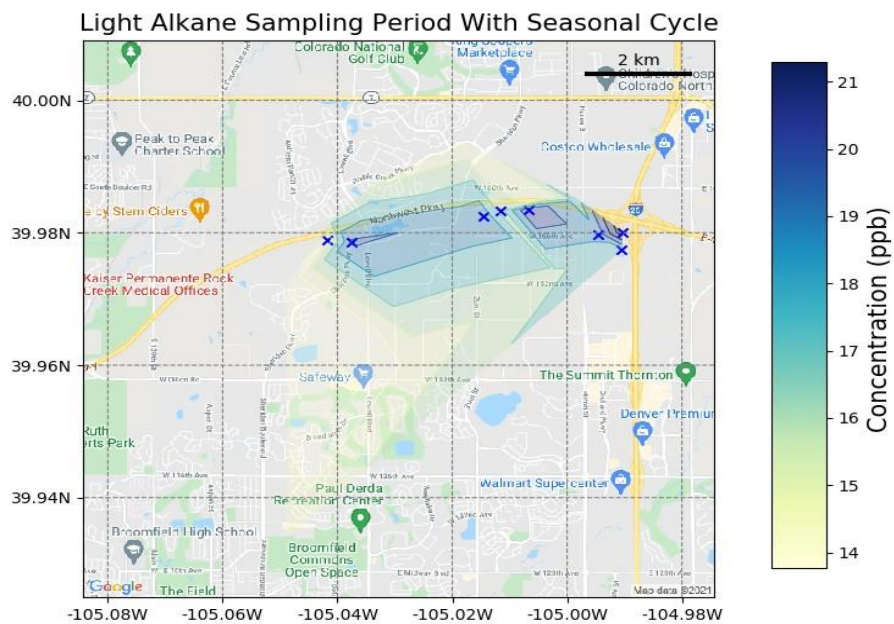
Figure 0-12: Average mixing ratios of the Light Alkane factor across the sampling network.
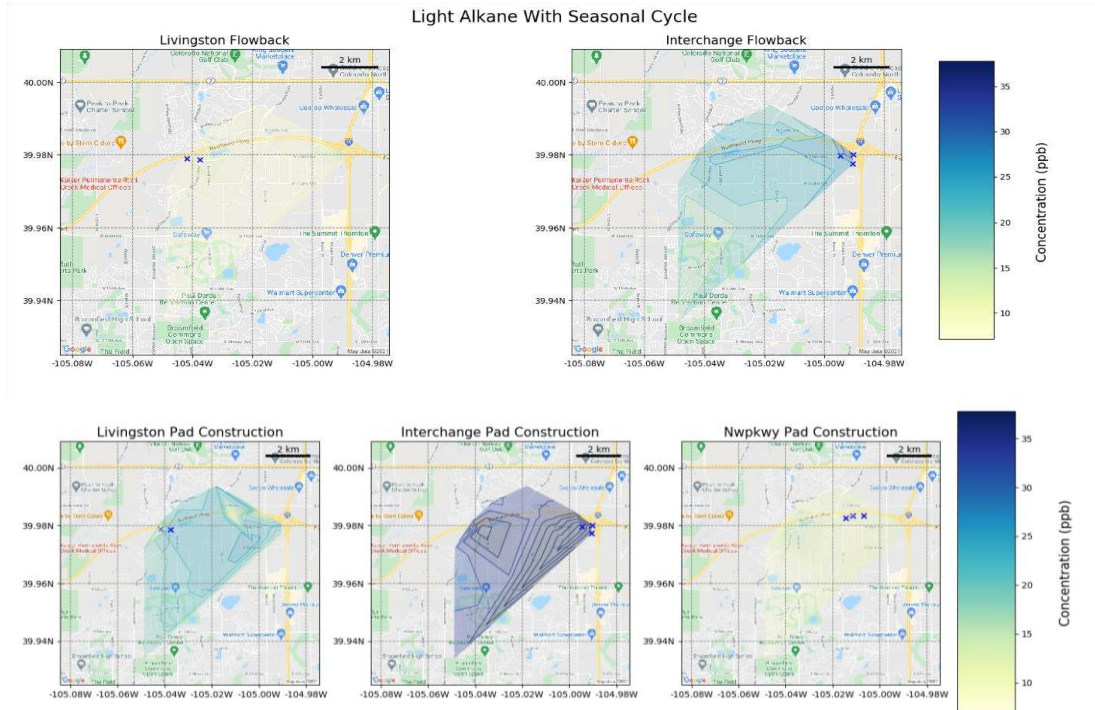
Figure 0-13: Examples of influence of the Light Alkane seasonal factor and difficulty discerning any local patterns within the spatial distribution.

To better distinguish between regional and local ONG influences, the seasonal cycle was calculated and removed from the time series using a Fourier transform. It was assumed that the regional ONG influence was well mixed and affected all sites equally throughout the sampling period. It was also assumed that the seasonal cycle was static from year to year. To quantify this seasonal cycle a Fourier transform was performed on the data from the Commons site, as it was consistently sampled throughout the full study period, and it was considered a regional background site separated from local ONG influences. Two weeks, 11/5/18 and 9/9/19, were unsampled during the observational period and values for these weeks were estimated using the mean of the values from the weeks prior and following. All sampled data from the Commons site was averaged into a seasonal cycle over the period and the frequency was evaluated from this average (Figure 0-14, left panel). The lowest frequency within the analyzed seasonal cycle corresponded to 53 weeks per cycle. The values associated with this cycle were subtracted from all observational data (Figure 0-14, right panel).
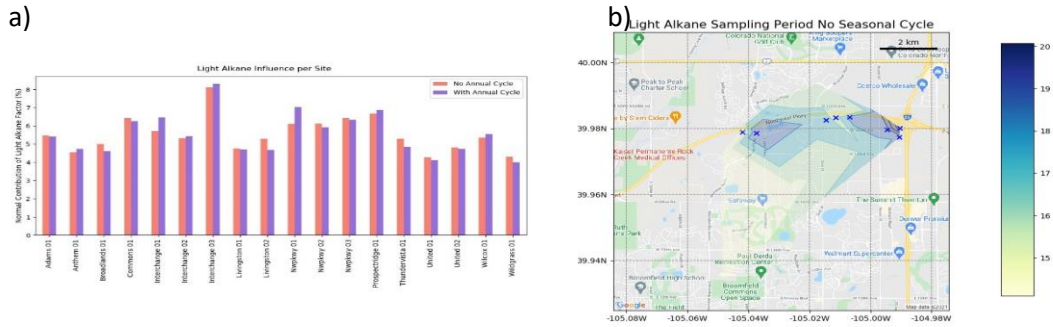
Figure 0-15: Panel a depicts normalized concentrations to the number of samples at each site. Overall site concentrations did not change dramatically suggesting that each site was influenced equally by the seasonal cycle. Panel b depicts the spatial pattern of the Light Alkane factor after removing the seasonal cycle.

Average concentrations at sites were not highly influenced by taking out the seasonal cycle (Figure 3-15). Some sites had a small increase in their average concentration while others decreased (Figure 3-15a). Spatially, the averages are similar to those with the seasonal cycle (Figure 3-15b), although there appears to be a slightly greater spatial association with the Livingston and Interchange sites after removing the seasonal cycle. With the seasonal cycle removed, the Light Alkane factor showed some spatiotemporal association with pad construction at Interchange, tubing operations at Livingston and Interchange, and flowback at Interchange (Figure 3-16). The association with pad construction is not expected, given the lack of subsurface ONG access during this operation, and was not observed at Livingston or NWPKWY. Pad construction at the Interchange site occurred between 1/2019 and 3/2019. In Figure 3-11 there is a clear spike during the Interchange pad construction period. However, IMPACT sites and other active ONG were impacted similarly suggesting this may be due to regional emissions. No other local ONG activity occurred during this period. The appearance of association at Interchange might simply reflect the prevalence of regional ONG sources NE of the CCOB sampling domain.
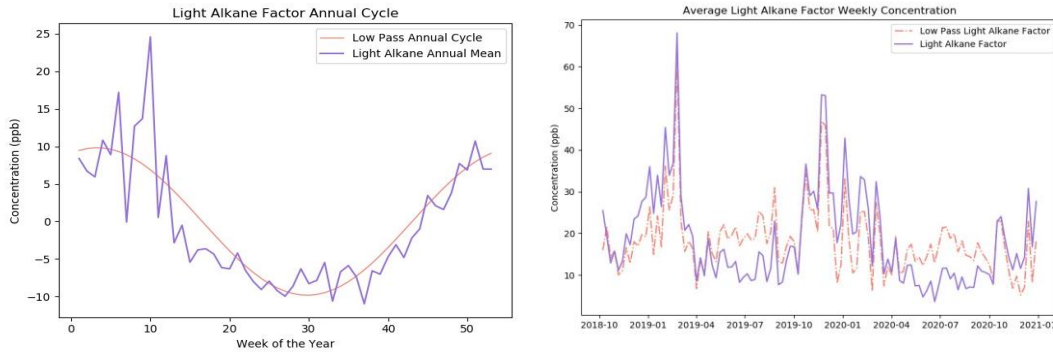
Figure 0-14: Left panel depicts the averaged seasonal cycle from the sampling period without the data mean (frequency is centered at zero). Purple is the averaged value, while the pink depicts the lowest frequency. The right panel shows the Light Alkane factor before and after the seasonal cycle was removed.
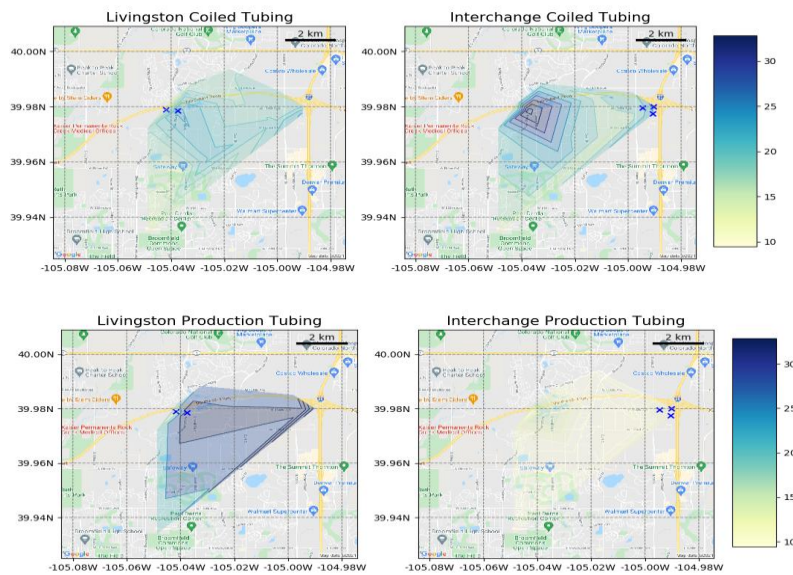

Figure 0-17: Concentrations associated with the two types of tubing reported by CCOB. Concentrations look to be more strongly associated with the coiled tubing activity as elevated concentrations are reported at both Livingston and Interchange.

There were two types of tubing operations that occurred at the ONG pads, coiled tubing operations and production tubing installation. To better understand how this factor was influenced by each type of tubing operation, the tubing spatial distribution was further broken down into the two tubing periods at Livingston and the two at Interchange. Figure 3-17 suggests that these types of emissions are more likely associated with coiled tubing, as increased emissions are seen at both pad sites during coil tubing operations while concentrations are only modestly increased at Interchange during production tubing.

The Light Alkane factor, although strongly associated with regional emissions, has also been

52

shown to have local sources. Emissions may be influenced, at a minimum, by coil tubing operations and flowback emissions. Some operations are of short duration, therefore, some other, especially short-duration operations might also be revealed as important contributors with higher time resolution sampling.
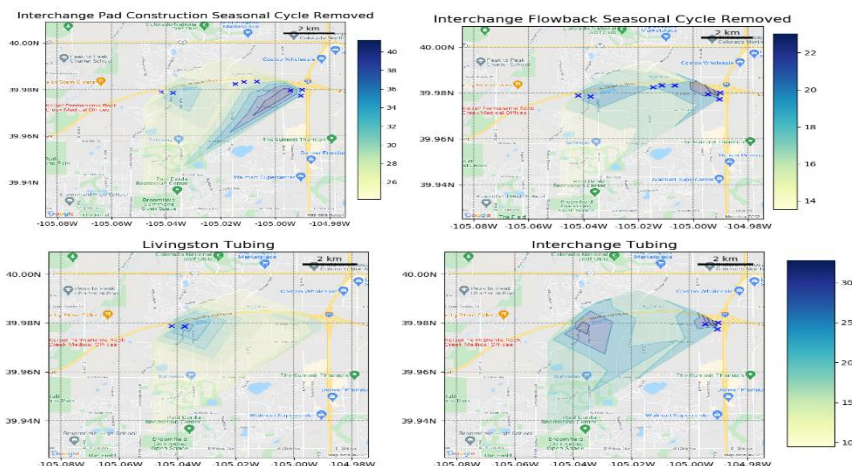

Figure 0-16: Light Alkane PMF factor with no seasonal influence. Concentrations are shown to be associated with, tubing, and flowback at Interchange and tubing at Livingston. Elevated concentrations are shown with pad construction, although other IMPACT and ONG sites, not

1.10.3.4 Ethyne factor

The Ethyne factor is so named due to the dominant contribution from ethyne (74% of ethyne is
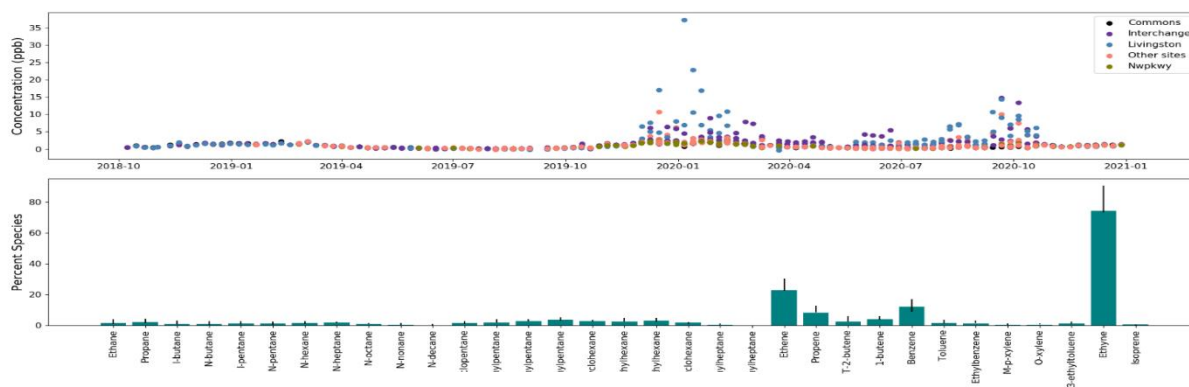

Figure 0-18: Ethyne factor timeline and associated compounds

apportioned to this factor). Thirty-three percent of ethene, twelve percent of benzene, and eight percent of propene were also associated with this factor. Ethyne is typically used as a tracer for combustion along with alkenes, a high i/n pentane ratio, and higher concentrations of toluene (McCarthy et al., 2013, Pollack et al., 2021, Gilman et al., 2013). Although this factor contained large portions of ethyne, and ethene, the

profile showed irregular contributions and no strong seasonal cycle as typically associated with a combustion emission profile. The factor's largest influence was during the 2019/2020 winter with secondary contributions in September 2020. The true source of this factor is not well understood and has received considerable attention as outlined below.

Since the source of this factor is not easily understood, it is useful to confirm that it represents an actual emission source and is not merely some artifact of the PMF analysis. Several other instruments deployed during the sampling period observed ethyne and benzene rich plumes, including measurements by Boulder AIR using a custom-built GC system, a PTR-MS deployed by CSU, and a CSU mobile plume tracking unit which used a cavity ring down spectrometer that measured methane and ethyne at 1 second time resolution and collected canister samples in ethyne-rich plumes.

During Fall 2020 the Boulder AIR GCs near the Livingston pad and at Soaring Eagle Park and the CSU PTR-MS located at Soaring Eagle Park measured repeated, high concentration VOC plumes that appeared to be transported from the direction of the Livingston pad. The composition of these plumes was unusual and not consistent with typical emissions from ONG operations. Concentrations of ethyne and benzene were high in these plumes and toluene/benzene ratios were very low, often below 0.2. In order to better confirm the source location for these unusual plumes, the CSU plume tracker was deployed to search for and further characterize the plume.

A drive on September 17th, 2020, captured a high ethyne plume which will be compared to the Ethyne factor for similarities. The plume tracker's driving path is shown in Figure 0-19a. High ethyne plumes were observed south of the Livingston pad on Sheridan Parkway (Figure 0-19b) while winds were coming from the direction of the pad. The plume-tracker sat in the plume during two instances, referred to as Plume 1 and Plume 2. The full timeline is shown in Figure 0-19c and each plume is broken down in Figure 0-20. Ethyne concentrations peaked at 68 ppb within plume 1 and 50 ppb in plume 2, far above background concentrations.
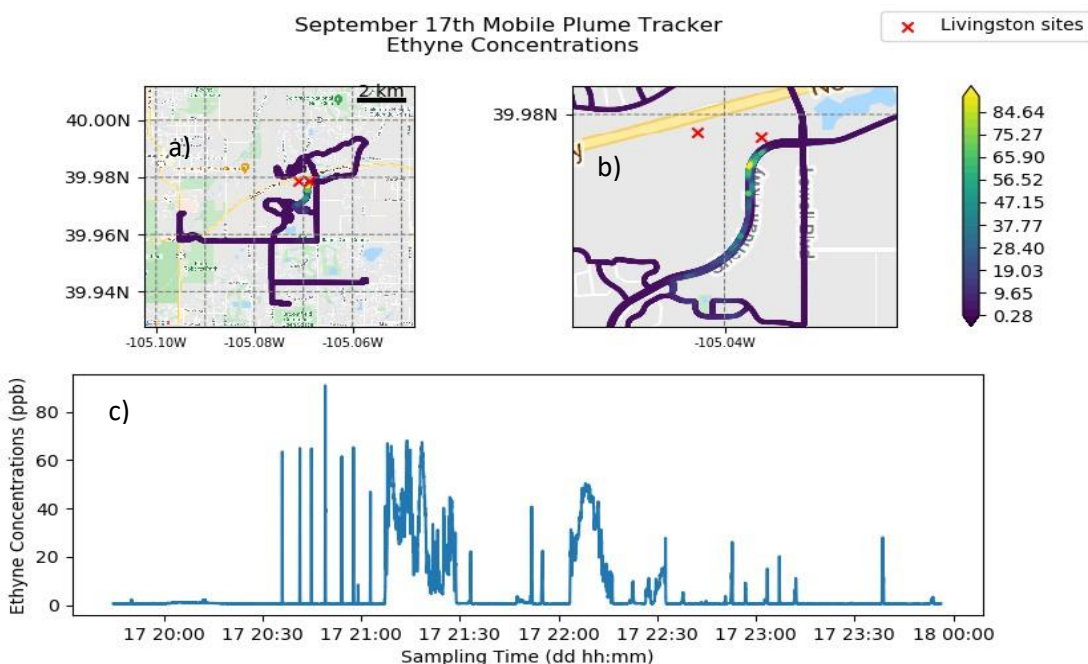
Figure 0-19: CCOB plume-tracker drive during September 17th, 2020. During the drive, an ethyne-rich plume was intersected several times shown by the ethyne concentration timeline. During two periods the plume tracker parked inside the plume and, six grab canisters

In total six 1-min grab canister samples were taken, four in the first plume and two in the second. Thirty-three compounds were reported and their concentration distributions within the two plumes are shown in Figure-20 a) and b). The canisters showed large concentrations of ethyne and ethene with average concentrations of 52 ppb and 36 ppb in the first plume and 50 ppb and 40 ppb in the second, respectively. The i/n pentane ratios for plume 1 and plume 2 were 0.99 and 1.04 with benzene-rich t/b ratios of 0.18 and 0.14, respectively. The abnormally large ethyne and ethene concentrations typically

suggest combustion, however, the low i/n pentane ratios and low toluene/benzene ratios suggest combustion is likely not the sources of these emissions. Ethane concentrations, a common ONG tracer, were not unusually high with a maximum of 28 ppb (Figure 3-22).

These observations from the plume-tracker, along with observations from the GC and PTR-MS systems at Soaring Eagle Park and Livingston effectively triangulated the location of this source,
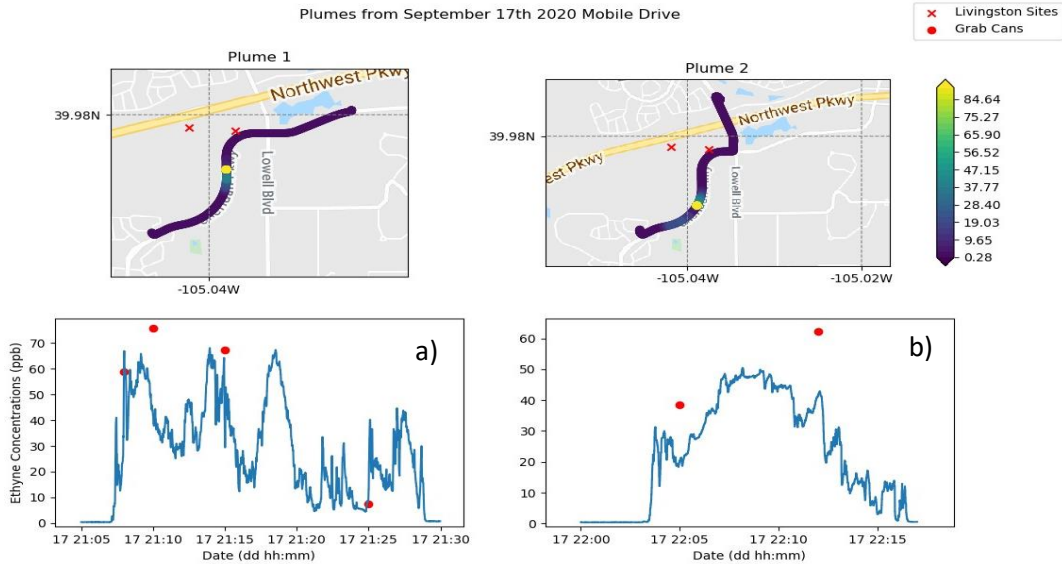

Figure 0-20: Plume 1 and Plume 2 locations within the September 17th drive. Ethyne concentrations from the analyzed grab canisters are shown along with the online mobile unit ethyne measurements.

constraining it to the location of the Livingston pad. These observations were shared with representatives from Extraction Oil and Gas. While the operator never confirmed a source for these emissions, a meeting scheduled to discuss the plumes was canceled by the operator after which the recurring plumes ceased to be observed. Remaining questions include the exact source of these unusual emissions plumes and whether they were occurring prior to their detection by high time resolution instruments deployed in summer 2020.

The ethyne PMF factor had maximum concentrations of 54.5 ppb for ethyne and 18.4 ppb for ethene. The i/n pentane ratio was 1.25 with a t/b ratio of 0.19. These parameters suggest the PMF analysis, even using weekly canister data, picked up an emission source with an unusual composition similar to that observed in transient plumes by the high time resolution measurements described above.
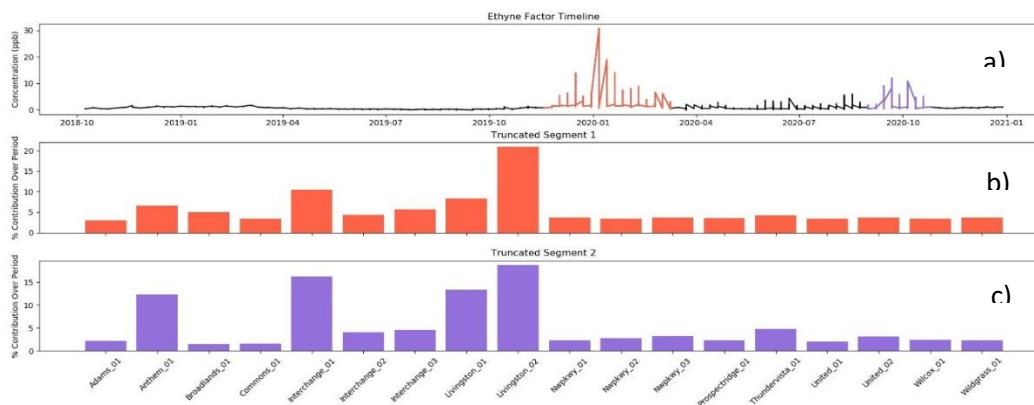

Figure 0-21: Ethyne factor contributions by site (panels b and c) during time periods with the greatest overall Ethyne factor contribution (panel a). During segments 1 (orange) and 2 (purple) sites near Livingston (Livingston 01, 02, and Anthem 01) and Interchange 01 show the largest influence.
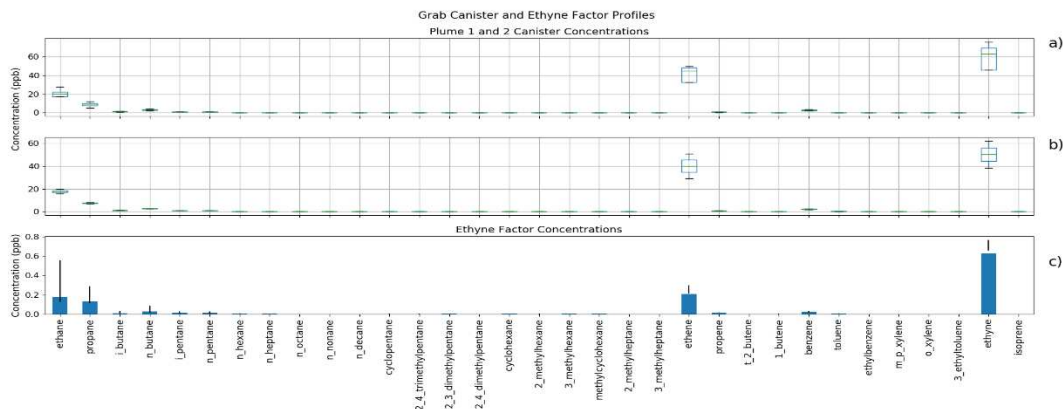

Figure 0-22: a), b) box and whiskers plots for concentrations in the grab canisters taken within plume 1 and plume 2 on the Sept. 17, 2020, plume tracker outing, respectively. Figures are given in terms of concentration (ppb). Panel c) depicts the concentrations of compounds in the sample with the highest Ethyne factor contribution.

Figure 3-22 compares the percent of compounds allocated to the Ethyne factor and the concentrations observed in the grab canister samples collected on the Sept. 17 plume-tracker drive. The Ethyne factor composition profile closely resembles the VOC composition in the grab canisters, with a similar compound profile and key compound ratios.

The Ethyne factor timeline shows two periods of large contributions during the winter of 2019/2020 and September/October 2020 (Figure 3-21 a). These contributing periods will be referred to as segment 1 and segment 2, respectively. Both segments show the largest contributions from the Livingston 02 site followed by Interchange 01, Livingston 01, and Anthem 01 (Figure 3-21 b & c).
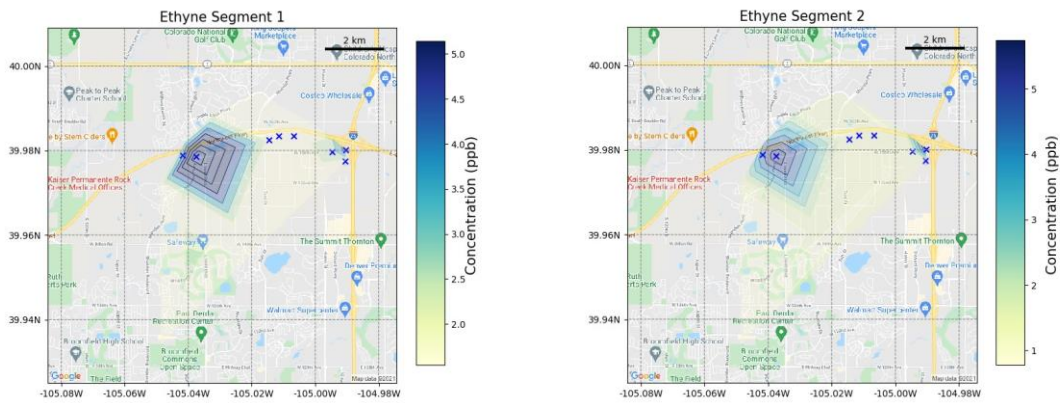

Figure 0-23: Spatial concentrations of segment 1 and segment 2 defined as the period between November 18th, 2019, and March 16th, 2020, and August 25th, 2020, and November 1st, 2020, respectively. There is a strong correlation between the Livingston pad in both segments and a small correlation with the Interchange pad.
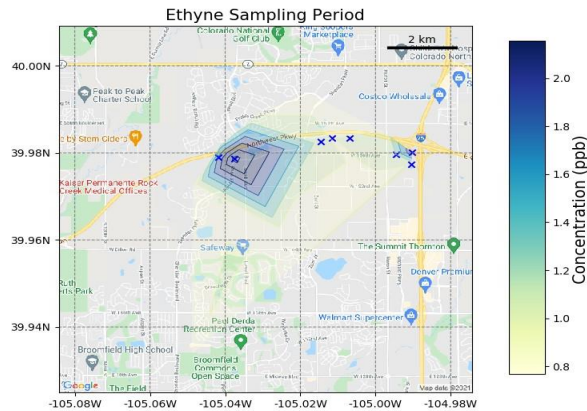

Figure 0-24: Ethyne factor sampling period. High concentrations are associated with the Livingston and Interchange Pad

A spatial analysis was performed for the full sampling period (Figure 0-24), and during the two high concentration periods shown in Figure 0-23. During the plume tracker outing, the primary source of these plumes was near the Livingston pad. The spatial analysis of the Ethyne factor shows a very similar

profile with most of the average mixing ratio originating from the Livingston pad. However, somewhat elevated concentrations are seen at the Interchange pad as well.

The two segments overlap with hydraulic fracturing and flowback activities at Livingston (Figure 0-25). Hydraulic fracturing occurred between 12/2/2019 and 2/13/2020 and falls into segment 1 of the Ethyne factor timeline while flowback of 4 wells at Livingston briefly overlapped segment 2 beginning in 4/15/2020 and ending 9/23/2020. There are slightly elevated levels at Interchange during flowback which took place between 10/2019 and 3/2020. However, there is not enough evidence to clearly correlate these pad activities with the observed Ethyne factor, especially since the factor composition is dissimilar to other measurements of fracking and flowback emissions (Hecobian et al., 2019). More likely, the factor represents the emission profile of a secondary activity – perhaps a malfunctioning piece of equipment or a maintenance activity – happening on the site and overlapping operational time periods.
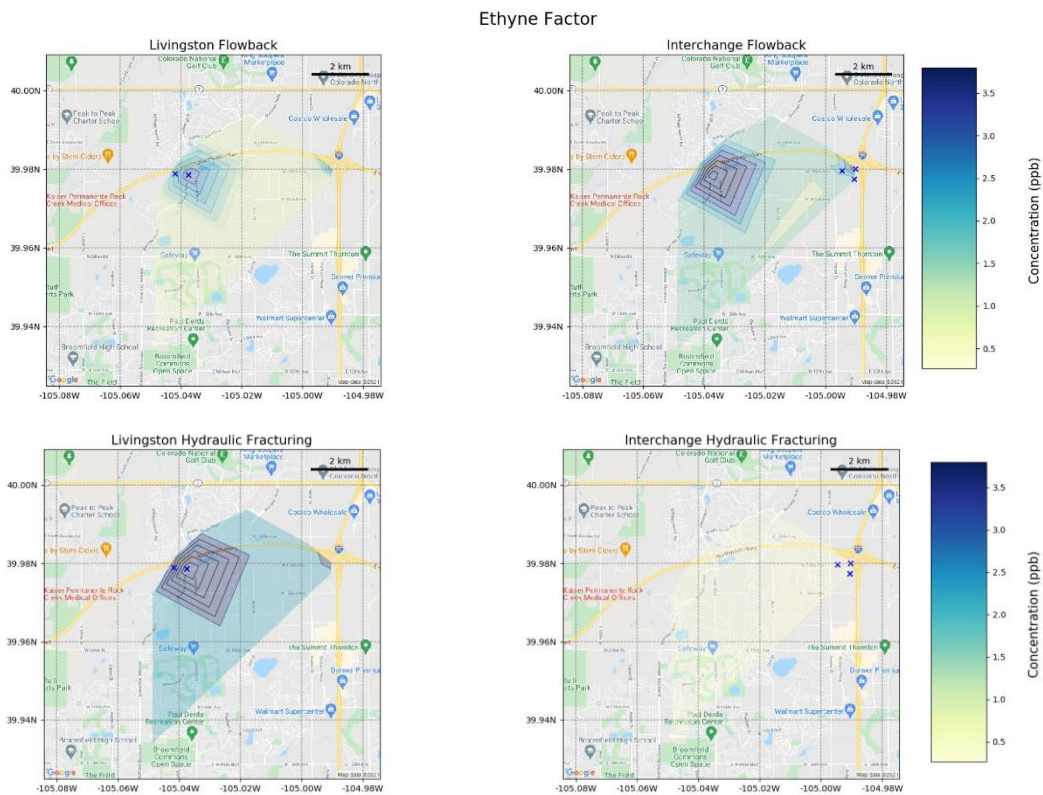

Figure 0-25: Average Ethyne factor mixing ratios during Interchange and Livingston flowback and hydraulic fracturing.

According to Whitby and Altwiker (1978), although automobile exhaust is typically the main

source of ethyne outside of industries or manufacturers that synthesize it, there may be additional significant atmospheric sources. Additional sources that emit ethyne due to a chemical reaction include petroleum refining, fuel combustion, waste burning, fires, diesel exhaust, jet engine exhaust and piston engine aircraft exhaust. Petroleum in CCOB was shipped off site for processing and waste burning was prohibited by CCOB (*Resolution NO. 2017-186*, 2017) and therefore it is unlikely this is the source. Diesel exhaust although associated with ethyne due to combustion processes, has a more robust emission spectrum and is also associated with heavy alkane and toluene emissions (Hecobian & Collett, 2019). Welding is utilized during various processes in the production and transportation of ONG for the creation of structures, gathering lines, and for maintenance and repair (Voestalpine, 2015).

Although ethyne is the largest contributing compound, the Ethyne factor is also associated with elevated concentrations of ethene, propene, and benzene. Ethene and propene are common oxyfuels for metal cutting (Bae et al., 2018), and there is evidence that benzene can be produced during the welding of painted steel (International Agency for Research on Cancer, 1990, National Center for Biotechnology Information, Acetylene, 2022, National Center for Biotechnology Information, Ethylene, 2022). Ethyne and benzene gases can also be produced through a paraffin hydrocarbon decomposition reaction catalyzed by the heat and plasma from the welding gun reacting with metal at the site being welded (Almostaneer et al., 2011). This suggests that this factor could be influenced by some type of maintenance activity occurring on the ONG pads that involves metal cutting, and welding and is categorized as an ONG associated factor, although the occurrence of these unusual plumes at night when no such operations could be seen on the pad raises questions regarding this hypothesis.
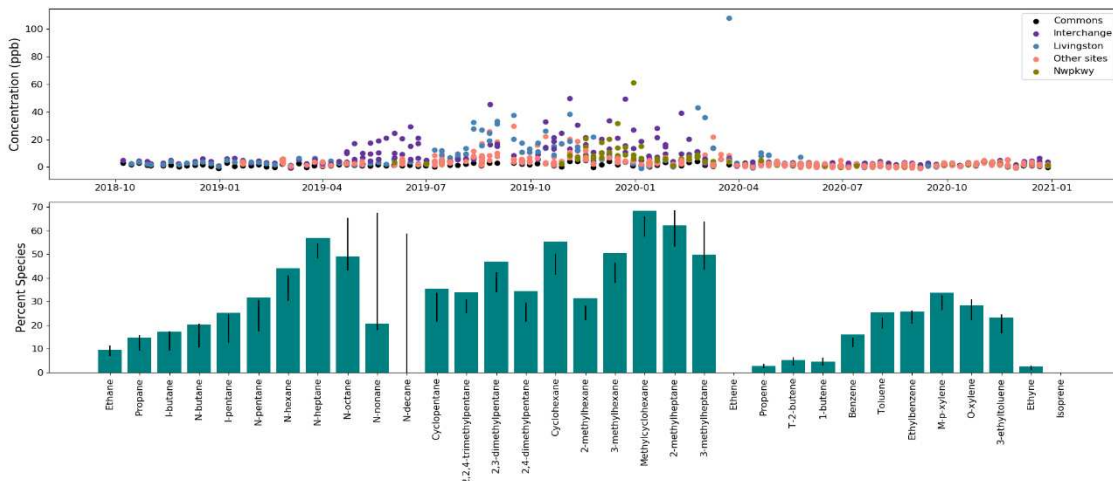
1.10.3.5 Complex Alkane factor

Figure 0-26: Complex Alkane timeseries and compound makeup. Samples taken at active ONG sites are labeled using separate colors while the remaining sites are plotted using the 'other sites' label.

The Complex Alkane factor is made up of several types of alkanes with the majority falling into the following categories: medium alkanes ($C_5 - C_9$), branched alkanes, and cyclic alkanes. Several aromatics (e.g., toluene, ethylbenzene, and xylenes) are also partly associated with this factor. Only fifteen percent of benzene was allocated to the Complex Alkane factor with a much larger concentration of toluene. The overall t/b ratio was 2.90, close to a typical combustion profile. The factor's i/n pentane ratio of 0.80 is more typical of an ONG profile. Previous work has suggested that PMF splits VOC factors by atmospheric lifetimes (Pollack et al, 2021). Toluene has a typical atmospheric lifetime of 2 days while benzene has a lifetime of 2 weeks which may explain why so little benzene was allocated to this factor enriched in higher reactivity compounds. Abeleira et al (2017) found a PMF factor in the Northern Front Range that contained larger concentrations of alkanes, cyclic alkanes, and aromatics and labeled it "ONG-Short Lived" and Pollack et al (2021) labeled a "Shorter-lived O&NG" based on an i/n pentane ratio ranging from 0.8 – 1.6 and higher concentrations of alkanes. These factors match closely to the one found here, leading this factor to be analyzed as a short-lived ONG factor.
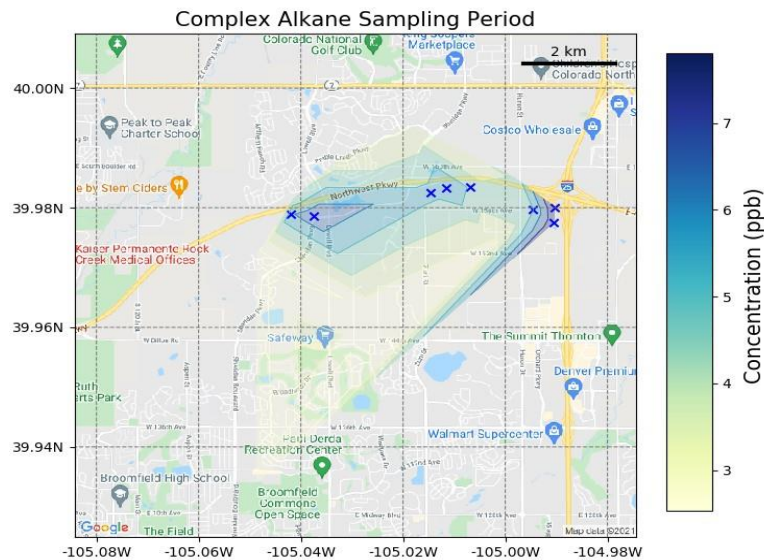
Figure 0-27: Average mixing ratios of the Complex Alkane factor over the sampling period.

A spatial analysis of average mixing ratios associated with this factor over the sampling period is shown in Figure 3-27. The spatial signature is very close to the Light Alkane factor's average mixing ratio (Figure 0-12) which is also associated with alkanes originating from ONG activities. Unlike the Light Alkane factor, however, this factor is not associated with a seasonal cycle, perhaps due to included compounds having a shorter lifetime that limits atmospheric build up. Absence of a seasonal cycle might also reflect the importance of operationally varying local ONG emissions on the factor's timeline.

The average concentration during each reported ONG activity was plotted on a map to determine areas of high and low concentrations (Figure 3-28). Higher than average concentrations were shown to originate from an active ONG pad during three activities: tubing at Livingston and Interchange, flowback at Interchange, and drilling at Livingston, Interchange, and Nwpkwy.

Figure 0- depicts the same information as Figure 0-28 but as ONG site timelines. The red dotted line shows the factor's 85th percentile or 7.04 ppb. During tubing and drilling at Livingston 6 of 10 and 32
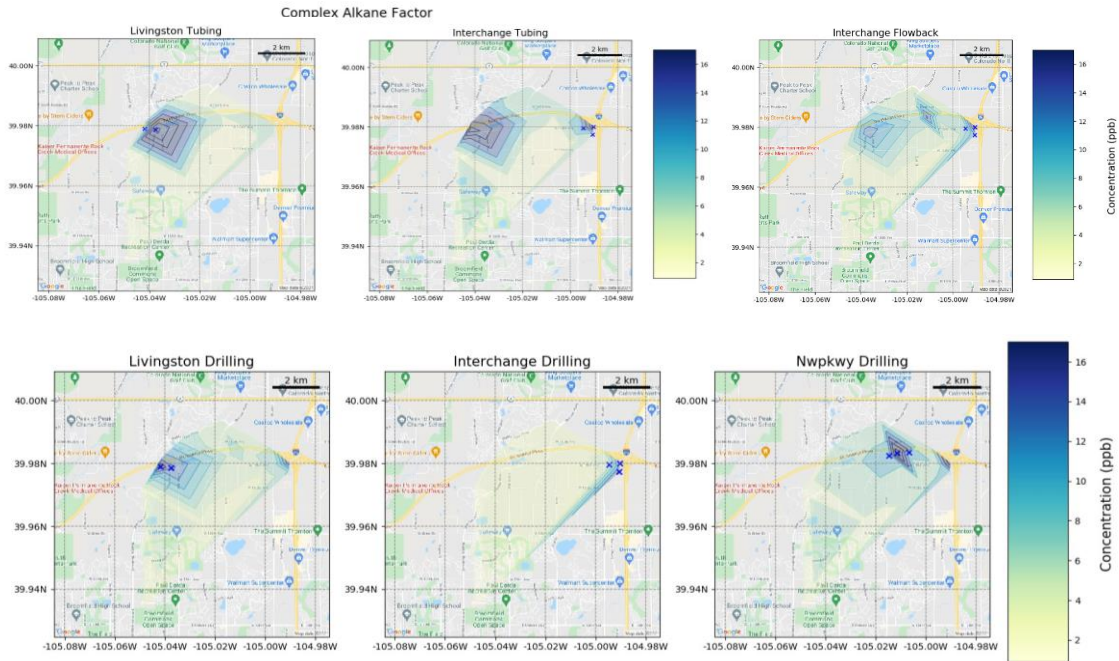
Figure 0-28: Average spatial concentrations during Livingston and Interchange tubing.

of 34 samples were greater than this value, respectively. However, only 5 samples of the 46 taken at the

Livingston site during flowback were above the factor's 85th percentile. Interchange showed large factor

concentrations during all three activities with 7 of 7, 17 of 28, and 43 of 68 samples above the 85th

percentile for tubing, drilling, and flowback, respectively. Nwpkwy only completed activities through

drilling during the study period. During drilling at Nwpkwy, 13 of the 17 samples returned concentrations

above the Complex Alkane factor's 85th percentile. Compounds associated with this factor are likely

emitted during tubing and drilling activities. The importance of this factor during flowback remains an

open question. It was clearly observed at Interchange but less so at Livingston. It should be noted that

VOC concentration increases overall were limited at Livingston during flowback, relative to observations

at Interchange. The difference may reflect improved operations management at Livingston, where wells

were completed after Interchange and where local government and nearby residents were closely
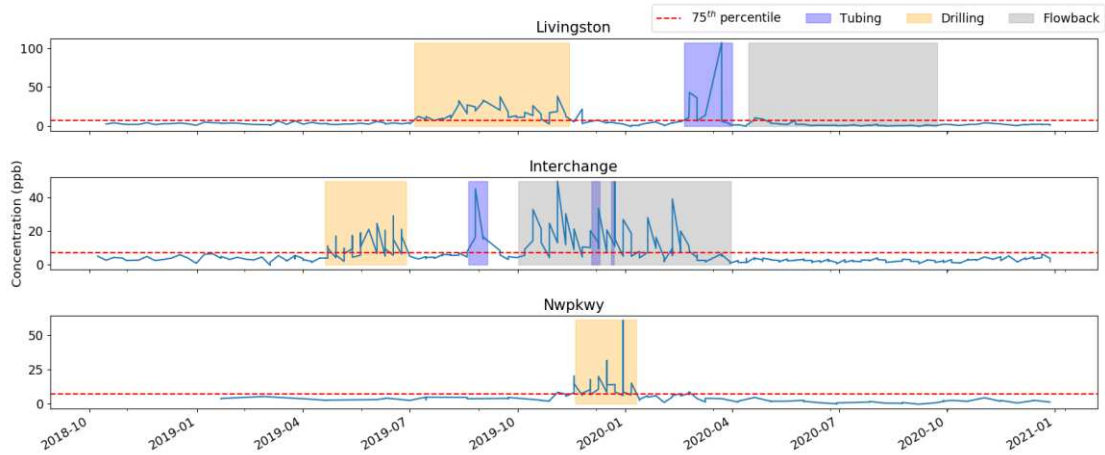
scrutinizing operations.

Figure 0-29: Complex Alkane timeseries at each active ONG site plotted against three associated ONG activities. The red dotted line shows the 85th percentile of the Complex Alkane factor or 7.04 ppb.
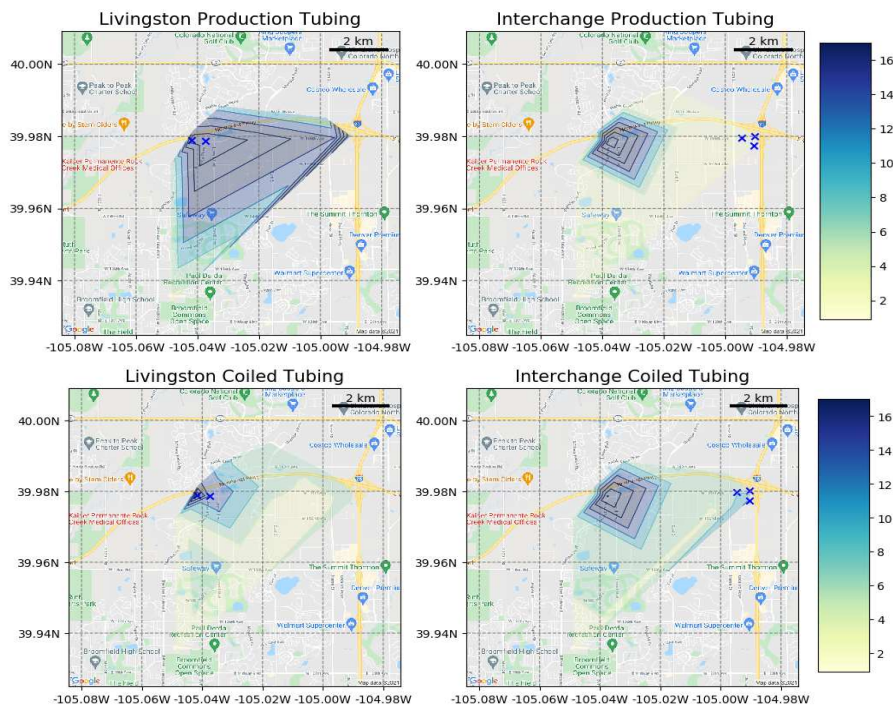

Figure 0-30: Compound emissions associated with the Complex Alkane factor from the Livingston and Interchange sites. Increased emissions are seen during coiled tubing at both sites.

Within the tubing operations at Livingston and Interchange, the coiled tubing phase produced higher than average concentrations at both the Livingston and Interchange pads, while only Livingston showed increased concentrations during production tubing operations.
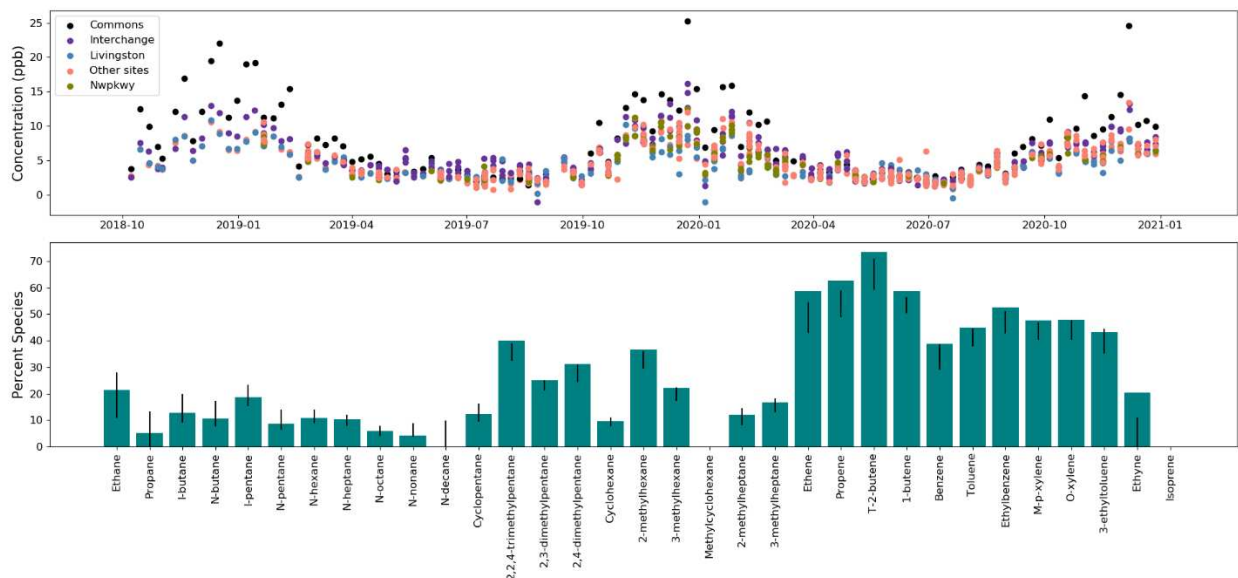
1.10.3.6 Combustion Factor

Figure 0-31: Combustion factor timeline and compound makeup as determined through PMF.

The combustion factor was so identified due to the high percentage of alkene compounds, an i/n pentane ratio of 2.33, a t/b ratio of 1.90, and a seasonal cycle with higher concentrations in the winter. Average factor concentrations are shown in Figure 3-29. The highest average concentrations are seen at the Commons 01 site. This site is located at a sports field in Broomfield which becomes inundated with cars during events and is also located in a more populated area surrounded by homes and close to heavily trafficked thoroughfares. It is also closer to the Denver metro area and its northern suburbs. These factors all likely contribute to locally elevated concentrations from combustion (e.g., traffic) sources.

To better examine spatiotemporal contributions from local combustion sources, the seasonal cycle was removed from the timeline. Due to Commons contributing most strongly to the combustion factor, Anthem 01 was used as the reference site. Anthem 01 was a neighborhood site consistently sampled throughout the study with (just two weeks were unsampled). Missing values for these two weeks were interpolated as the mean of the weeks prior and following. Observations from Anthem 01 were averaged to create an average seasonal cycle (Figure 3-31 a) which underwent a Fourier transform where

a lowpass filter was applied to return the lowest frequency -- one cycle per 53.2 weeks. Values from the

lowpass filter were subtracted from the original time series data to obtain the filtered timeseries (Figure

3-31 b).

Once the seasonal cycle was removed, the factor's influence on each of the sites was once again

calculated. There was no significant change in the spatial pattern and no correlation with any of the ONG

activities. Therefore, this factor is not considered as an ONG factor.
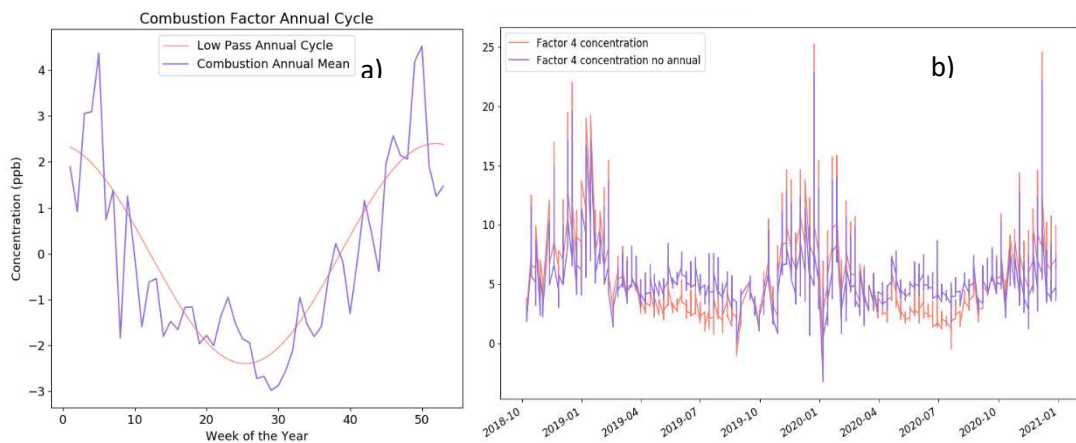

Figure 0-33: Fourier transform of the annual cycle from Anthem 01. A frequency of 53.19 weeks per year was removed and the weekly average of all samples is shown in the Average Combustion Factor Weekly Concentration.
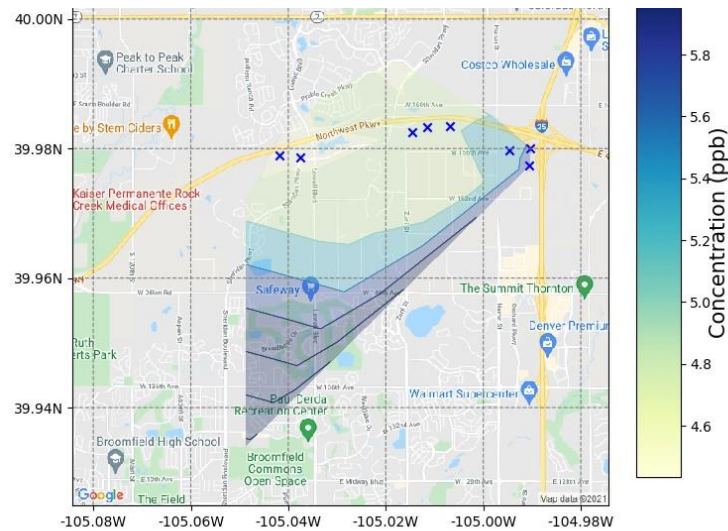

Figure 0-34: Average spatial concentrations after the extraction of the seasonal cycle. Concentrations do not appear to be correlated with any ONG sites but appear to be more closely associated with proximity to I-25 and major roads in southern Broomfield.
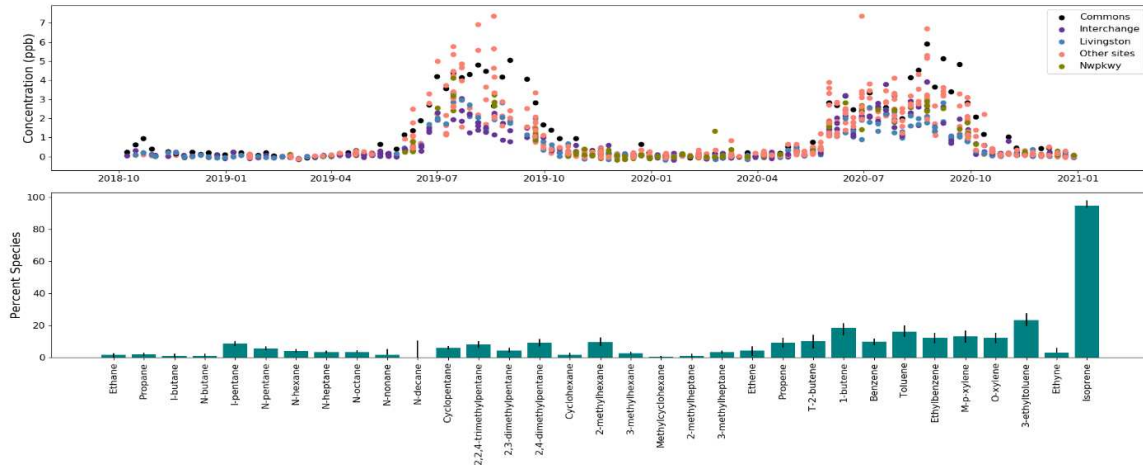
1.10.3.7 Background Factor

Figure 0-35: Shows the Background factor profile and compound composition. 'Other sites' are the remaining IMPACT sites. The factor was strongly influenced by isoprene which was reflected in the factor timeline which shows higher concentrations in the summer and very small mixing ratios in the winter. No site visually contributes to the factor more than another.

The Background factor was associated with a strong seasonal cycle and included 95% of the isoprene concentrations. Several aromatic compounds also contributed to the factor. A similar factor was found in a study done by Hecobian and Collett (2019) who found a Background factor consisting of mainly isoprene and some mixed aged vehicular exhaust including alkenes and aromatic VOCs. The contributions of biogenic and anthropogenic emissions likely indicate these compounds covary in the atmosphere. This factor was analyzed without removing the seasonal cycle, mainly due to factor concentrations dropping to zero during the winter months. When a simple seasonal cycle was removed, an unintended secondary frequency was added to the transformed data.

A spatial analysis of factor contributions is shown in Figure 3-34. The three active CCOB ONG pads appear to be along a corridor of lower average factor concentrations. This is likely due to their location with a lack of nearby biogenic sources due to a barren landscape and central highway (E-470).
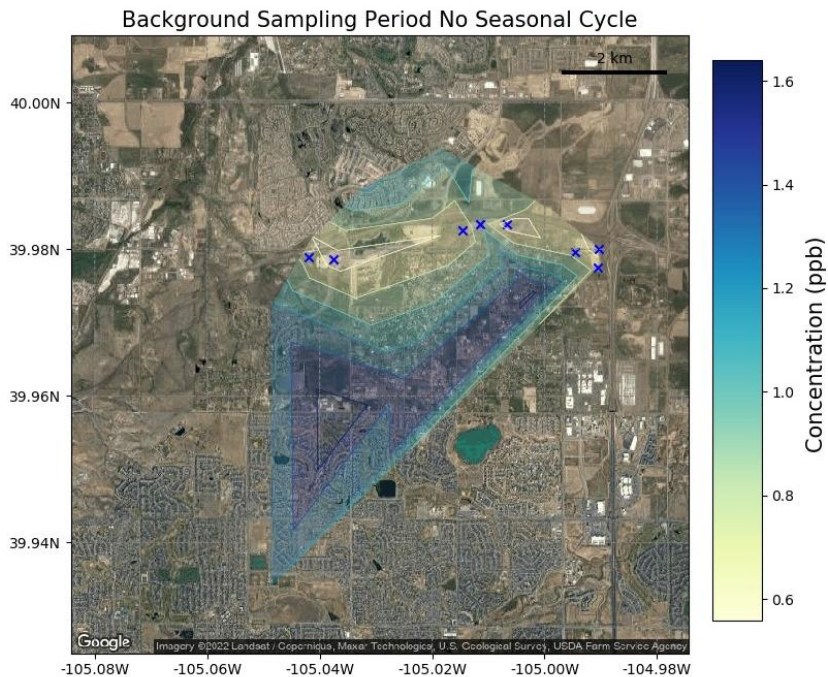
Figure 0-36: Average concentrations from each site are plotted on a map of CCOB. A satellite map was used to help depict possible biogenic sources through imagery. High mixing ratios appear to the south of the sampling region and look to begin again to the north of the E-470 highway.

1.10.3.8 Benzene analysis

Benzene is classified as a Hazardous Air Pollutant (HAP) meaning it is known or suspected to cause cancer or other serious health effects (*Oil and Natural Gas Production Facilities: National Emission Standards for Hazardous Air Pollutants (NESHAP)*, 2021). Benzene is emitted by combustion processes and is found in ONG deposits. Consequently, it can be emitted by a wide range of activities in the region, including ONG drilling, completion, and production activities as well as traffic, industrial operations, and wildfires. Because it is relatively abundant in emissions and has one of the lowest health guideline levels for human exposure, its emission is highly relevant to public health.
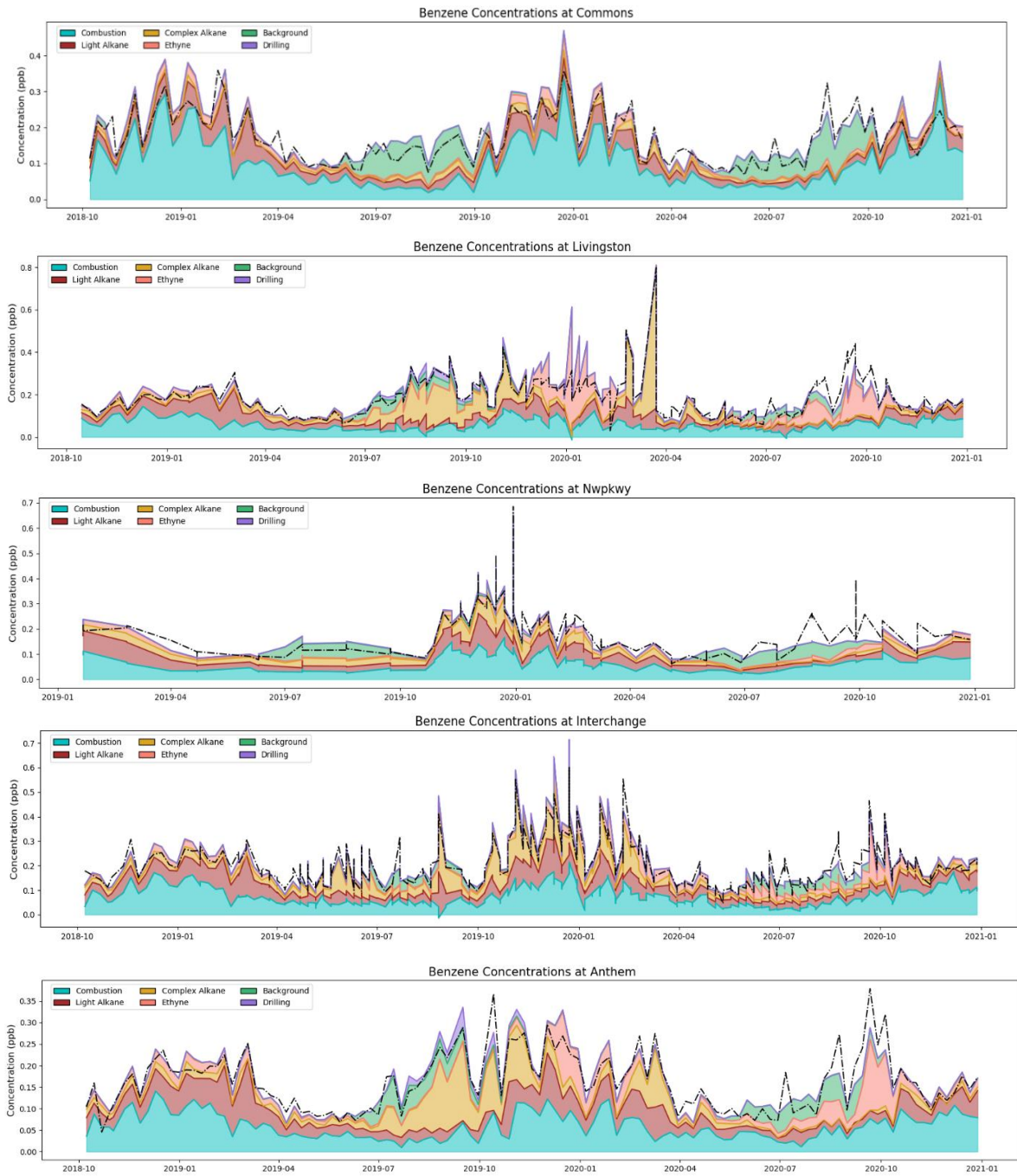
Figure 0-37: Contribution of benzene over the sampling period from each PMF factor against observed benzene concentrations by location. ONG sites are summed. Factors are stacked from largest contributing source to least based over all sites.

Time-resolved contributions to measured benzene at individual sites by each PMF factor are shown in Figure 3-37. The PMF algorithm fit the Benzene profile well with a coefficient of determination of 81%. Overall, the combustion factor accounted for the single largest contribution to average benzene concentrations across the full sampling period. There are localized periods in which the benzene concentrations are strongly accounted for by PMF profiles other than combustion. The Complex Alkane factor showed strong influence at the Livingston and Anthem sites between 7/2019 and 4/2020 with a large spike at Livingston occurring during tubing operations. There are also two distinct periods in which the Ethyne factor accounts for most of the benzene seen at Livingston and Anthem. These two periods align with segments 1 & 2 discussed in earlier sections. In the summer, the Background factor accounts for most of the benzene at the Commons and Nwpkwy sites.

The combustion factor accounted for 39.0% of reconstructed benzene profile (0.07 ppb average per sample) across the entire network and sampling period, followed by the Light Alkane factor at 22.2% (0.04 ppb average per sample), the Complex Alkane factor at 16.0% (0.03 ppb average per sample), the Ethyne factor at 12.1% (0.02 ppb average pers sample), the background at 9.7% (0.02 ppb average per sample), and the Drilling factor at 1.2% (0.002 ppb average pers sample). Adding together ONG-related factors, the average total ONG contribution to benzene is 51.5%.
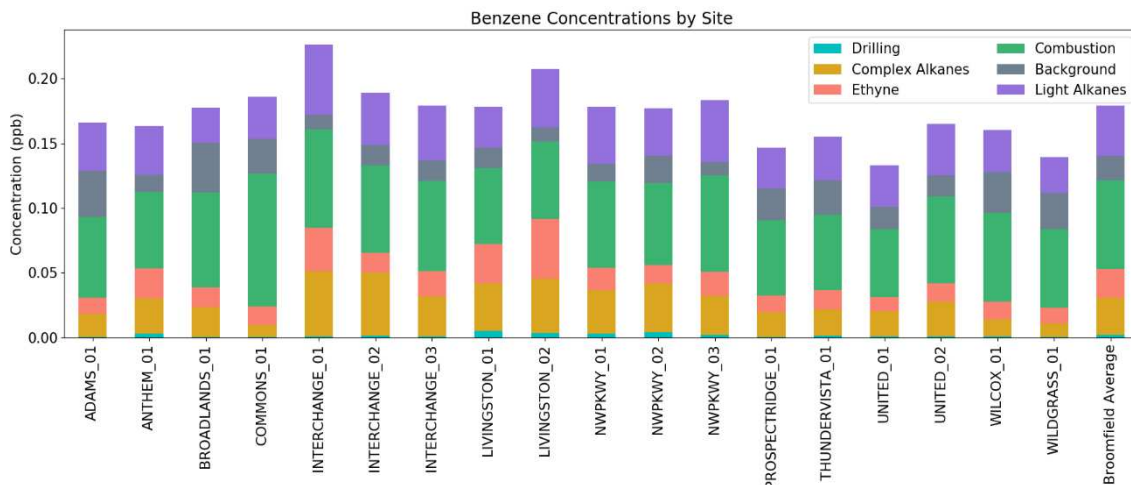

Figure 0-38: Average benzene concentrations at each site within the CCOB network

Benzene concentrations were broken down by site and factor contribution. The largest average benzene concentrations were observed at the Interchange 01 site, followed by Livingston 02. The combustion factor is the largest contributor to benzene across all sites and most notably at the Commons site as the site was found to be the most heavily influenced by the combustion factor. The Ethyne factor is shown to disproportionately contribute to average benzene at the Livingston and Interchange pads, consistent with the origination of this emission factor from these pads.

1.10.4 Spatial Impacts Summary

An exploratory method using multiple linear regression was applied to the ONG PMF factors to determine if IMPACT site timelines could be significantly explained by four driving sites, the three active ONG sites (Livingston, Nwpkwy, and Interchange) and the regional background site (Commons). The full analysis can be found in Appendix B. Local versus regional ONG impacts on sites around CCOB are difficult to determine based strictly on PMF factor analysis due to large contributions of both regional and local ONG operations to ambient concentrations, especially in the DJ Basin. IMPACT PMF timelines were reconstructed as a combination of the driving profiles to try to quantitatively estimate impacts from specific local operations. The theory behind this analysis is that sites in the CCOB receive varying contributions of ONG-related VOCs from both regional and local ONG emissions based on changing activity profiles and meteorology. Assuming the four driving profiles adequately represent the influence of local and regional ONG emissions, is it possible to determine how IMPACT sites are individually influenced by local ONG activities vs. regional emissions? This analysis was only performed for PMF factors found to relate to local ONG activities including the Ethyne factor, Light Alkane factor, Complex Alkane factor, and the Drilling factor.

Multiple linear regression was chosen as it fit the data best for reasons that follow. For this type of analysis, all five sites – the four drivers and one impacted receptor – needed to have an observation during the same week. The number of samples per analysis ranged from 15-49 weeks which did not allow for a more complex analysis method without the chance of overfitting. When calculating a coefficient for the influence of each driving timeline, linear regression analyzes each driver while holding others constant which allows for direct comparison between regressed coefficients. Coefficients represent the predicted change in the dependent variable (IMPACT site) for a unit change in each independent variable (ONG or background site), when driving timelines are theorized to be prior to the predicted variable (Hoyt et al., 2006), as they are here. A p-value significance test was performed on each coefficient to determine if it the relationship found mapped to the larger population of the dependent IMPACT site variable.
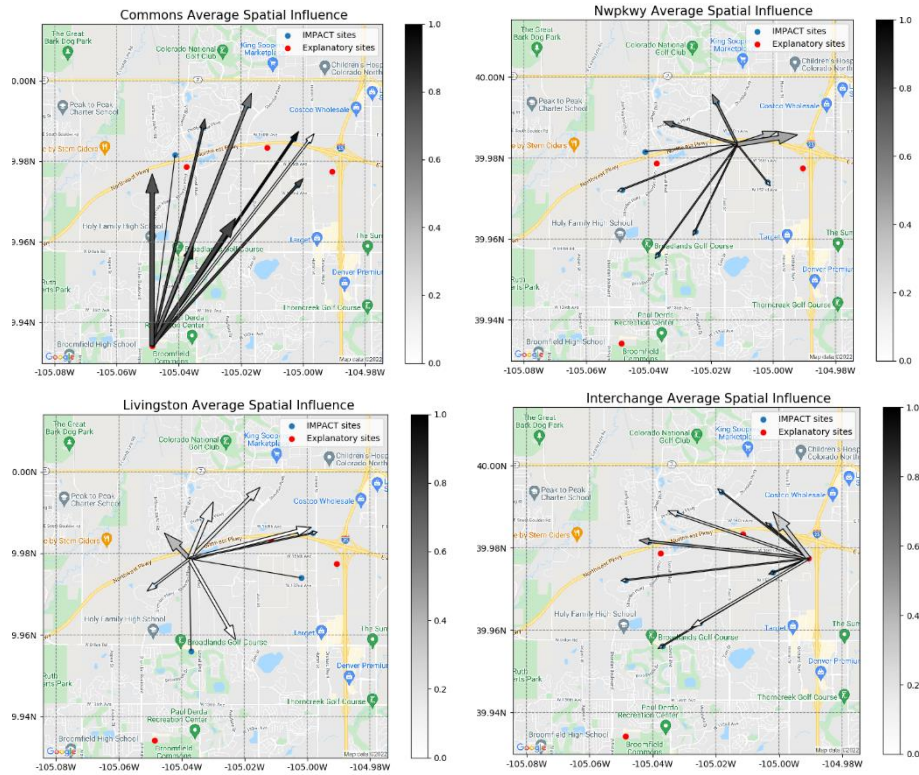
Figure 0-39: Summary of linear regression and causal impacts by the local and regional ONG sites. The width of each arrow represents the number of factors found to significantly impact the surrounding sites while the color represents the average coefficient.

Figure 3-37 depicts a summary of the linear regression findings. The four factors explored, Drilling, Ethyne, Complex Alkane, and Light Alkane, influenced the IMPACT sites differently. The arrow width in

Figure 0-3 represents how many of the four factors had a significant influence on the IMPACT site. Larger widths indicate that more factors were a significant driver of concentrations at that IMPACT site. Colors represent the average regression coefficient of all significant factor coefficients. If two factors were found to be a significant driver of an IMPACT site, this color represents the average of the two factor coefficients.

Overall, the regression approach worked well with an average coefficient of determination equal to 0.75, meaning this method captured most of the variance observed at the IMPACT sites. Commons, the regional background site influenced the most sites with the highest average coefficient as seen in Figure 0-3. Active ONG sites significantly explained sites to the north more consistently than to the south, with sites closer in distance typically associated with a larger coefficient. Overall, these results suggest that regional emissions exert the strongest influence on variations in VOC concentrations at many CCOB locations but that local ONG operations also impact air quality at nearby IMPACT sites.

There are a number of limitations to this analysis. First, linear regression assumes a linear relationship between independent and dependent variables. Relationships between emissions sources and observational locations likely can not be described solely by a linear relationship. Many dispersion models use a Gaussian dispersion which takes wind direction and speed into account (Chen et al., 2020). Second, the analysis as conducted assumes that the influence of a driving site on an IMPACT site is fixed and constant over the period of analysis while we know that ONG activities and emissions vary in time across the study period. Third, the true relationship between impact and emissions also includes a time lag. Due to the low time-resolution, weekly sampling, this time lag relationship could not be captured within this model. Finally, within this framework, independent variables are not truly independent as all sites are influenced by the regional background. When there are no local ONG emissions, a certain concentration means that either profile, the ONG site of interest or the Commons background/regional site, can reasonably explain the IMPACT site variance.

1.11 CAMML
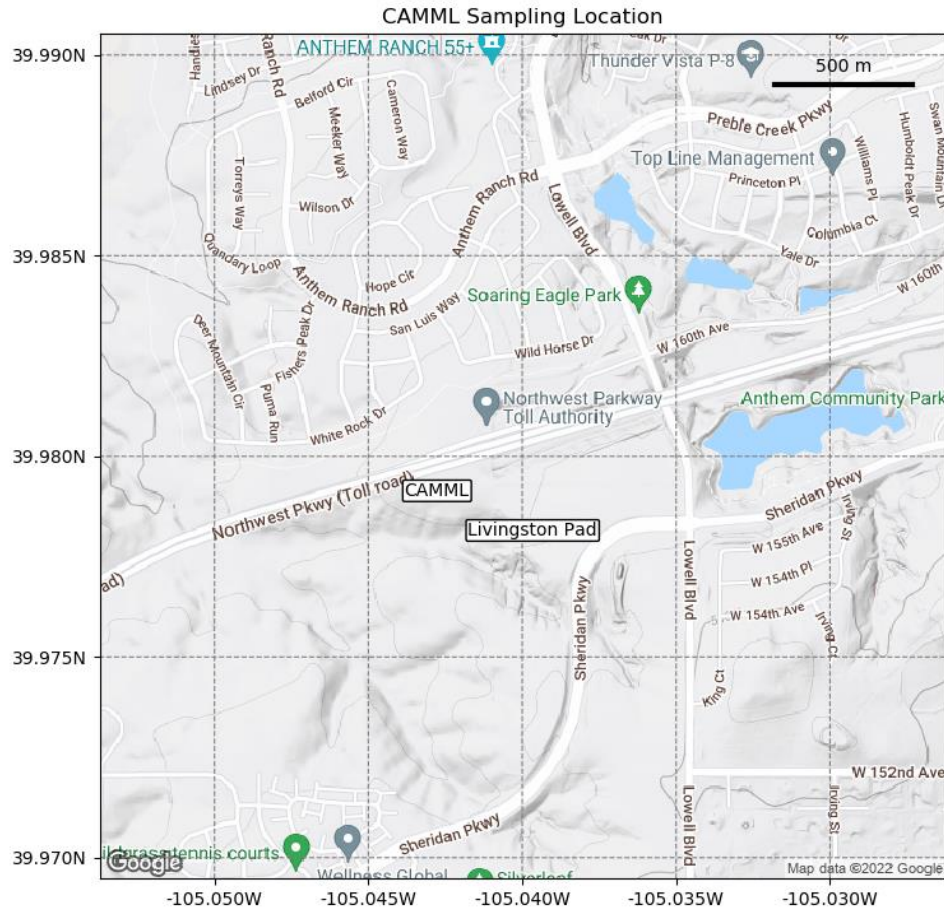
Figure 3-40: CAMML sampling location located NW of the Livingston pad.

The Colorado Department of Public Health and Environment deployed an online GC and other air quality monitors in its Colorado Air Monitoring Mobile Laboratory (CAMML) to observe five periods of ONG preproduction near the Livingston pad in the City and County of Broomfield (CCOB). The instrument was deployed to the northwest of the Livingston pad and sampled during the baseline before any pre-production or production phases occurred, during drilling, hydraulic fracturing, mill out, and flowback. Sampling periods are depicted in Figure 3-38. The deployment schedule made seasonal trends difficult to quantitatively analyze.

Figure 0-41: CAMML sampling periods

1.11.1 Compound Variations

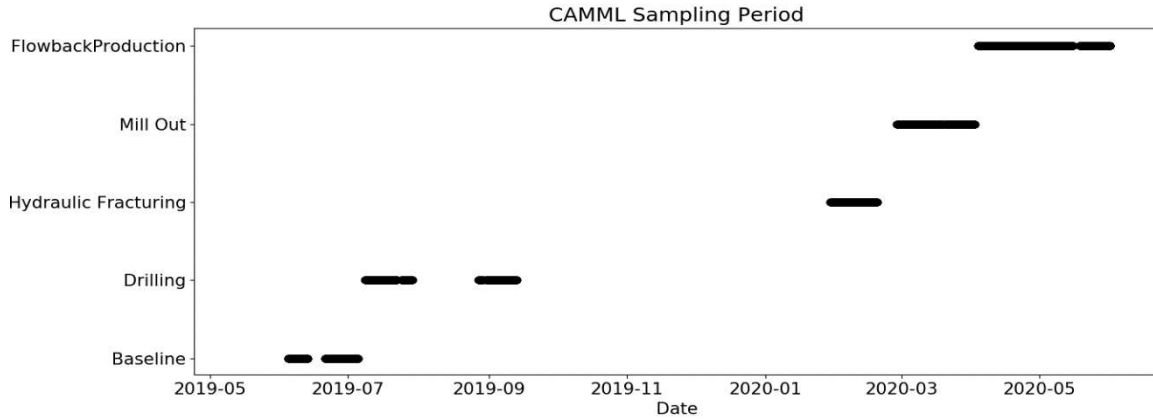The average diurnal variations of BTEX concentrations are plotted according to activity type in Figure 0-4. The drilling period (fall 2019) shows the largest concentration levels and diurnal variability for all BTEX compounds where the largest peaks were observed in the early evening. BTEX concentrations appeared to be most strongly influenced by the drilling period which is notable given that almost no benzene was apportioned to the weekly canister PMF Drilling factor. BTEX concentrations peak at hour 19 during the drilling period. Wind direction was examined further to determine if this time of day was associated with a predominant transport pattern. Figure 3-40 shows that there was no apparent dominant wind direction during all hours or between 18:00 and 20:00. The weekly canister PMF Drilling factor did
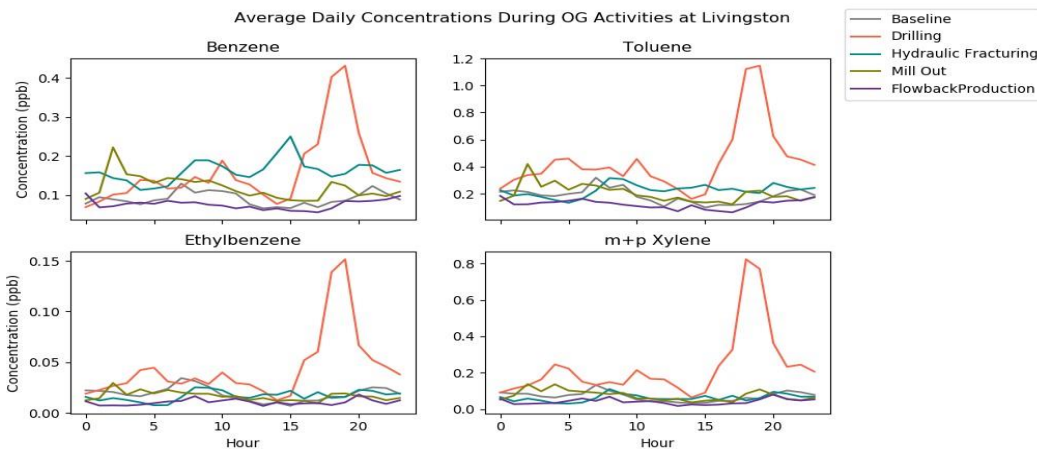

Figure 0-42: Average daily concentrations during each deployment of the CAMML. OG activities correspond to the Livingston pad.

find benzene emissions to be strongly associated with drilling at Livingston and headspace analysis of the Neoflow drilling mud used at Livingston was rich in n-decane and other heavy alkanes. Benzene and n-decane have a coefficient of determination of 0.92 during the Drilling period, indicating that the two compounds strongly covary, while this drops to 0.65 for other development periods with an overall coefficient of determination equal to 0.85 for the entire period.
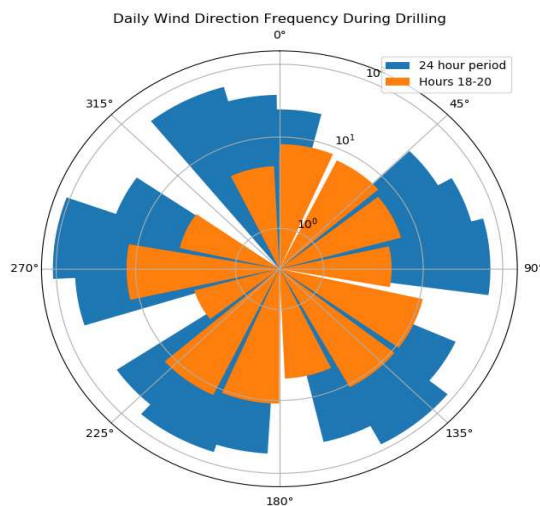
Figure 0-43: Daily wind direction frequencies during the drilling period. The concentric axis is on a log scale. Blue shows the full 24-hour period while orange is strictly when the BTEX spike occurs in Figure 3-40. There appears to be no associated wind direction at this specific time of day.

1.11.2 PMF Factors

Twenty-six compounds were analyzed by PMF in the CAMML hourly resolution dataset, including ethane, propane, isobutane, n-butane, cyclopentane, isopentane, n-pentane, isoprene, n-hexane, methylcyclopentane, benzene, toluene, n-octane, ethylbenzene, m+p-xylene, o-xylene, n-nonane, n-decane, n-undecane, PM2.5, PM10, NO_x, O_3, and methane anomalies. N-undecane was labeled as weak due to a S/N ratio of 0.7 and n-dodecane was labeled bad due to a S/N ratio below 0.5. NO, NO_2, and total CH_4 were not included in the analysis due to overlap with included NOx and methane anomalies. Five factors were judged to represent the dataset best. A four-factor solution did not include a combustion factor while a six-factor solution broke up a particulate matter factor in an unintuitive manner.

The five-factors in the PMF solution (Figure 3-42) were interpreted as representing an ozone factor, light alkanes, combustion, particulate matter, and complex alkanes. No biogenic Background factor resulted from the CAMML PMF factor set. For five factors, PMF fit isoprene at an $r^2 = 0.03$ and only at eleven factors did the model fit isoprene with an $r^2 > 0.15$ at 0.96. Additional factors at an eleven-factor solution did not make physical sense and therefore the biogenic factor was foregone. The intermittent measurement schedule by operation rather than consistently across seasons may have hampered identification of a biogenic factor.

The five CAMML factors were analyzed using the built in DISP and bootstrap methods. The largest change in Q -- the minimization function -- after running DISP was -0.139, which was much less than 1% of the Q robust values, and no factor swaps occurred. The bootstrap analysis was run 100 times and the Complex Alkane factor was mapped to the combustion factor 4 out of the 100 times. Given the small values of these error estimations, the five-factor solution was considered robust enough to analyze. In the five-factor solution, the compounds labeled "Strong" had an average $r^2 \sim 0.78$. N-decane – which was the only compound labeled "Weak"—had an $r^2 = 0.86$. The following analysis gives a brief overview of each factor and the reasoning behind the factor name chosen.

The combustion factor had t/b and i/n pentane ratios of 2.16 and 1.68, respectively. Both ratios suggest a combustion source. The most prominent compound in the factor was NO_x – a combustion emission. Other compounds associated with this factor, at lower levels, include BTEX and the methane anomaly.

The Light Alkane factor had high concentrations and fractional contributions of lighter alkanes. Ethane is a good marker for ONG activity given that its atmospheric sources are almost exclusively from natural gas activities (Orak et al., 2021). Colorado's Front Range has a high number of ONG wells and emissions from these operations that affect the region, along with local emissions at the Livingston pad. Thirty-eight percent of the methane anomaly concentrations were allocated to this factor. The ONG

nature of this factor is also reflected in an i/n pentane ratio of 0.77 and a t/b ratio of 0.47. This t/b ratio is very low and may partly reflect differences in atmospheric lifetimes between benzene and toluene (Pollack et al., 2021).
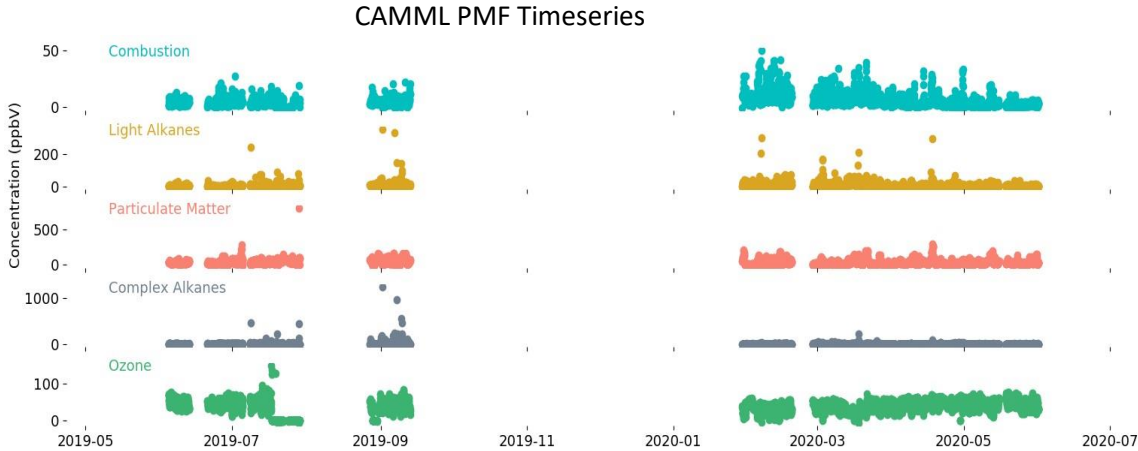
Figure 0-44: CAMML factor temporal profile for all five PMF factors.
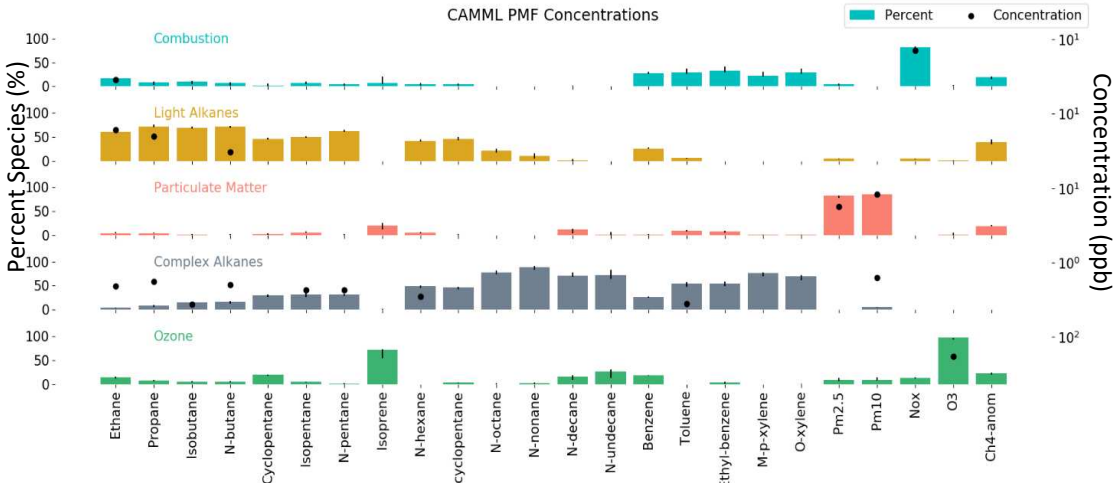
Figure 0-45: CAMML factor compound profiles for all five PMF factors

The Complex Alkane factor shows a similar compound makeup to fresh oil and gas emissions (Hecobian et al, 2019b). This factor also showed higher mixing ratios during the drilling period with 62% of the overall concentration being accounted for during this period with only 21% of the total number of observations. This factor may represent a mixture of the Complex Alkane and Drilling factors obtained in

PMF analysis of the weekly CCOB VOC data. Alkanes are emitted from various sources associated with ONG production including fuel evaporation and fuel combustion in the industrial processing of fuels (Bari and Kindzierski 2018). Like the weekly PMF Complex Alkane factor, the t/b ratio is larger than expected for an ONG profile at 4.33. However, this may reflect an atmospheric lifetime splitting between toluene and benzene (Pollack et al., 2021). The i/n pentane ratio was 0.98. The diurnal cycle over the entire sampling period shows a peak in concentrations in the evening, similar to the peak shown in BTEX concentrations in Figure 3-39.

The Ozone factor contained much of the ozone and isoprene in the dataset. This factor did not include any toluene and therefore had a t/b ratio of 0. The contributions from the factor are consistent across the sampling period suggesting a regional influence. The i/n pentane ratio for the factor was 4.32. Most of the isoprene concentrations were allocated to this factor which may have been due to similar diurnal variations.
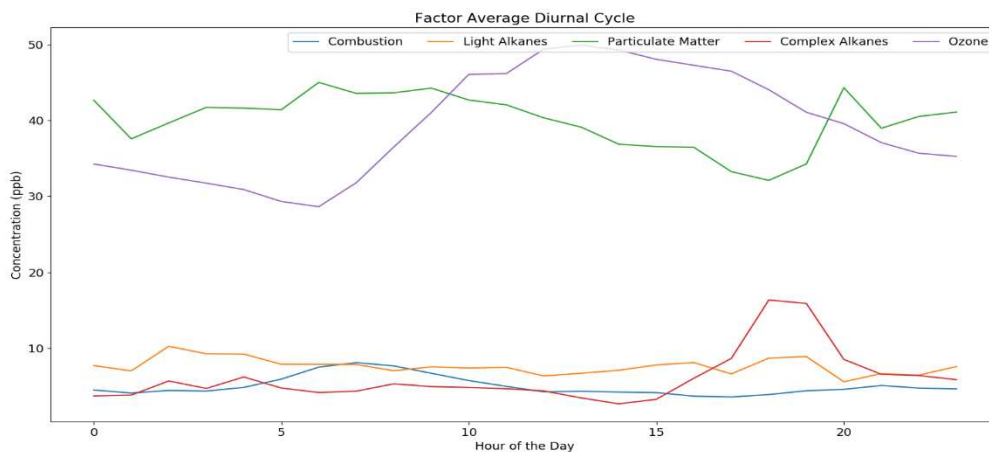
Figure 0-46: CAMML diurnal cycle over CAMML sampling period

The particulate matter factor had the largest contributions from both $PM_{2.5}$ and PM_{10} with only minor contributions of other analyzed species. Its separation from the other VOC related factors suggests that key PM sources differ from those dominating VOC levels in the Broomfield atmosphere. The diurnal cycle of the factor does not correlate with any of the other factors (Figure 3-43) further separating it from the other VOC related factors.

1.11.3 PMF factor discussion
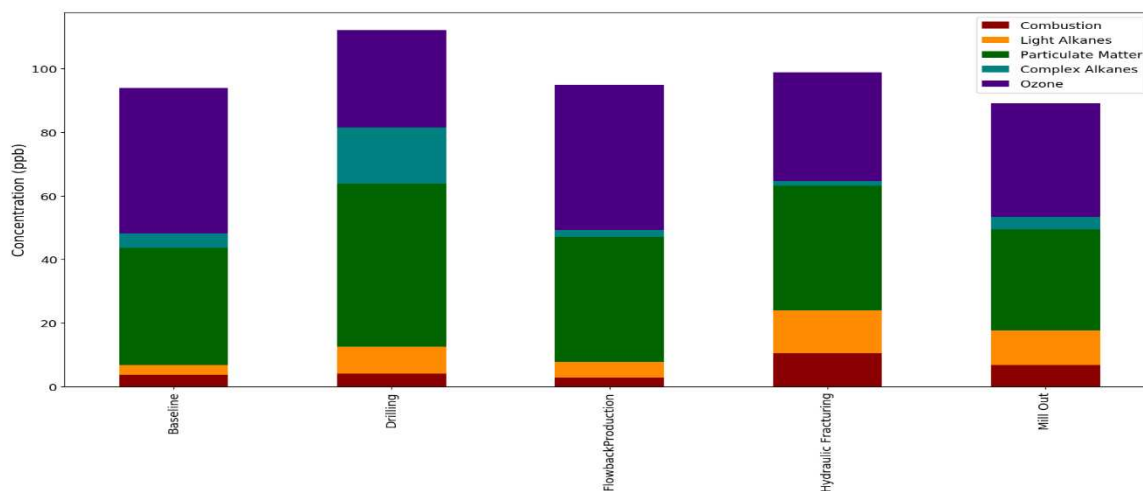
Figure 0-47: Average CAMML factor concentrations by ONG activity

Average factor concentrations were grouped by ONG activity in Figure 3-44. The Complex Alkane factor was shown to have the largest contribution during the drilling period and further suggests that this factor may be influenced by compounds emitted from the drilling mud as well as other subsurface ONG emissions. Ozone mixing ratios increase in the summer due to enhanced photochemistry and therefore the highest concentrations of this factor are to be expected during the Baseline and Flowback periods as they overlap with the warmest months. The Hydraulic Fracturing period, which occurred in winter 2020, showed elevated concentrations in the Combustion and Light Alkane factors. The cause of this increase is difficult to discern due to seasonal cycles associated with higher mixing ratios in the winter for both regional light alkanes and combustion emissions.

Box and whisker plots (Figure 3-45) were analyzed for the CAMML PMF factors, grouped by pad activity, to help assess whether elevated concentrations may reflect local emissions and not simply a regional influence coupled with the effects of a seasonal cycle in meteorology and dispersion. Activity periods occur during a shorter period of the year so breaking down the factors by activity helps limit the influence of seasonal cycles. If an activity period is associated with elevated local emissions, we expect more outliers to be present on the upper end of a factor's concentration distribution. The Combustion

and Ozone factors do not show many outliers associated with any activity period. Therefore, it is likely these factors are mainly driven by regional emissions and their seasonal cycles. The Light Alkane factor shows the most outliers associated with the drilling period, followed by hydraulic fracturing, and mill out. Enhanced emissions of compounds in this factor (ethane, propane, isobutane, and n-butane) are anticipated during these ONG preproduction activities. The Complex Alkane factor showed the largest anomalies during the drilling period followed by mill out. These findings are similar to the Drilling and Complex Alkane factor in the CCOB weekly data. Interestingly, The PM factor shows many outliers across several activity types. Note, however, that the PM factor also shows many high outliers during the baseline monitoring period. This suggests that factors driving local PM concentrations are probably not associated with ONG activities.
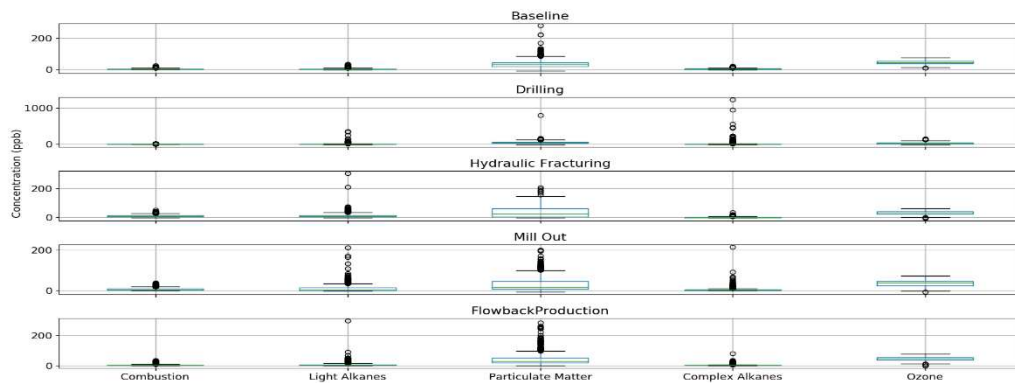

Figure 0-48: Box and whiskers plot of five CAMML factors broken down by ONG activity periods to better characterize local vs regional emissions.
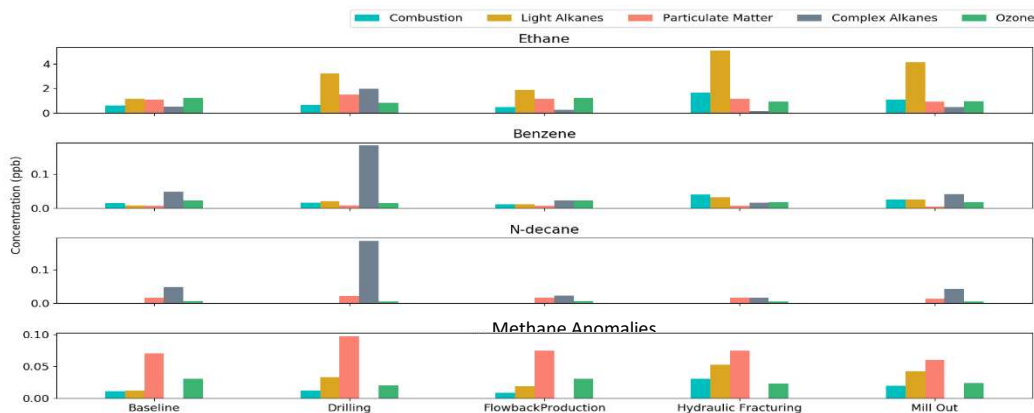

Figure 0-49: Concentrations of four compounds associated with the five CAMML PMF factors during each ONG activity period.

Concentrations of four compounds (ethane, benzene, n-decane, and methane anomalies) are analyzed in terms of their contributions from the individual PMF factors during each ONG activity period (Figure 3-46). One surprising result is the large contribution of anomalous methane to the PM factor, during baseline and all ONG activities. Not surprisingly, the light alkane factor, which we interpret as being associated with a combination of local and regional ONG emissions, is generally the biggest contributor to ethane concentrations, especially during Livingston pad activities. Both benzene and n-decane concentrations increase during the Livingston drilling period, where the increase is particularly associated with the Complex Alkane factor.

1.11.4 Wind Direction Analysis

Wind direction and wind speed were measured during the CAMML sampling period at a time resolution of minutes. Wind data were broken down into vector form and averaged to the VOC hourly sampling period. The data were then reconstructed using the averaged vectors.

To understand the sources of these factors, each factor was analyzed in association with the wind direction data. Concentrations were plotted on a wind rose to determine if higher than average mixing ratios were associated with a wind direction. The CAMML trailer was located to the northwest of the Livingston pad and therefore high concentrations originating from the southeast may indicate transport
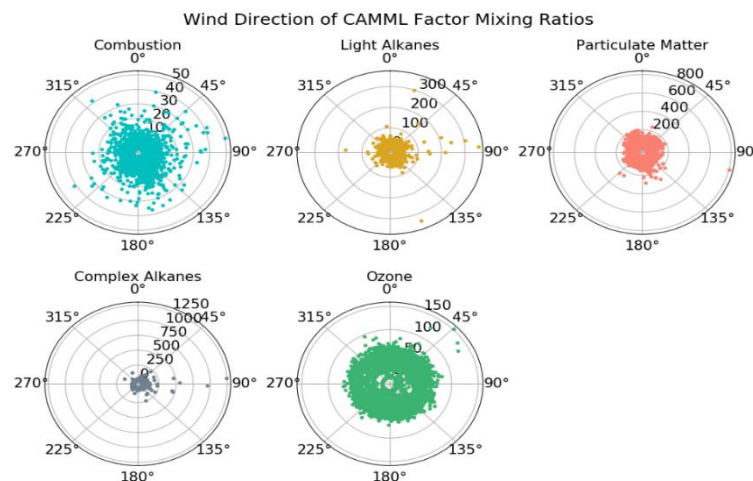

Figure 0-50: Wind direction given by the polar axis plotted against factor concentration given by the concentric axis. Both light and Complex Alkane factors show higher concentrations associated originating from 90 degrees and associated with easterly winds.

from the pad. If there were no associated local emissions, concentrations would be expected to show no preference towards direction, and if there were multiple strong local sources, high mixing ratios may be associated with multiple directions.

Figure 0- shows the concentrations over the CAMML sampling period and their associated wind direction. Wind direction is shown by the polar axis while the radial axis shows the associated concentrations. The Combustion factor shows elevated concentrations associated with multiple directions while the Ozone and PM factor have a consistent range of concentrations from all directions. Both patterns suggest that these factors are not associated with a single source and are more likely a regional or moving source. The Light Alkane and Complex Alkane factors show elevated concentrations associated mainly with 90 degrees or east. This is in the general direction of the Livingston pad. Both factors were broken down further to determine if these were associated with any ONG activities.

During baseline sampling, the Complex and Light Alkane factors have higher concentrations associated with multiple directions. When drilling begins, higher mixing ratios become associated with the east to SE direction, towards the Livingston pad. Light Alkane factor concentrations reach ~300 ppb during
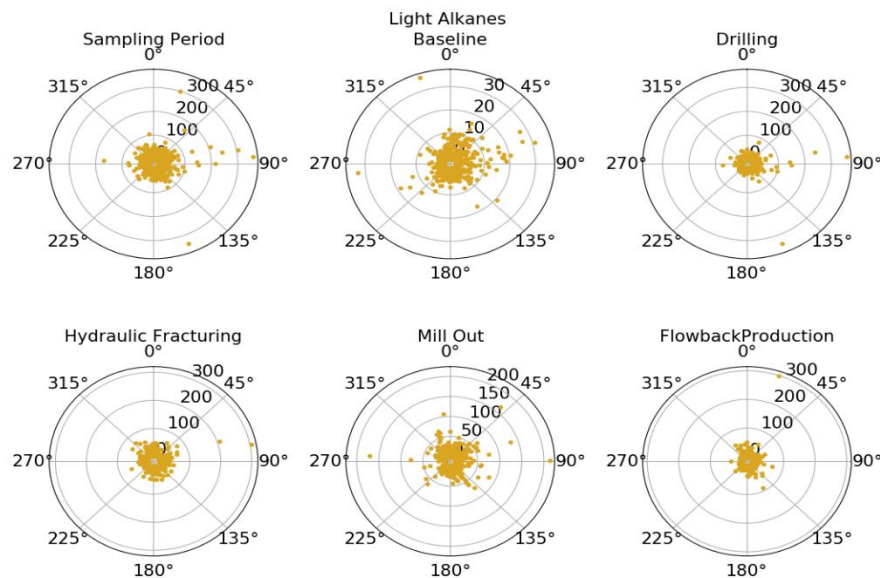
Figure 0-51: Light Alkane CAMML factor associated with observational wind direction. Wind direction is labeled on the polar axis and factor concentration is on the concentric axis in ppb.

drilling, hydraulic fracturing, and flowback. These result yield similar findings to the box and whiskers plot analysis. Similarly, the Complex alkane shows the largest concentrations, up to 1,250 ppb during the drilling period. Elevated concentrations are also observed during the mill out activity.

Wind direction correlations with high concentrations is difficult to fully determine. The online GC system reported VOC concentrations by integrating an air mass over an hour while wind direction was reported every minute. High concentration plumes may be carried from one direction over a short period of time while the average wind direction over the hour may be different. Several atmospheric barriers may have existed when sampling occurred, including sound walls and elevation differences as seen in Figure 3-38.

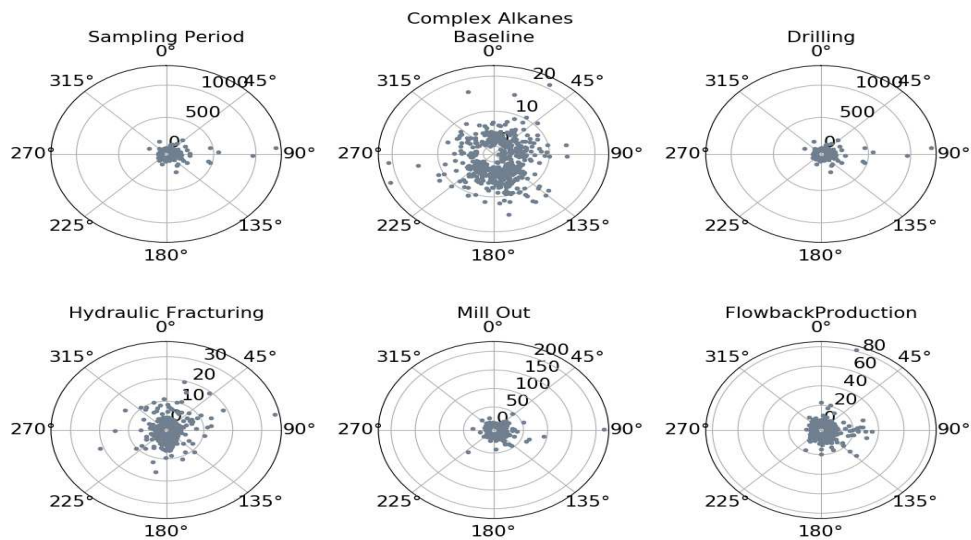*Figure 0-52: CAMML Complex Alkane factor samples with associated observational wind direction. Wind direction is on the polar axis while concentrations in ppb are on the concentric axis.*
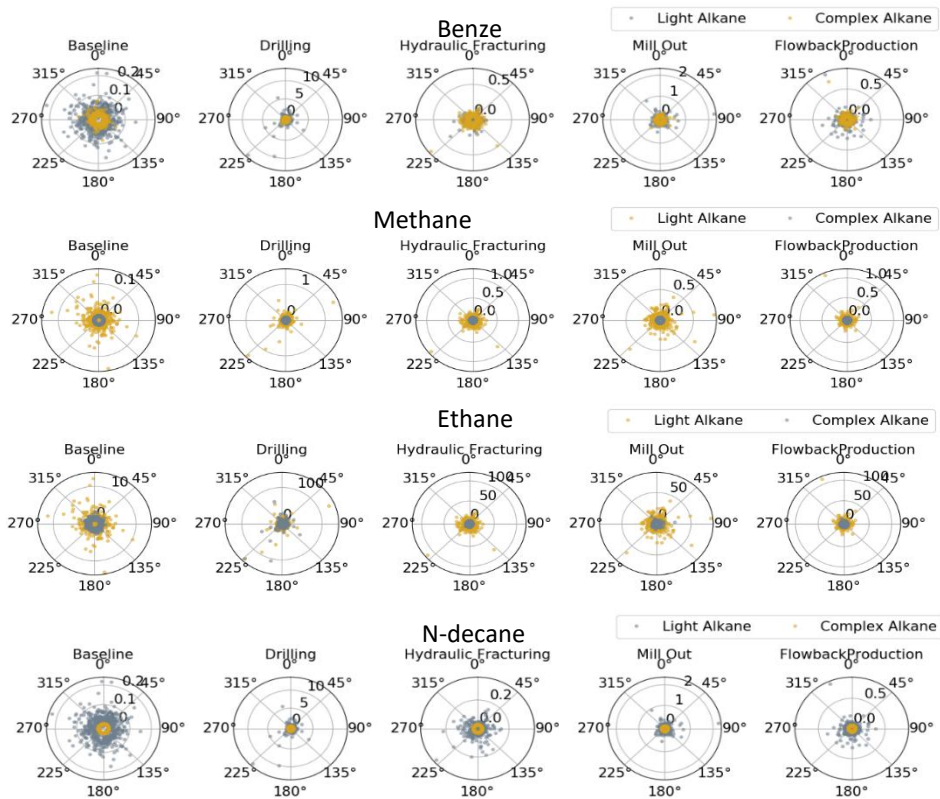
Figure 0-53: Key tracer compounds and associated wind directions during ONG activities. Wind direction is depicted on the polar axis and compound concentration on the concentric axis.

CONCLUSIONS

Weekly and hourly air pollutant concentrations were measured in the City and County of Broomfield (CCOB) to better determine emission sources impacting the area and how they changed over the course of development of several large, multiwell oil and gas pads. Weekly samples were analyzed for methane and a large number of VOCs, including alkanes, alkenes, and aromatics. Hourly measurements included a smaller number of VOCs, along with methane, NOx, ozone, and PM. The weekly data included samples across a large, spatially distributed sampling network that included near-pad and more distant sites. The hourly data were collected from a single site near the Livingtson pad.

The hourly and weekly air pollutant concentration data sets were analyzed using EPA's Positive Matrix Factorization (PMF). The weekly CCOB data was found to be best explained by six factors which represented the Background, Light Alkanes, Complex Alkanes, Combustion, Ethyne, and Drilling. Four of the six factors are believed to be influenced by the local ONG production. The Combustion and Background factors did not have any significant relationship to the local ONG production. The Light Alkane factor was associated with tubing operations at both the Livingston and Interchange pads. The Complex Alkane factor was associated with the drilling at all three active ONG sites, production tubing operations at Livingston, and coiled tubing operations at both Livingston and Interchange. The Interchange pad experienced very high concentrations of the Complex Alkane factor during the flowback period, while Livingston did not. Emissions from the drilling mud used at Nwpkwy and Livingston were found to significantly contribute to the Drilling factor. The source of the Ethyne factor remains unknown but it is believed to originate from the ONG pads. These plumes of increased ethyne, ethene, and benzene are speculated to be from some type of equipment malfunction or pad maintenance activity. The Combustion and Background factors did not have any relationship to the local ONG production.

The contributions of the different weekly PMF source factors to concentrations of benzene, a key

air toxic, were examined. Looking across the full study, the largest single contributor was the Combustion factor at 39%. The four ONG-related factors together accounting for 51.5% with the Light Alkane factor as the largest contributing ONG-related factor at 22%. Average contributions of the ONG-related factors were higher at near-pad sites especially during active operations.

The spatial extent of local ONG emissions on other sites across CCOB were examined by looking at temporal and spatial patterns of PMF factor levels. This analysis included two approaches: a visual examination of spatial gradients in factor strength during specific operational phases at a particular wellpad (e.g., drilling operations at the Livingston pad) and a study-long reconstruction of receptor site PMF factor timelines using a multilinear regression (MLR) approach. The spatial gradient analysis clearly illustrated a falloff in the influence of local pad emissions with distance. Sites nearest active ONG pads were associated with larger significant regression coefficients. An increase in distance was typically associated with a decrease in regression coefficients interpreted as the causal influence. For the MLR analysis, receptor site timelines were regressed against four other time series from the three ONG sites and the background site. The best reconstruction was found for the Light Alkane factor with an average $r^2 = 0.90$. Sites to the north and south of the CCOB ONG operations were best described by the background time series, while sites nearest the active ONG pads were more strongly influenced by local emissions. The Ethyne factor had an average model fit of $r^2 = 0.80$ and the only IMPACT receptor site with significant influence by the ONG sites was Anthem 01, located near Livingston. The Complex Alkane factor had an average $r^2 = 0.73$ and the maximum influence by local ONG emissions was approximately 30%. The Drilling factor timeline on average had the poorest reconstruction across sites, with an average $r^2 = 0.52$. The Anthem site was shown to be most dependent on the Livingston Drilling factor timeline which accounted for 61% of the Anthem variability. The MLR approach is limited by a lack of complete independence between the explanatory time series, since for many VOCs regional emissions influence the ONG timelines in much the same way that they influence the background site, and by the nature of the

approach taken where single regression coefficients were derived for each explanatory time series. In reality, the influence of individual local emission sources on a receptor site will change over time due, for example, to changes in prevailing meteorology.

Hourly VOC, methane, NO_x, O3 and PM concentrations were measured by the CDPHE CAMML during several individual phases of wellpad development. PMF analysis of hourly data collected by the CAMML resulted in five factors, including Ozone, Particulate Matter, Combustion, Light Alkanes, and Complex Alkanes. An absence of systematic, year-round measurements with the CAMML limited the ability to resolve a biogenic factor. The PM, combustion, and ozone profiles did not correlate to any ONG activity type. The wind direction analysis confirmed this with no large concentrations originating from a single direction. The light and Complex Alkane factors showed high concentrations originating from the E and NE directions during drilling, hydraulic fracturing, and mill out.

FUTURE WORK

Past studies of ONG emissions have largely focused on emissions of methane. Those that have focused on VOC emissions, often look at production activities. The limited duration of pre-production activities and, challenges in accessing these operations for measurement and documenting activity timelines, and large variability in pre-production practices by ONG operators and their subcontractors, all combine to limit current understanding of health and air quality impacts during well drilling and completion activities. Within CCOB, the tubing operations and drilling accounted for the higher-than-average emissions. Flowback, which was previously identified (Hecobian et al., 2019) as a large source of VOC emissions, had less impact in CCOB, likely due to improved practices that were utilized, including closed loop systems for fluid handling and limitations on on-site tanks for waste storage. Even withing CCOB ONG operations, differences were seen between emissions at different pads. For example, flowback emissions were more evident at the Interchange pad than at Livingston. Differences in drilling emissions were also observed and associated with a change in the drilling mud utilized – a change made in response to odor complaints from residents. It is important to note that other ONG sites around the DJ Basin and across the US are not implementing all of the best management practices put in place in CCOB and therefore likely exhibit very different, probably larger, wellpad emissions. For these reasons, there is considerable need to examine emissions and air quality impacts at other locations with different pre-production practices. This is especially important in marginalized communities where residents may not have the same voice to influence operator agreements that promote emissions reducing operational practices and in different government jurisdictions where operator requirements are less stringent. The rapidly evolving nature of pre-production practices also means there is a need to continually assess changes in emissions over time. The reduction in flowback emissions seen in CCOB is a good example. As best management practices are more widely adopted to mitigate flowback and fracking emissions, drilling

operations and transition activities like coil or production tubing operations or maintenance activities may become relatively more important.

While the dense spatial sampling network employed in the CCOB air monitoring program provided unusually good insight into local changes in air quality associated with particular operations at different wellpad sites, quantitative assessment of these impacts was challenging due to the length of individual weekly samples. Good spatial resolution accompanied by increased temporal resolution is likely to better inform impacts of wellpad emissions on nearby residents. Of course operating a VOC speciation network across many sites with high (e.g., hourly or faster) time resolution is an expensive proposition. One approach that has offered some benefits in CCOB is the installation of continuous photoionization detector (PID) based sensors that provide 1-min time-resolved measurements of "total" VOCs (the PID sensor has differential response to individual VOCs and therefore the aggregate sensitivity varies in time as VOC composition changes) to capture what often prove to be transient impacts (a few minutes duration) of emission plumes emanating from well-pads. The PID sensors are equipped with canisters that can be triggered and later analyzed offline to document VOC composition and concentration levels to characterize acute exposure episodes. These sensors are economical enough that a network can reasonably be deployed to document ONG emission impacts across neighborhoods at a timescale that can be better tied to changing meteorology and emissions.

Ethyne is a compound historically associated with combustion. This study shows that strong emissions may be associated with equipment malfunctions or maintenance activities on ONG pads. Ethyne, in future studies, should be considered as an important compound to observe.

Previous studies have applied a multivariate regression using propane and ethyne as ONG and combustion tracers respectively to show the variability in these species can represent the other observed VOC variability (Gilman et al., 2013, Pollack et al., 2021). Applying this analysis technique to this data would be an interesting additional step not taken here, although much of the ethyne observed within this

study appears to not be associated with combustion sources and a different species like ethene or t-2-butene may prove a better combustion tracer for this dataset.

Ozone is a prominent issue in the Front Range of Colorado. The reactivity of observed VOC species is quintessential to understanding how to mitigate the issue. To better understand this problem, species and factor reactivity can be calculated to better understand which specific pre-production practices pose a larger problem for high ozone concentrations, similar to Abeleira et al. (2017).

The linear regression technique may be an interesting analysis with a dataset more suited to the analysis technique. In the future, having increased temporal resolution coupled with spatial resolution could yield interesting results. A lasso or ridge technique may be applied to help coefficients make more physical sense and share statistically significant coefficients across site emissions.

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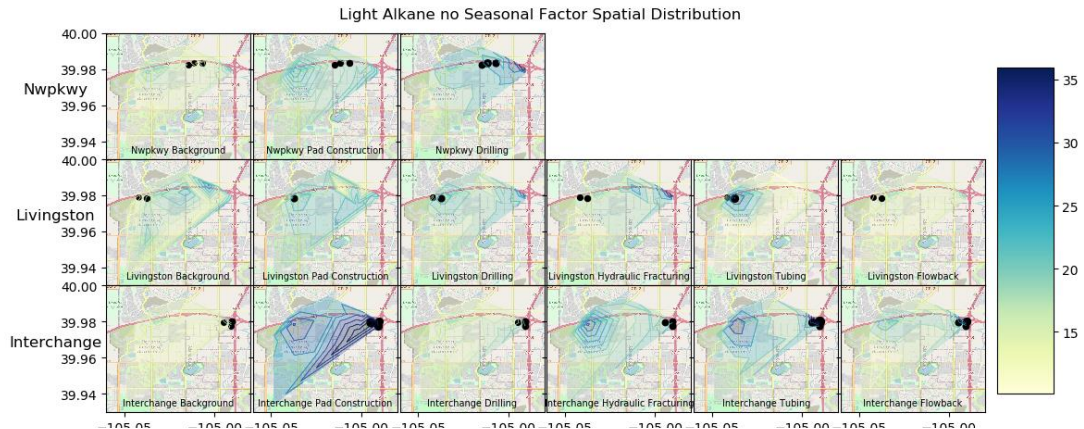
Figure 7-1: Light Alkane factor without the seasonal cycle. Black dots indicate active pad of interest and size corresponds to average concentrations during this period. Higher than average concentrations are shown to be associated with pad construction at Interchange, and tubing at Livingston and Interchange.
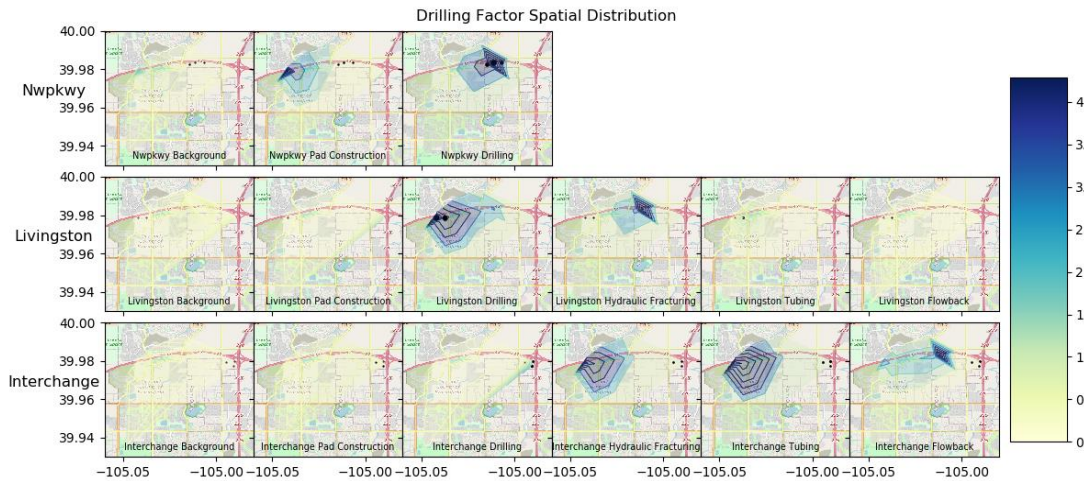

Figure 7-2: Drilling factor spatial figure. Black dots indicate active pad of interest and size corresponds to average concentrations during this period. Higher than average concentrations are shown to be associated with drilling at both Nwpkwy and Livingston.
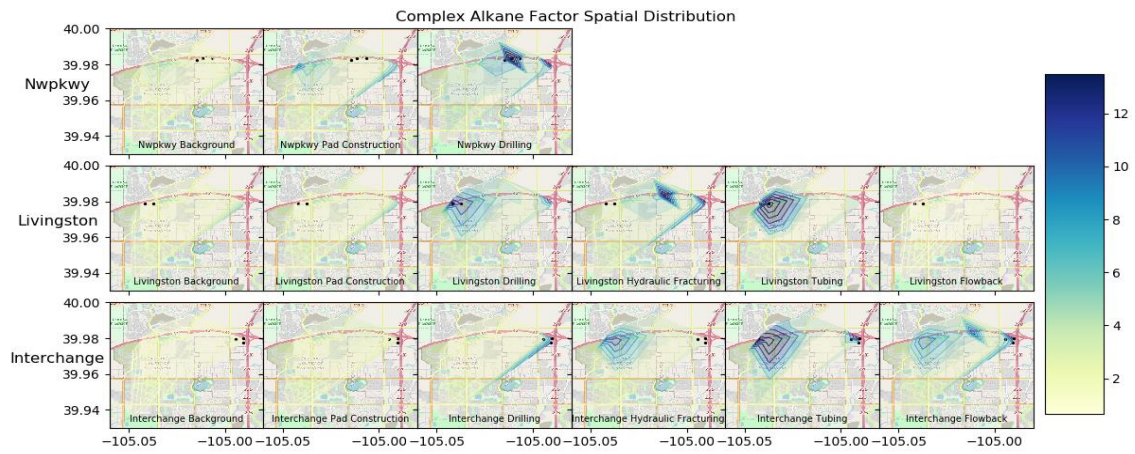
Figure:7-3: Complex Alkane factor without the seasonal cycle. Black dots indicate active pad of interest and size corresponds to average concentrations during this period. Higher than average concentrations are shown to be associated with drilling at all three active ONG sites, tubing at Livingston and Interchange, and Flowback at Interchange.
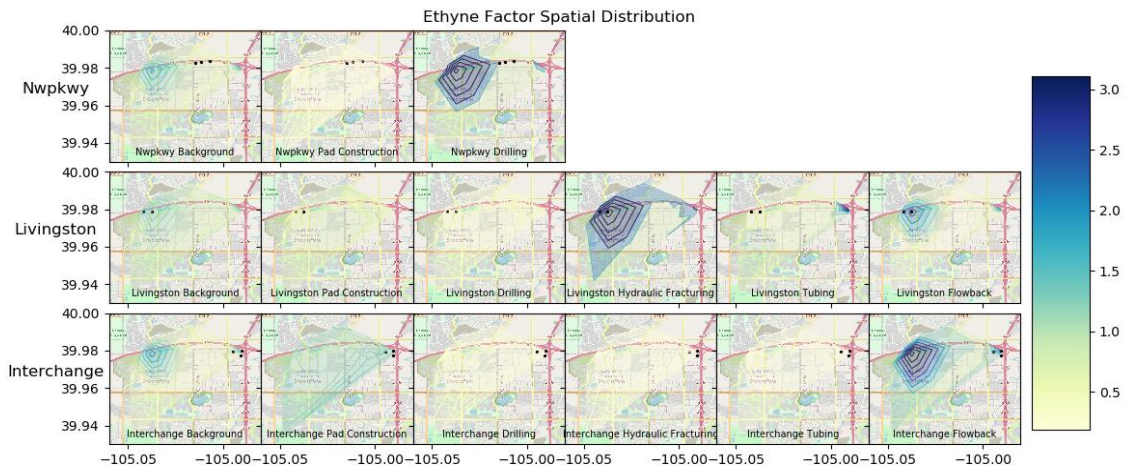

Figure 7-4: Ethyne factor without the seasonal cycle. Black dots indicate active pad of interest and size corresponds to average concentrations during this period. Higher than average concentrations are shown to be associated with hydraulic fracturing at Livingston, and flowback at Livingston and Interchange.

Figure 7-5: Combustion factor without the seasonal cycle. Black dots indicate active pad of interest and size corresponds to average concentrations during this period. High average concentrations are not shown to be correlated with active ONG activities.
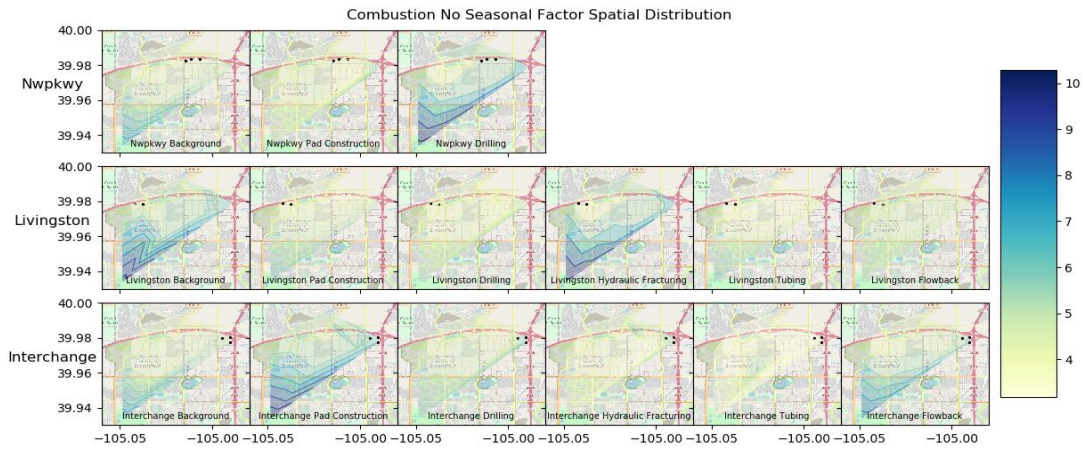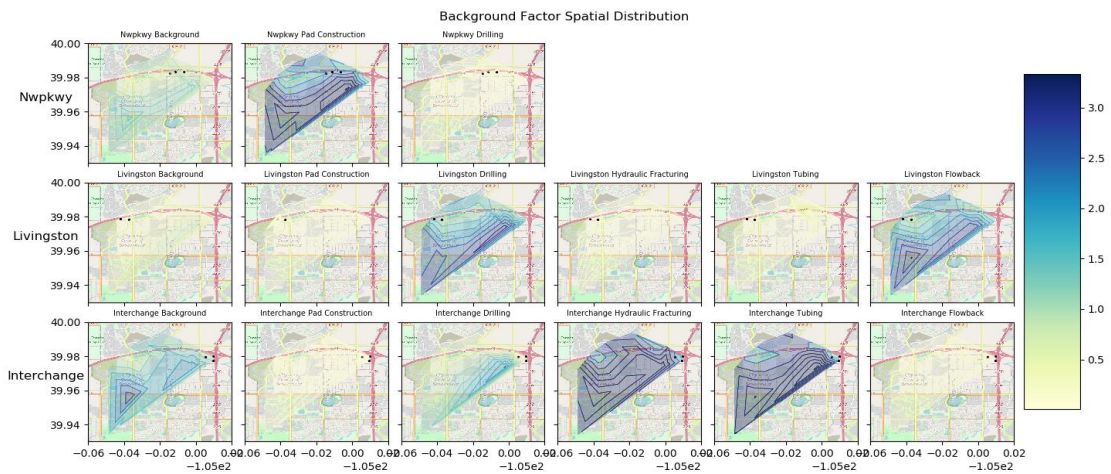
A.

Figure 7-6: Background factor spatial figure. Black dots indicate active pad of interest and size corresponds to average concentrations during this period. There does not look to be a correlation between

APPENDIX B: ONG IMPACTS THROUGH LINEAR REGRESSION

CCOB sites were monitored to understand how local ONG development, among other sources, influenced the surrounding areas. CCOB monitoring sites, as outlined above, were impacted by both local and regional sources. These sources have been characterized using EPA PMF which determined six sources; four of these – Light Alkane, Complex Alkane, Drilling, and Ethyne – were associated with ONG activities. However, the influence from local versus regional ONG is still unknown. To help characterize if IMPACT sites (school and neighborhood sites not directly at an ONG site, excluding the Commons background site) were more impacted by local or regional emissions, IMPACT site PMF factor concentration timelines were reconstructed using four explanatory time series from Livingston, Interchange, Nwpkwy, and Commons. Due to the coarse temporal resolution of the weekly samples a simple multi-regression model was used with an instantaneous impact, meaning no time lag was included. Physically, one would expect emissions to reach impact sites at some lagged time; however, the transport times (minutes to hours) between CCOB sites are much shorter than the weekly measurement timeline, so application of a time lag does not make sense in this analysis.

The reconstructed profiles, or target sites, included the IMPACT locations of Anthem 01, Wildgrass 01, Adams 01, Thundervista 01, United 01 & 02, Wilcox 01, Prospectridge 01, and Broadlands 01. The motivation behind this analysis was to assess of the four explanatory timelines could explain the IMPACT sites best through linear regression. A site is designated as significantly affected by local ONG emissions if the regression coefficient of one of the active ONG pads was significant at the 95% confidence interval. The coefficient of each predictive driver in each regression is determined through holding the other predictive driving variables constant. This allows for the influence of the predictive variable (active ONG or Commons site regional background) coefficient to be determined while holding all other predictive variable timelines constant. Therefore, the influence of each predictor location can be compared. The

IMPACT site timelines were individually regressed on the active ONG and regional background sites using

Anthem 01	Wildgrass 01	Adams 01	Thundervista 01	United 01	United 02	Wilcox 01	Prospectridge 01	Broadlands 01
49	34	27	32	20	29	23	20	15

equation 5-1:

8-1

$$\hat{y} = \Sigma_{j=1}^{N}\beta_j \boldsymbol{y_{ji}} + \beta_{0_i}$$

where β_{0i} is the population y-intercept for the regression model i, β_j is the regression coefficient for predictor j holding all other predictors constant, $\mathbf{y_{ji}}$ are the driver values of driver j for model i, and $\hat{y}_i$ are the predicted values of the target. An assumption in this regression is that all sources are observed: local (Livingston, Interchange, and Nwpkwy) and regional (Commons). Mean squared error (MSE) was used as the cost function shown in equation 5-2.

8-2

$$MSE = \frac{1}{N}\Sigma_{i=1}^{N}(y_i - \hat{y})^2$$

All active ONG pads had two or more local measurement sites: two at Livingston, three at Interchange, and three at Nwpkwy. Samples that were taken during the same week of the year at a single pad (eg. 1 taken at Livingston 01 and 1 taken at Livingston 02 during the 3rd week of the year) were averaged to create a single timeline for each active ONG pad site. The ordinary least squares (OLS) model from the Python statsmodels.api module was used for the implementation of this model. This module returns the overall model statistics which were used to help determine coefficient significance.

The coefficients of significant variables from the ONG sites are interpreted as a causal influence of ONG emissions at the IMPACT site. Each target site had a different number of observations; therefore, only weeks that had an observation at all five sites – four from the predictor sites and one from the target impact site – were used in the analysis. The number of data points used to recreate the IMPACT timelines are shown below:

This analysis provides the average influence of ONG profiles on the surrounding area. A coefficient for each site and profile is calculated from the regression analysis. Coefficients are averaged in the conclusions of the section to get an overall value for the influence of ONG sites on IMPACT sites. The impacts of emissions are highly influenced by the local wind direction and wind speed. Winds in Broomfield, Colorado, are predominately from the west. The weekly sampling time period, along with the two-year timeline will give insights into the average direction and dispersion of these emission profiles.

Figure 8-1: Figure and data obtained from Iowa Environmental Mesonet from the Northwest Parkway site located east of the CCOB Interchange sampling site. Predominate winds are from the west, northwest.
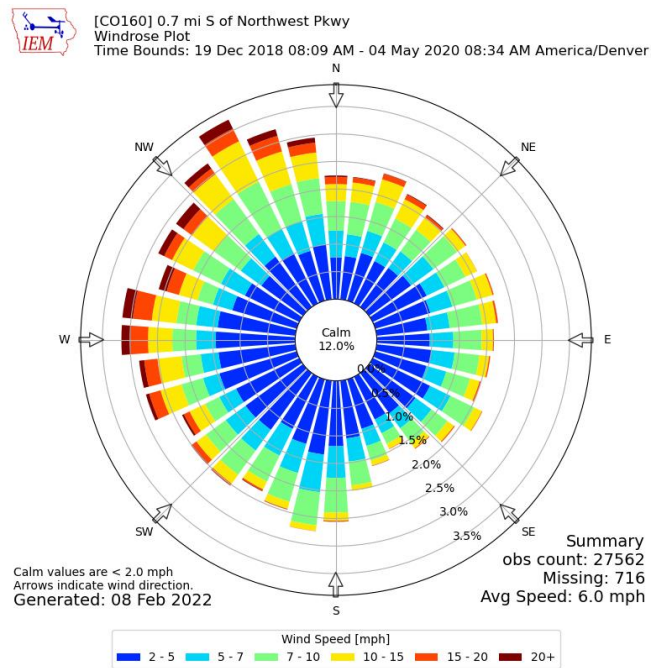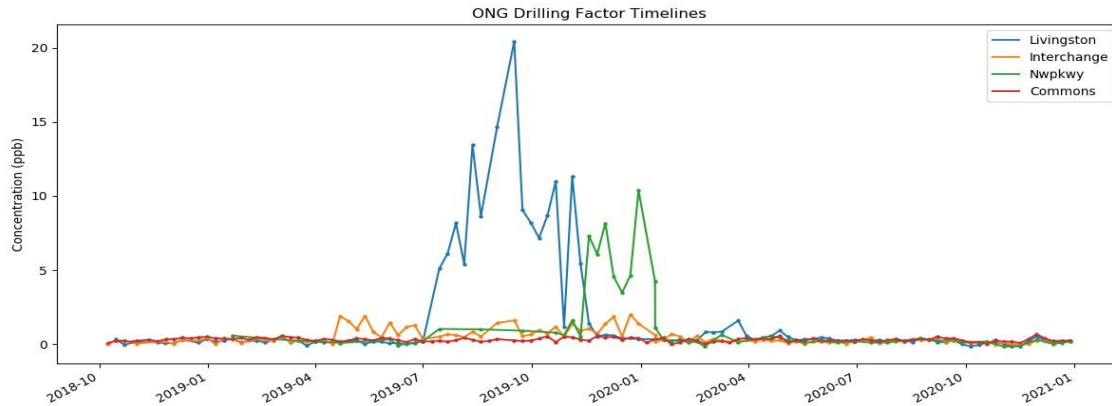
8.1 Drilling factor Impact

Figure 8-2: Timelines used as the explanatory variables to reconstruct the Drilling factor using linear regression.

PMF Drilling factor timelines for the four predictor sites are shown in Figure 3-37. As discussed above, the Drilling factor was most pronounced during drilling operations at the Livingston and NWPKWY pads. PMF Drilling factor timelines and Drilling factor timelines reconstructed using the regression analysis are plotted for each IMPACT site in Figure 3-38.-. Each plot shows one timeline using all four predictor site coefficients (r^2), and another only containing significant coefficients (sigr^2). Overall, the model had an average $r^2 = 0.48$ and $sigr^2 = 0.56$ with a maximum of 0.83 at United 02 and minimum $r^2 = -0.42$ and $sigr^2 = 0.06$ at Wildgrass 01. The small regression coefficient seens at Wildgrass is likely a factor of average wind direction. Wildgrass is located southwest of the Livingston pad and dominant winds are from the west (Figure B-1). Sites that had larger r^2 values tended to be in the northern part of the sampling region where influence of emissions from drilling operations at Livingston and NWPKWY might be anticipated.
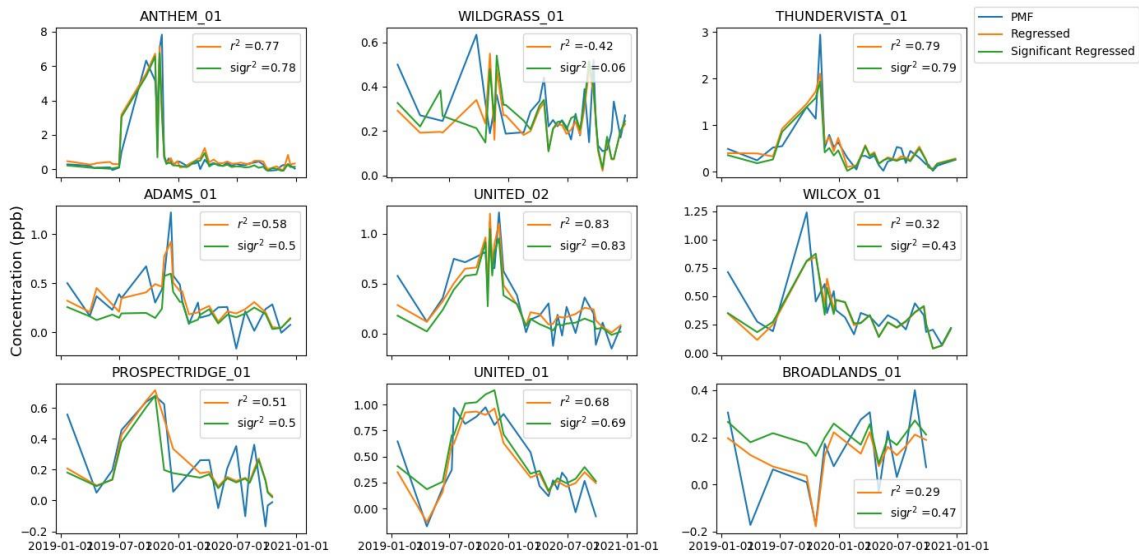
Figure 8-3: PMF Drilling factor and a linear regression reconstruction of IMPACT site profiles. A linear regression using all four explanatory sites is plotted in orange and the reconstruction using only significant coefficients is plotted in green.

A linear dependence between the Drilling factor timeline at Livingston and those at Anthem 01, Thundervista 01, United 01 & 02, Wilcox 01, and Prospectridge 01 was found. Livingston had the largest statistically significant impact on the Anthem 01 site with a coefficient of 0.6. Anthem 01 is located directly north of the Livingston pad. The Thundervista, Prospectridge, and United 01 & 02 sites were located north/northeast of the Livingston pad. Thundervista was influenced the most strongly with a coefficient of 0.13, followed by United 01 (0.08), Prospectridge (0.06), and United 02 (0.04).

The analysis indicated that the Interchange Drilling factor timeline only significantly impacted United 02 (coefficient = 0.40), which is located northwest of the Interchange pad. Recalling that the Drilling factor timeline at Interchange was small in magnitude, it may actually be that the similarity between the Interchange and United 02 Drilling factor timelines merely reflects similar impacts on both sites from drilling operations using Neoflow at Livingston and/or NWPKWY.

Adams 01, United 01 & 02 timelines each showed a significant dependence on the NWPKWY Drilling factor timeline. All three sites are relatively close to NWPKWY. Most IMPACT site Drilling factor timelines were best reconstructed using the background timeline from the Commons site. The regional

background explained an average variance of 0.85 for seven IMPACT sites. Anthem 01 and United 02 were the only sites that did not show significant influence from the background. Anthem 01 was strongly driven by the Livingston Drilling factor timeline and United 02 by Interchange, as discussed above. The PMF Drilling factor is associated with the type of drilling mud used at Livingston and Nwpkwy. This analysis shows that sites located near active ONG pads to the north/northwest were affected most strongly by drilling emissions.

Table 8-2: Regression coefficients of the Drilling factor linear regression. Significant coefficients, at the 95th percentile, are shown in bold.

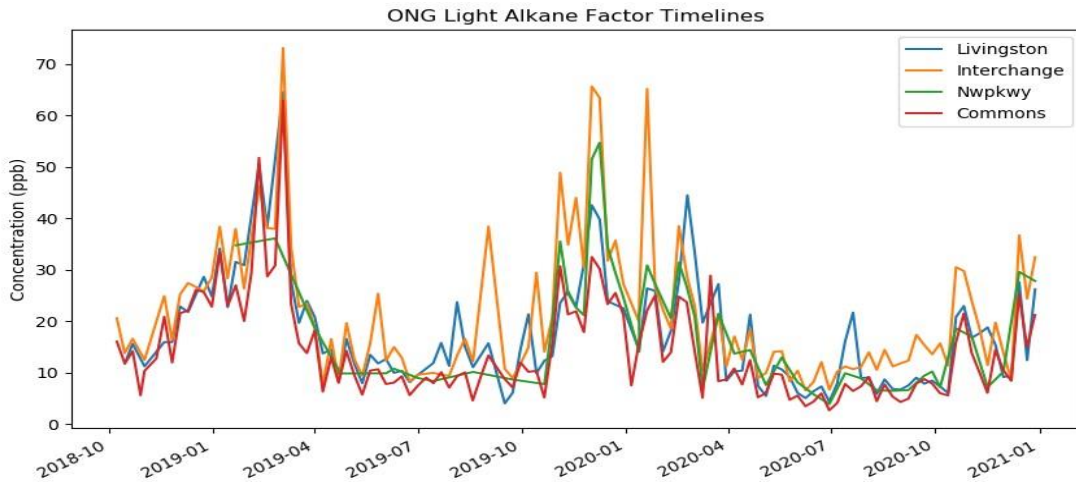|	Livingston	Interchange	Nwpkwy	Commons
Anthem 01	**0.6**	0.08	-0.05	0.77
Wildgrass 01	0.02	-0.13	0.0	**1.01**
Thundervista 01	**0.13**	0.11	0.01	**0.94**
Adams 01	0.01	0.17	**0.06**	**0.69**
United 01	**0.08**	-0.17	**0.11**	**0.98**
United 02	**0.04**	**0.4**	**0.05**	0.33
Wilcox 01	**0.07**	-0.04	0.02	**1.01**
Prospectridge 01	**0.06**	0.0	0.05	**0.5**
Broadlands 01	0.0	-0.23	0.02	**0.82**

8.2 Light Alkane factor Impact

Figure 8-4: The four explanatory variable timelines from the PMF Light Alkane factor.

The Light Alkane factor is made up largely of longer-lived alkanes. There is a strong influence on these compounds' concentrations from regional ONG emissions and, therefore, each explanatory time series contains a fair amount of regional influence. As shown in Figure B-4, the Light Alkane factor timeline at the Commons 01 background site is, overall, similar to those found at the active CCOB ONG sites. The variance in concentrations across sites increases when local ONG activities began in early 2019.

Overall, these four explanatory timelines were able to recreate the observed variance very well with an average $r^2 = 0.93$ and $sigr^2 = 0.92$. Anthem 01 had by far the worst fit ($r^2 = 0.54$) 50% of the variance Anthem 01 timeline variance is explained by only using the Livingston Light Alkane factor suggesting that Livingston pad emissions had a large influence on the site. All other profiles had a coefficient of determination greater than 0.92 with increased results when only using the significant timeseries.
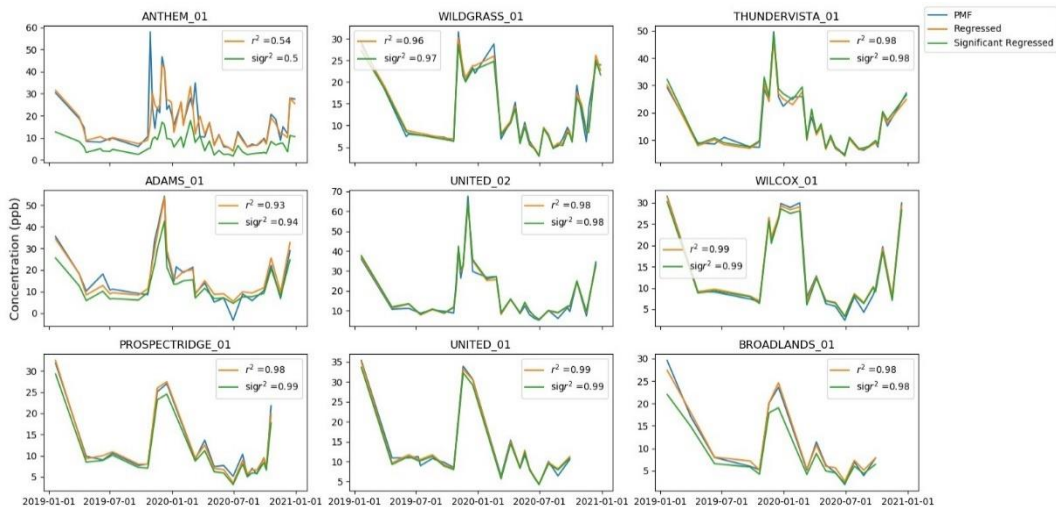
Figure 8-5: Impact site linear regression model of the PMF Light Alkane factor using the four explanatory variables

Five of the nine sites (Anthem, Wildgrass, Thundervista, United 01, and Prospectridge) were found to have a significant dependence on the Livingston Light Alkane factor timeline. As with the Drilling factor, Anthem 01 had the most variance explained by the Livingston site with a regression coefficient of 0.4 followed by Thundervista (0.24), Prospectridge (0.23), and Wildgrass (0.19). Thundervista and Prospectridge are located to the northeast of the Livingston pad where Prospectridge is further in distance than Thundervista. Winds are predominately from the west which may help explain why these sites have a larger influence than Wildgrass which is located to the southwest but closer in distance. Adams 01 (0.67), United 02 (0.54), United 01 (0.34), Thundervista (0.22), and Wilcox 01 (0.08) showed a significant dependence on the Interchange ligh alkane factor timeline. Adams 01 and the United sites are fairly close by and similar in distance from the Interchange pad while Thundervista and Wilcox are further to the west. Nwpkwy significantly influenced United 02 (0.87) and Thundervista (0.47) which are both located to the north of the Nwpkwy pads. Finally, the Commons site light alkane timeline once again had the largest significant coefficients for most IMPACT sites, especially those further North and South within the sampling area, suggesting that the light alkanes at most sites were overall influenced more strongly by regional emissions rather than local ones.

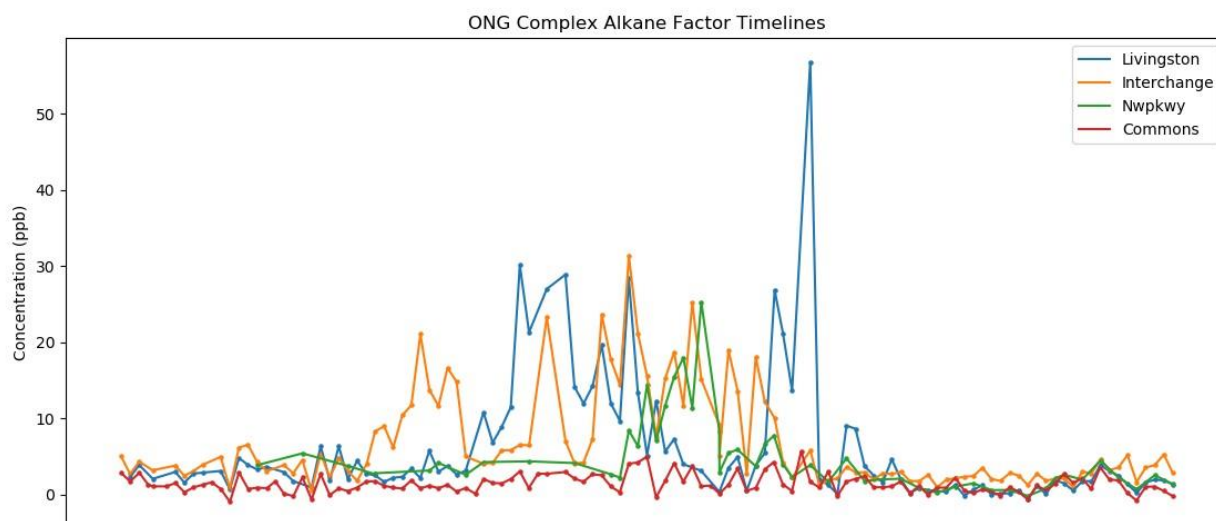|	Livingston	Interchange	Nwpkwy	Commons
Anthem 01	**0.4**	0.02	0.27	0.32
Wildgrass 01	**0.19**	0.04	-0.02	**0.79**
Thundervista 01	**0.24**	**0.22**	**0.47**	-0.08
Adams 01	-0.01	**0.67**	0.08	0.24
United 01	**-0.13**	**0.34**	0.04	**0.92**
United 02	-0.03	**0.54**	**0.87**	**-0.49**
Wilcox 01	0.06	**0.08**	-0.03	**1.01**
Prospectridge 01	**0.23**	0.04	0.05	**0.82**
Broadlands 01	0.02	-0.07	0.21	**0.82**

8.3 Complex Alkane Impact

Figure 8-6: The four explanatory variable timelines taken from the complex alkane PMF factor.

depicts the four driving profiles used in the linear regression model for the Complex Alkane factor. The compounds in the Complex Alkane factor have an atmospheric lifetime from hours to days so ONG timelines likely only depict local emissions. The model did an okay job at fitting the variance of each IMPACT timeline. The average variance explained across all the sites was $r^2 = 0.62$ and $sigr^2 = 0.68$. The Adams 01 site had the worst fit model with an $r^2 = 0.33$ and $sigr^2 = 0.46$ due to only having Commons as a significant driver.

Anthem 01 was strongly influenced by Livingston (0.28), however, had the largest dependency on Interchange (0.36). This may be due to higher rate of Complex Alkane emissions associated with the Interchange pad during the flowback period (see section 1.10.3.5 Complex Alkane). The Livingston pad additionally showed a linear impact on Wildgrass 01, Thundervista 01, Wilcox 01, Prospectridge 01 and United 01. Along with Anthem 01, Interchange significantly influenced Thundervista 01 and United 02. Wildgrass 01, United 01 02, Prospectridge 01, and Broadlands 01 were all linearly dependent on the Nwpkwy site. It is difficult to decern how much of these impacts are due to limited sampling during high concentration episodes at Livingston and Interchange. Most sites, except for Anthem 01 and United 01, were linearly dependent on the Commons site suggesting locations were mainly impacted by regional complex alkanes.
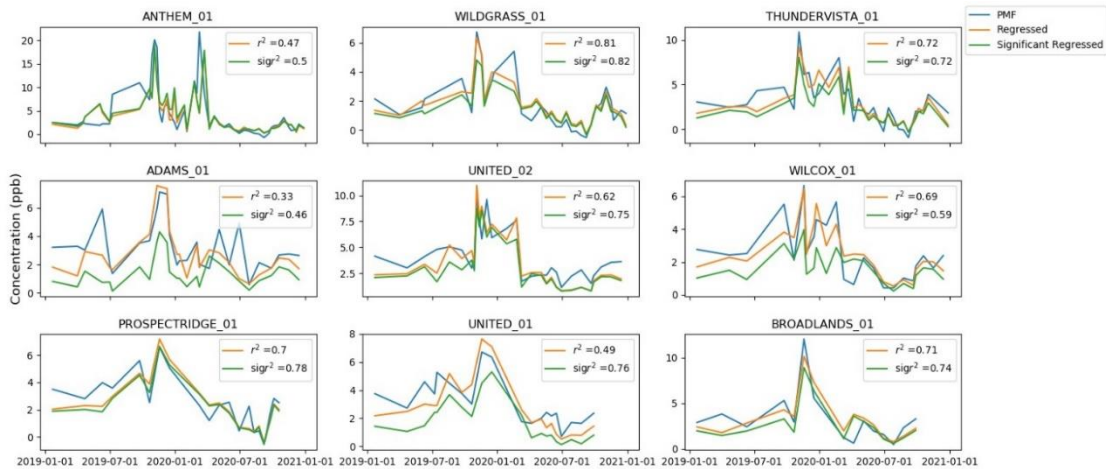

Figure 8-7: Regressed profiles for the impact sites using the chosen four drivers. The PMF timeline is shown in blue, the regressed equation using all coefficients is shown in orange, and the timeline only using the significant coefficients is shown in green.

Table 8-4: Regression coefficients for the IMPACT sites using the four explanatory variable timelines. Coefficients that are significant at the 95th percentile are in bold.

	Livingston	Interchange	Nwpkwy	Commons
Anthem 01	**0.28**	**0.36**	-0.15	0.23
Wildgrass 01	**0.07**	0.05	**0.13**	**0.43**
Thundervista 01	**0.08**	**0.1**	0.13	**0.6**

Adams 01	0.07	0.12	0.06	**0.86**
United 01	**0.12**	0.11	**0.27**	0.28
United 02	0.08	**0.14**	**0.24**	**0.59**
Wilcox 01	**0.12**	0.06	0.11	**0.67**
Prospectridge 01	**0.18**	0.03	**0.2**	**0.56**
Broadlands 01	0.05	0.06	**0.25**	**1.04**

8.4 Ethyne Impact

The Ethyne factor had an unknown source that likely originated from the Livingston pad with some emissions from Interchange. During the summertime in Colorado, ethyne has a lifetime of 13 days (Pollock et al 2021). Due to the short lifetime, local emissions were well captured, and IMPACT site variance was well explained by the model with an $r^2 = 0.80$ and $sigr^2 = 0.83$. Adams 01 was found to have no significant drivers and Broadlands 01 had the least variance explained with an $r^2 = 0.54$ and $sigr^2 = 0.31$.
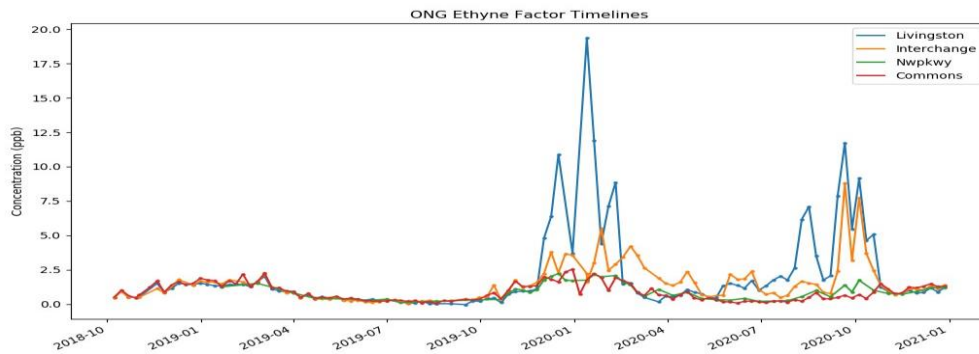

Figure 8-8: The four driving Ethyne factor profiles used in the linear regression analysis
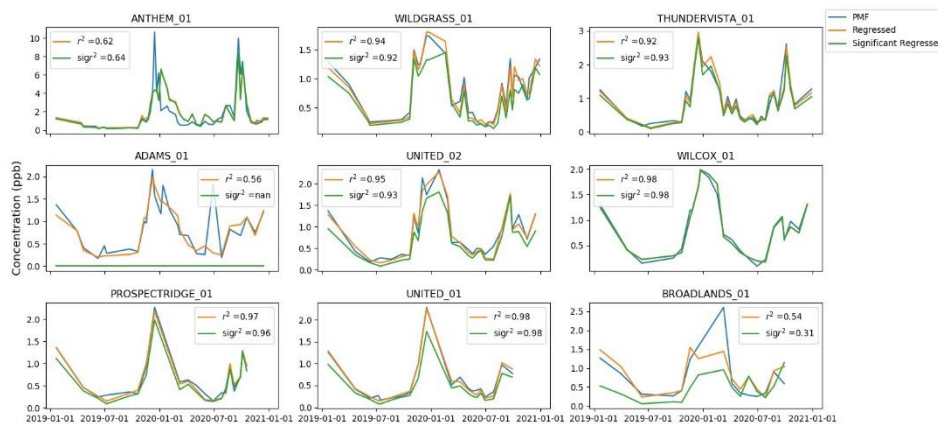

Figure 8-9: Regressed profiles for the impact sites using the chosen four drivers. The PMF timeline is shown in blue, the regressed equation using all coefficients is shown in orange, and the timeline only using the significant coefficients is shown in green.

The largest factor mixing ratios were observed at the Livingston and Interchange pad. Livingston significantly explained Anthem 01, Thundervista 01 and Wilcox 01 showing the largest contribution to the Anthem 01 site (0.27). Anthem 01, however, had a stronger linear dependence on the Interchange site (0.6). shows the Interchange timeline has a similar trend as the Livingston one, with a lower contribution. This may help to explain the dependence of Anthem 01 on Interchange given that the sites are far apart in physical space. The Nwpkwy and Commons sites had the largest significant coefficients on IMPACT sites. Both profiles were not strongly affected by the ethyne rich plumes (Figure B-8). This suggests mixing ratios at the IMPACT sites were not strongly influenced by the high concentrations the Ethyne factor allocated to Livingston and Interchange.

Table8-5: Linear regression coefficients for the IMPACT sites using the four explanatory variables. Coefficients in bold are significant at the 95th percentile.

	Livingston	Interchange	Nwpkwy	Commons
Anthem 01	**0.27**	**0.6**	-0.26	0.35
Wildgrass 01	0.02	**0.04**	0.1	**0.77**
Thundervista 01	**0.1**	0.03	**0.76**	0.06
Adams 01	0.03	0.13	0.07	0.64
United 01	0.01	0.0	**0.78**	0.22
United 02	-0.01	**0.09**	**0.65**	0.26
Wilcox 01	**-0.03**	**0.04**	**0.53**	**0.44**
Prospectridge 01	-0.01	**-0.05**	**0.94**	0.21
Broadlands 01	-0.07	**0.36**	-0.17	0.99

8.5 Spatial Summary

Table b-shows the number of times that a driver profile significantly influenced an IMPACT site with its average coefficient in parenthesis. The Livingston profile was the strongest significant driver for all four profiles of Anthem 01 and Thundervista 01. These sites are the closest sites to the north of the Livingston pad. Anthem 01 showed a higher average coefficient (0.39) over all regressed profiles indicating that it was influenced stronger than Thundervista (0.14) which is likely due to distance between sites. United 01, 02, and Prospectridge showed 3 out of four profiles significantly explained by the

Livingston pad. The coefficient decreases with distance with Prospectridge (0.16) being the closest to Livingston and United 02 (0.04) being the furthest away.

Interchange significantly explained all four timeseries for the United 02 site explaining an average of 29% of the variance. United 02 was the closest site in distance to the Interchange pad located to the northwest. The Adams 01 site, located to the west/southwest of the Interchange pad, was the second closest site but only showed influence during one ONG related profile. This may be due to several reasons including, infrastructure blocking an atmospheric pathway to the Adams sampling location or the Interchange profile not being the strongest driver of two of the regressed profiles (Drilling and Ethyne). Interchange largely influenced two of the Anthem timelines, Ethyne and Complex Alkanes, with an average coefficient of 0.48. Interchange driving Anthem 01 in the Ethyne factor is likely due a similar covarying timeseries but with decreased concentrations. The significant influence during the Complex Alkane factor may be due to the increased emissions from the Interchange site during flowback.

The Nwpkwy site was also a significant driver for the United 02 site (average = 0.42) during all four regressed profiles. United 02 was located directly across the highway the Nwpkwy pad. Both United sites were closest in distance to the Nwpkwy pad. United 01 was only significantly explained by Nwpkwy for three of the four sites with no significance found from the Light Alkane factor associated with Nwpkwy which is likely due to the activities at Nwpkwy only finishing through drilling. United 01 had 9 less samples than United 02 which may contribute to the non-significant association during high Light Alkane compound emissions.

The Commons site showed a large influence over many of the sites for the Drilling factor, Light Alkane factor, and Complex Alkane factor. There were only two sites that had a linear dependence on the Commons site for the Ethyne factor, however. This finding may be due to the similarity between the Nwpkwy and Commons factor profiles where sites with a higher background influence were mapped to the Nwpkwy profile. The Commons and Nwpkwy Ethyne factor timelines covaried with a coefficient of

determination equal to 0.68 while Livingston and Interchange covaried with the Commons site with an

r^2 = 0.05 and 0.16, respectively.

Table: 8.6: The number of significant coefficients associated with each of the impact sites. Each number is out of four, given that four PMF profiles were reconstructed using multiple linear regression. The average coefficient for the number of significant values

	Livingston	Interchange	Nwpkwy	Commons
Anthem 01	4 (0.39)	2 (0.48)	0	0
Wildgrass 01	2 (0.13)	1 (0.04)	1 (0.13)	4 (0.75)
Thundervista 01	4 (0.14)	2 (0.16)	2 (0.62)	2 (0.77)
Adams 01	0	1 (0.67)	1 (0.06)	2 (0.79)
United 01	3 (0.11)	1 (0.34)	3 (0.37)	2 (0.95)
United 02	1 (0.04)	4 (0.29)	4 (0.42)	2 (0.54)
Wilcox 01	3 (0.07)	2 (0.06)	1 (0.53)	4 (0.78)
Prospectridge 01	3 (0.16)	1 (0.05)	2 (0.48)	3 (0.63)
Broadlands 01	0	1 (0.36)	1 (0.25)	3 (0.89)