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New Insights into Fossil Fuel Volatile Organic Compound Emissions and Chemistry using $\text{H}_3\text{O}^+$
and NO$^+$ Chemical Ionization Mass Spectrometry

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B.S., Massachusetts Institute of Technology, 2012

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This thesis entitled:
New Insights into Fossil Fuel Volatile Organic Compound Emissions and Chemistry using H$_2$O$^+$ and NO$^+$
Chemical Ionization Mass Spectrometry
written by Abigail R. Koss
has been approved for the Department of Chemistry and Biochemistry

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Dr. Jose-Luis Jimenez

Date_____________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Volatile organic compounds (VOCs) are ubiquitous in the troposphere. They can have significant human health effects, and contribute to the formation of ozone and secondary organic aerosol. The insight we gain from taking detailed, precise measurements of VOCs is essential to understanding chemical processes in the atmosphere, and to making informed policy decisions about air quality. This thesis describes the development of chemical ionization mass spectrometry (CIMS) techniques to measure VOCs, specifically $\text{H}_3\text{O}^+$ CIMS (proton-transfer-reaction mass spectrometry, PTR-MS) and NO$^+$ CIMS, and the application of those techniques to VOC chemistry related to fossil fuel production and use.

Instrument development in this work includes (1) the development and characterization of a high-resolution $\text{H}_3\text{O}^+$ time-of-flight chemical ionization mass spectrometer ($\text{H}_3\text{O}^+$ ToF-CIMS, or PTR-ToF-MS) and (2) the development and evaluation of NO$^+$ chemical ionization mass spectrometry (NO$^+$ CIMS).

Applications have focused on air quality issues in oil and natural gas producing regions in the US, which have experienced a recent, rapid increase in production. In these regions, VOC and NO$_x$ emissions have raised concerns about the release of air toxics, greenhouse gases, and ozone precursors. This thesis describes the deployment of PTR-MS and $\text{H}_3\text{O}^+$ ToF-CIMS in two major field intensives investigating the oil and natural gas extraction industry: the Uintah Basin Winter Ozone Study in 2013, and the Shale Oil and Natural Gas Nexus study in 2015. An additional mobile laboratory project demonstrates the utility of NO$^+$ CIMS to measure on-road VOC emissions.

$\text{H}_3\text{O}^+$ and NO$^+$ CIMS are powerful techniques that provide detailed and highly time-resolved information about VOCs in ambient air. This thesis adds to our knowledge of VOCs in oil- and gas-producing regions, contributes a framework for interpreting PTR-ToF-MS measurements in oil and gas producing regions, and provides a foundation for NO$^+$ CIMS measurements of ambient air.
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Chapter 1. Introduction

1. VOCs in the atmosphere

Volatile organic compounds (VOCs) are one of the most fascinating and complex classes of chemicals in Earth’s atmosphere. They are ubiquitous in the troposphere and intrinsically related to life: plants are responsible for three-fifths of the non-methane organic gases emitted to the atmosphere, biological activity in the oceans emits another fifth, and the remaining fifth comes from biomass burning and human activity (Figure 1.1). Chemical transformation of VOCs in the atmosphere can create less volatile species that contribute to the formation and growth of aerosols. Photochemistry involving VOCs and nitrogen oxides leads to the formation of ozone. Aerosols, ozone, and many VOCs are harmful to human health, and ozone and aerosols are radiative forcing agents. In the United States, anthropogenic emission of VOCs is regulated under the Clean Air Act.

In the United States, production and use of fossil fuels have consistently accounted for about half of anthropogenic VOC emissions over the past 45 years (EPA). However, the various contributions to this category, and the total emissions, have changed considerably over time. Since 1970, the total VOC emissions from highway vehicles have decreased by a factor of 10; in 1970, this source accounted for half of anthropogenic VOC emissions, while today it accounts for only 13% (Figure 1.2). Conversely, emissions from petroleum and related industries have been rising substantially since the mid 2000’s.

This thesis describes the development and application of methods to measure VOCs associated with fossil fuel sources. The majority of the work focuses on air quality impacts from oil and natural gas.
extraction. An additional section describes the application of a new measurement technique to on-road vehicle emissions. This chapter provides background information on VOC chemistry from these sources, VOC measurement technology, and a thesis summary.

2. VOC emissions from fossil fuel sources

The recent rise in emissions from petroleum industry reflects a rapid and dramatic increase in domestic production in several regions with “unconventional” reservoirs (tight oil and gas, Figure 1.3). This surge has been largely driven by improvements in extraction technology such as hydraulic fracturing and directional drilling. VOC emissions from oil and natural gas extraction activity can influence global climate, and local and regional air quality.

Replacing coal with natural gas may have climate and air quality benefits: natural gas produces less CO₂ and other pollutants (Jackson et al., 2014; de Gouw et al., 2014). However, methane, the main component of natural gas, is a potent greenhouse gas, with a global warming potential 30 times that of CO₂ over a 100 year time frame (IPCC, 2013). If a natural gas extraction field leaks a sufficient amount of methane, the climate benefits of using natural gas could be offset. There are different numbers for the “break-even” leak rate, but it is likely around 3% of production (Alvarez et al., 2012). Top-down estimates from aircraft suggest that leak rates in some basins are higher than this, and that regulatory inventories generally underestimate methane emissions (Miller et al., 2013; Karion et al., 2013; Moore et al., 2014; Brandt et al., 2014; Pétron et al., 2014; Peischl et al., 2015).

![Figure 1.3. Oil and gas production from several key unconventional production regions. Data and map from US Energy Information Administration.](image-url)
Regional air quality can be adversely affected by extraction activity. VOCs emitted by oil and gas operations contribute to extremely high ozone episodes in rural areas of Utah and Wyoming in the winter (Schnell et al., 2009; Edwards et al., 2014), and can enhance ozone and possibly fine particulate levels near urban areas in the summer (Kemball-Cook et al., 2010; Olaguer, 2012; McDuffie et al., 2016; Roohani et al., 2017).

Air toxics, including small aromatics (benzene, toluene, ethylbenzene, and xylenes, or “BTEX”), formaldehyde, hydrogen sulfide (H₂S), polycyclic aromatic hydrocarbons (PAHs), and methylene chloride, can be emitted from production sites in significant quantities, during the initial drilling phase but also afterwards during the production phase (Colborn et al., 2014; McKenzie et al., 2012; Adgate et al., 2014; Macey et al., 2014; Li et al., 2014; Warneke et al., 2014). Several studies have indicated that air toxic emissions may be important on a very local scale, to people who work on well pads, or whose homes are near production sites (Bunch et al., 2014; Colorado State University, 2016).

Most studies of VOC emissions from oil and gas operations have measured a relatively limited set of non-methane VOCs, typically including BTEX, alkanes, and occasionally small oxygenates such as methanol and formaldehyde. Several studies have achieved much higher VOC chemical detail, including quantification of larger (>C5) alkanes, cyclic alkanes, more highly-alkyl-substituted aromatics, alkenes, halocarbons, and a wide range of photochemically produced species (Simpson et al., 2010; Gilman et al., 2013; Swarthout et al., 2013; Utah Division of Air Quality, 2014). The higher chemical detail has been valuable for modeling studies (Edwards et al., 2014; Ahmadov et al., 2015; McDuffie et al., 2016).

While VOC emissions from the production of fossil fuels have been rising, emissions from one of their end uses – vehicles – have fallen dramatically (Figure 1.2). A corresponding decrease in ambient mixing ratios of many VOCs has been described in Los Angeles (Warneke et al., 2012) and London (von Schneidemesser et al., 2010). The decrease is attributable to more stringent emissions standards, leading to improved emissions reduction technology in both vehicles and fuels (Sawyer et al., 2000; Sandhu and Frey, 2012; McDonald et al., 2013). The VOC composition of vehicle-related emissions has been extensively
characterized from laboratory and tunnel studies (Kean et al., 2001; Schauer et al., 2002; Gentner et al., 2013; May et al., 2014), but up-to-date field measurements of VOCs are still important. They are necessary to know whether regulations are working, which emission sources are the most effective regulatory targets, and to answer current science questions, such as whether gasoline or diesel fuel usage contributes more to ambient secondary organic aerosol formation (Gentner et al., 2012; Bahreini et al., 2012). The recent Volkswagen scandal has also illustrated the importance of having real-world in-situ measurements as well as laboratory and dynamometer studies (Thompson et al., 2014).

What types of VOCs are found in fossil fuels? Both crude and refined fuels are dominated by the same types of compounds – alkanes, alkenes, aromatics, and cyclic alkanes – but the relative distribution of these compounds varies (Figure 1.4). Crude fuels have highly variable composition depending on the source reservoir, and can include relatively high abundances (a few weight %) of nitrogen, oxygen, and sulfur-containing VOCs and related volatile species such as H$_2$S (Speight, 2006). Extraction activity by the fossil fuel industry can release VOCs, like methanol, that are not found in the crude fuel (Mansfield et al., 2016). Tailpipe exhaust can additionally contain oxygenates such as ethanol and formaldehyde (Gentner et al., 2013).

In the atmosphere, these compounds undergo oxidation reactions and form a wide range of products. Generally speaking, the reactivity of these groups with the OH radical increases in the order: alkanes < cycloalkanes < aromatics < alkenes (Atkinson and Arey, 2003). Alkenes

![Figure 1.4. VOC speciation in crude and refined fuels. Data points are sized by relative abundance by weight. Crude oil is a representative profile combined from Smith (1968); National Research Council (1985); Drozd et al. (2015). Natural gas profile from Uinta Basin conventional gas profile (Western Regional Air Partnership, 2012). Diesel and gasoline exhaust profiles from Gentner et al. (2013).]
additionally undergo reaction with O₃ and NO₃. First-generation products of alkanes and cycloalkanes include a range of carbonyls, alkyl nitrates, and (hydro)peroxides (Calvert et al., 2008); aromatics produce glyoxal, phenols, nitrophenols, benzaldehydes, and furanones (Wagner et al., 2003; Wyche et al., 2009); alkenes form carbonyls, hydroxynitrates, furans, oxiranes, and nitrates, among other products (Calvert et al., 2000). First generation products react further to produce more highly oxidized species, fragmentary compounds, peroxy nitrates (PANs), and ultimately CO and CO₂.

3. Measurement of VOCs using Proton-transfer-reaction mass spectrometry

It is clear that comprehensive and precise measurements of VOCs are required to understand the chemistry leading to the formation of ozone and particulates, and to properly assess the need for and effect of regulations. However, VOC measurements are challenging. Goldstein and Galbally (2007) estimate that 10⁴ to 10⁵ individual organic species have been detected in the atmosphere, and many more remain as yet undetected. VOCs are highly chemically diverse, and the composition of the VOC mixture can change dramatically depending on emission sources and chemistry. VOCs in air are typically very dilute, requiring instrumentation with part-per-trillion (ppt) detection level capability.

A number of methods have been developed to address the challenges of measuring VOCs in-situ. One class of techniques is based on gas chromatography (GC). GC techniques can provide very specific VOC identification, measure a wide range of compounds, and have very high sensitivity when used with cryogenic or adsorbent pre-concentration (Nozière et al., 2015). However, GC techniques have several drawbacks. They have limited time resolution, with typical sample periods of 15 minutes to several hours. Several pre-treatment steps such as remote collection with a whole-air-sampler, removal of water and ozone, and cryogenic pre-concentration may be required, which may create sample artifacts or loss of specific classes of VOC (Kuster et al., 2004; Lerner et al., 2017).

Mass spectrometry techniques provide a complementary approach. Although less chemically specific information is provided (only the mass-to-charge ratio of a VOC is measured), mass spectrometry techniques can measure much faster and require less sample pre-treatment. They are better suited to
measurement from a mobile platform, or for other studies such as eddy covariance investigations where very high time resolution is necessary. Combined with co-deployment of a GC technique, highly time resolved and chemically specific VOC information can be obtained.

One especially popular direct mass spectrometry analysis technique in atmospheric chemistry is proton-transfer-reaction mass spectrometry (PTR-MS). PTR-MS was first developed in the mid-1990s by the Lindinger group in Innsbruck, Austria (Lindinger et al., 1998) and has found widespread use not only in atmospheric chemistry, but also in medical diagnostics, the food and flavor industry, and security applications (Blake et al., 2009; Biasioli et al., 2011).

PTR-MS is a chemical ionization method, the goal of which is to create ions with little excess energy. The resulting mass spectrum contains few fragment ions, and may be used to analyze complex sample mixtures, such as VOCs in air. A reagent ion $RH^+$ is created and mixed with analyte molecules $A$. The thermodynamics are described by the “proton affinity” of the neutral molecules, which is the energy released when a neutral molecule is protonated. If the reaction $RH^+ + A \rightarrow R + A^H^+$ is exothermic (in other words, if the proton affinity of $A$ is higher than that of $R$), then the proton transfers from the reagent ion to the analyte molecule, which can then be measured with a mass spectrometer.

Although proton transfer reactions can be accomplished with a number of reagents, most commonly methane, isobutene, or ammonia; in atmospheric applications, “PTR-MS” almost exclusively refers to proton transfer using protonated water ($H_3O^+$) reagent ions. $H_3O^+$ is generated from water vapor in an ion source (in the PTR-MS instruments used in this work, the ion source is an electrical discharge in a hollow cathode). $H_3O^+$ ions are then mixed with VOC-containing air in a drift tube region. A strong electric field is applied along the length of the drift tube to prevent cluster formation and accelerate the ions into the mass analyzer section of the instrument (de Gouw and Warneke, 2007).

In theory, PTR-MS can detect molecules with a proton affinity higher than that of water (PA = 691 kJ mol$^{-1}$); this includes aromatics, alkenes larger than ethene, alkanes larger than hexane, alkyl-substituted
cycloalkanes, and a wide range of oxygenated and other polar molecules, including carbonyls, alcohols, acids, furans, etc.

The PTR-MS response to a particular VOC A can be described relatively simply (de Gouw and Warneke, 2007). As molecules of A travel through the drift tube, they react with H₃O⁺ with rate k over reaction time t. The number of AH⁺ ions created is equal and opposite to the H₃O⁺ lost. If only a small fraction of H₃O⁺ are lost ([A] is small), then the number of AH⁺ created is approximately linear with k, [H₃O⁺], and [A]:

\[ [AH^+] = [H_3O^+](1 - e^{-k[A]Δt}) \approx [H_3O^+]k[A]Δt \]

The reaction time t, the time needed to traverse the drift tube, depends on drift tube length L, number density N, electric field E, and ion mobility μ:

\[ Δt = \frac{L}{\mu E} = \frac{L}{\mu N} \times \left(\frac{E}{N}\right)^{-1} \]

(The ion mobility is usually reported as the mobility under standard conditions, \( \mu_0 \approx \mu N/N_0 \)).

The measured ion signal of AH⁺ (I_AH⁺), normalized to the primary ion signal (I_H3O⁺), is then linearly related to the volume mixing ratio of A ([A]/N):

\[ \frac{I_{AH^+}}{I_{H_3O^+}} = \frac{[AH^+]}{[H_3O^+]} \times \frac{T_{AH^+}}{T_{H_3O^+}} = \frac{T_{AH^+}}{T_{H_3O^+}} \times \frac{kL}{\mu} \times \left(\frac{E}{N}\right)^{-1} \times \frac{|A|}{N} \]

where \( T_{AH^+} \) and \( T_{H_3O^+} \) are the relative transmissions of the VOC and reagent ions between the drift tube and detector. The volume mixing ratio of VOC A can therefore be determined by measuring the ion signal of AH⁺, normalizing to the ion signal of H₃O⁺, and applying a linear calibration factor.

In practice, more reactions than simple proton transfer are possible in a PTR-MS instrument, and factors other than proton affinity and reaction rate constant contribute to the instrument response. Some H₃O⁺ reactions, such as with alcohols and alkanes, are dissociative, and significant fragmentation occurs. Other reactions involve ligand-switching between a water cluster and VOC molecule. Sensitivities can also be humidity-dependent. Characterization of a PTR-MS instrument response to a wide range of VOCs is described in Chapter 3.
The measurement capability of PTR-MS instruments has improved dramatically over the past two decades. One major advance has been the application of time-of-flight mass analyzers to PTR-MS. Until very recently, PTR-MS most commonly used a quadrupole mass analyzer. (This includes the instrument described in Chapter 2). Typically, quadrupole PTR-MS instruments are operated in selected-ion-scan mode (SIS), where a limited set of ions are chosen, and the quadrupole successively steps from one ion to the next, spending a certain dwell time on each. This limits the overall duty-cycle of the instrument and the de-facto time response. ToF instruments can measure all masses simultaneously, and modern PTR-ToF have high enough sensitivity for this characteristic to be advantageous. Additionally, modern PTR-ToF instruments are capable of high resolution (>4000 m/Δm), which allows the separation of isobaric species, and the determination of the exact elemental composition of many ion masses.

Another advance has been the development of “switchable reagent ion” instruments (Jordan et al., 2009a). These are PTR-MS instruments that have been modified to use reagent ions other than H$_3$O$^+$. Alternative reagent ions are used in order to detect trace gases not easily measurable with H$_3$O$^+$ and to separate isobaric and isomeric ions. Modifying a PTR-MS instrument can be relatively easy, and has obvious cost benefits over using a separate CIMS instrument. Most commonly, NO$^+$ and O$_2$ have been investigated as alternate reagent ions; use of NH$_4^+$, Kr$^+$, and other ions has also been explored. Prior to this work, only a few applications of NO$^+$ CIMS had been reported and the application to ambient air measurement was limited. The development of an NO$^+$ CIMS instrument and its application to VOC measurement are described in Chapter 5.
4. Thesis overview

In this thesis, I describe the development of CIMS techniques, specifically H$_3$O$^+$ CIMS (PTR-MS) and NO$^+$ CIMS, and the application of those techniques to VOC emissions and chemistry related to fossil fuel production and use. The chapters are as follows:

Chapter 2. Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event

The UBWOS 2013 study was conducted at a ground site in the Uintah Basin, Utah, an oil and gas producing region that experiences very high winter ozone. I used quadrupole PTR-MS to investigate photochemical aging of VOCs. Using an OH-chemistry driven box model constrained to measured VOC ratios, I determined ambient OH concentrations, defined the aromatic VOC source composition and emission rate, and inferred significant formation of unquantified secondary species. Co-deployment of a PTR-time-of-flight instrument (PTR-ToF) emphasized the potential for scientific advances using improved PTR-MS technology.

Chapter 3. Development of a high-resolution H$_3$O$^+$ time-of-flight chemical ionization mass spectrometer (H$_3$O$^+$ ToF-CIMS)

We developed our own PTR-ToF instrument based on the Aerodyne CIMS (the NOAA H$_3$O$^+$ ToF-CIMS). This instrument had higher sensitivity than contemporary commercially available instruments and is designed for mobile lab deployment. We extensively characterized the instrument performance. I have included detailed characterization of the effect of the RF-only segmented quadrupole ion guides, which are part of the latest generation of commercial PTR-ToF and Aerodyne CIMS.

Chapter 4. Observations of VOC emissions and chemical products over US oil- and gas-producing regions using high-resolution H$_3$O$^+$ ToF-CIMS (PTR-ToF-MS)

The new PTR-ToF instrument was deployed on the NOAA WP-3D Orion aircraft during the SONGNEX 2015 campaign, targeting western US oil and gas fields. Using PTR-ToF, we observed several previously unreported VOCs, including cyclic nitrogen-containing species and cycloalkane oxidation
products. I also compare mixing ratios of aromatics, oxygenated species, and hydrogen sulfide (H₂S) between production regions. The differences reflect regional sources, chemistry, and regulations. This work includes the first detailed VOC measurements in the Permian Basin, the largest oil and gas field in the United States.

Chapter 5. Evaluation of NO⁺ reagent ion chemistry for online measurements of atmospheric volatile organic compounds

The SONGNEX PTR-ToF deployment highlighted several weaknesses of the PTR-MS technique. PTR-MS has difficulty detecting many compounds found in fossil fuels, and provides no isomeric information (e.g. separating aldehydes and ketones). CIMS using NO⁺ has the potential to address these issues, but its application to atmospheric chemistry had not been thoroughly evaluated. Using a modified PTR-ToF instrument and a GC interface, I quantified the selectivity of NO⁺ for a number of aliphatics, created a guide to interpreting NO⁺ CIMS measurements of urban air, and demonstrated separation of carbonyl isomers and fast in-situ measurement of C12-C15 alkanes in ambient air.

Chapter 6. Direct measurement of on-road VOC emissions from vehicles using NO⁺ ToF-CIMS

The newly developed NO⁺ ToF-CIMS was deployed on a mobile laboratory in a pilot study to measure real-world highway vehicle emissions. The high time resolution of the NO⁺ ToF-CIMS allows the measurement of emission plumes from individual vehicles. This ability bridges the gap between dynamometer studies, which provide detailed information about specific vehicles but may not reflect fleet averages, and tunnel studies, which provide fleet-averaged emissions. Application of positive matrix factorization clearly identified the important emission sources, their VOC composition, and contribution to total VOC emissions.

Chapter 7. Summary and conclusions
Chapter 2. Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event

Abstract

High concentrations of volatile organic compounds (VOCs) associated with oil and natural gas extraction were measured during a strong temperature inversion in winter of 2013 at a rural site in the Uintah Basin, Utah. During this period, photochemistry enhanced by the stagnant meteorological conditions and concentrated VOCs led to high ozone mixing ratios (150 ppbv). An analysis of aromatic VOCs measured by quadrupole proton-transfer-reaction mass-spectrometry (PTR-MS) is used to estimate (1) VOC emission ratios (the ratio of two VOCs at the time of emission) relative to benzene, (2) aromatic VOC emission rates, and (3) ambient OH radical concentrations. These quantities are determined from a best fit to VOC:benzene ratios as a function of time. The main findings are that (1) emission ratios are consistent with contributions from both oil and gas producing wells; (2) the emission rate of methane \((27-57 \times 10^3 \text{ kg methane hr}^{-1})\), extrapolated from the emission rate of benzene \((4.1 \pm 0.4 \times 10^5 \text{ molecules cm}^3 \text{ s}^{-1})\), agrees with an independent estimate of methane emissions from aircraft measurements in 2012; and (3) calculated daily \(\text{OH}\) concentrations are low, peaking at \(1 \times 10^6 \text{ molecules cm}^3\), and are consistent with Master Chemical Mechanism (MCM) modeling. The analysis is extended to photochemical production of oxygenated VOCs measured by PTRMS and is able to explain daytime variability of these species. It is not able to completely reproduce nighttime behavior, possibly due to surface deposition. Using results from this analysis, the formation rate of measured secondary compounds was compared to the oxidation rate of primary species. The oxidation rate of primary species is a factor of two higher than the measured secondary species formation rate. The disparity is likely due to substantial formation of unquantified oxygenated products.


1. Introduction

Natural gas, crude oil, and natural gas liquids are major fuel sources -- accounting for 54% of 2013 US domestic energy production -- and extraction of these resources has been rising substantially since the mid 2000’s (US Energy Information Administration, 2016). This activity is associated with a range of possible environmental issues. Emissions due to extraction can: increase atmospheric concentrations of methane, a greenhouse gas (Miller et al., 2013; Brandt et al., 2014); directly impact local air quality through release of air toxics (Moore et al., 2014; Adgate et al., 2014; Li et al., 2014); and contribute to photochemical ozone formation (Schnell et al., 2009; Carter and Seinfeld, 2012; Edwards et al., 2014). Many scientific aspects of these processes are uncertain. Emissions budgets of methane and VOCs are poorly constrained and frequently do not agree with inventory estimates (Miller et al., 2013; Brandt et al., 2014). Many variables can affect the composition of emissions, including well life-cycle stage, extraction techniques, whether the well is producing oil or gas, and diverse infrastructure/equipment components (Litovitz et al., 2013; Allen et al., 2013; Moore et al., 2014). Wintertime ozone events, while sharing some similarities with ozone formation typically seen in urban areas during the summer, occur in different meteorological and chemical conditions and have attracted several recent measurement and modeling investigations (Kotamarthi and Holdridge, 2007; Schnell et al., 2009; Carter and Seinfeld, 2012; Edwards et al., 2013; Edwards et al., 2014).

The Uintah Basin, located in northeastern Utah, is a region of intense oil and natural gas extraction activity. In 2013, approximately 4000 active oil-producing and 6500 gas-producing wells were located in a 10000 km² area, with an additional 1000 wells added each year for several previous years (State of Utah Division of Oil Gas and Mining, 2017). In January and February of 2012-2014, a suite of chemical and meteorological instrumentation was deployed at Horse Pool, a remote site in the eastern part of the basin. Little active photochemistry was observed in 2012, but in 2013 ground snow cover was accompanied by
several sustained periods of strong temperature inversion. Temperature inversions trap ozone precursors emitted by oil and natural gas activity (VOCs and NOx) and ozone close to the surface. Increased actinic flux from reflective snow cover contributes to heightened ozone-producing photochemistry (Edwards et al., 2014). The gradual buildup of VOCs and ozone during a several day period of these conditions can lead to very high mixing ratios – in this case, up to 5ppmC non-methane hydrocarbon and 150ppb ozone. VOCs are a fundamental component of the photochemistry that occurred during these events, and so it is important to quantify (1) the rate at which VOCs are emitted from primary sources (“emission rate”), (2) the source composition of the VOC mixture (“emission ratios”), and (3) the degree of VOC oxidation.

In this chapter, I analyze the photochemical aging of VOCs during an ozone formation period in 2013 using a box model. I first examine primary, aromatic VOCs with a method that considers reaction with OH and constant primary emission. This analysis provides information on the emission rate and emission ratios of these VOCs, and the typical daily concentration of OH. I next investigate oxygenated VOCs with a method that includes production and loss via OH chemistry and loss to photolysis. This approach identifies oxygenated VOCs with substantial primary sources and suggests rates of carbonyl formation from photochemistry. Finally, I calculate the organic carbon mass balance of primary and product species. This defines overall VOC speciation and determines the fraction of product species measured with the Horse Pool instrumentation.

2. Methods

2.1 Measurement site and instrumentation.

The Horse Pool site is located in the central eastern part of the Uintah basin, approximately 30 km south of Vernal, Utah. Meteorological, gas, and particle-phase measurements were deployed concurrently at the site from 15 Jan. - 29 Feb. 2012, 23 Jan. – 22 Feb. 2013, and 15 Jan. – 13 Feb. 2014. Data referenced in this paper are primarily from a proton-transfer-reaction mass-spectrometer (PTR-MS), deployed in both 2012 and 2013, and a gas chromatograph with flame ionization detection (GC-FID), deployed in 2013. Measurements from 2014 are not discussed in this analysis.
PTR-MS uses chemical ionization with H$_3$O$^+$ ions to selectively detect VOCs (de Gouw and Warneke, 2007). The technique is particularly sensitive to aromatic and small oxygenated VOCs, but cannot detect small alkanes due to their low proton affinity relative to water. The instrument deployed at Horse Pool uses a quadrupole mass filter with unit mass resolution that scanned through a set of selected ions every 38 seconds. Data are averaged to a 1-minute time scale. Calibrated measurement accuracy is generally better than 20%, with a precision of 10%. The instrument is not able to distinguish between isomers; e.g. a measurement of C8 aromatics comprises the sum of ethylbenzene, o-, m-, and p- xyles. A high-resolution PTR time-of-flight mass spectrometer (PTR-ToF) from Ionicon Analytik owned by the University of Wyoming was also deployed at the site, for a shorter period of time (Warneke et al., 2015). Comparison with this instrument indicates negligible contribution from isobaric compounds (e.g., benzaldehyde contributing to the measurement of C8 aromatics). Some measurements from the Ionicon PTR-ToF instrument are discussed in Chapter 4.

The GC-FID deployed at Horse Pool resolves C2-C7 saturated and unsaturated hydrocarbons. Ambient air passes through water and carbon dioxide traps, then into a liquid nitrogen cryogenic VOC trap. VOCs are captured in the cryogenic trap for five minutes every half hour. After the five-minute sampling period, compounds are injected onto a 50m Al$_2$O$_3$/KCl PLOT column and analyzed using flame ionization detection. The accuracy and precision are dependent on compound and sample flow rate, but are generally <20% and <5%, respectively. The instrument has been previously described in more detail by Kuster et al. (2004).

Other measurements used in this paper include gas-chromatography mass-spectrometry (GC-MS) operated in 2012 (Gilman et al., 2010), methane cavity ring-down spectroscopy (CaRDS, Picarro) operated in 2013 (Crosson, 2008; Peischl et al., 2012), organic aerosol via quartz filter collection/thermal desorption in 2013 (Bates et al., 2004), snow organic carbon using a Shimadzu TOC-VCSH instrument in 2013, and organic peroxy nitrate (PAN) species by chemical ionization mass spectrometry (Slusher et al., 2004). Some sulfur-containing species were measured (Li et al., 2014) but are not discussed in this manuscript. Further

2.2 Data treatment

A stagnation event associated with high levels of ozone formation occurred from 29 Jan. to 10 Feb. 2013. A subset of this period, 31 Jan. 2013 20:48 (LT) through 08 Feb. 2013 05:29, is analyzed here (Figure 2.1). This period captures the majority of the ozone formation event, is characterized by a strong temperature inversion, and avoids periods of higher wind on 31 Jan. and 08 Feb. Selecting these meteorological conditions minimizes changes in VOC concentrations and ratios due to stronger mixing into or out of the basin.

Figure 2.1. Ozone formation event and analysis period selection.
The analyzed period (colored) was selected to avoid high wind events on Jan 31 and Feb 8. (center) and include strong temperature inversions (bottom) to minimize mixing of VOCs in or out of the basin. Meteorological data courtesy of NOAA Physical Sciences Division. Temperature data from tethered balloon sonde operated by NOAA Global Monitoring Division.
Primary hydrocarbons and oxygenated compounds investigated are listed in Table 2.1. The majority of analysis was applied to compounds measured by PTR-MS. The fast time resolution of this instrument (1 minute) allows the separation of plumes of VOCs from nearby sources from the more regionally widespread, accumulated emissions in the basin. Additionally, restricting analyzed compounds to a single instrument helps eliminate instrumental variation. Additional compounds from the GC-FID data set were used to investigate the balance of primary and secondary species.

<table>
<thead>
<tr>
<th>PTR-MS Primary compounds</th>
<th>OH rate constant (10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</th>
<th>Average mixing ratio ppbv (1 σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>1.22</td>
<td>3.30 (1.92)</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.63</td>
<td>4.00 (2.76)</td>
</tr>
<tr>
<td>C8 aromatics</td>
<td>16.4(^a)</td>
<td>1.74 (1.36)</td>
</tr>
<tr>
<td>C9 aromatics</td>
<td>16.9(^a)</td>
<td>0.365 (0.271)</td>
</tr>
<tr>
<td>C10 aromatics</td>
<td>24.2(^a)</td>
<td>0.071 (0.055)</td>
</tr>
<tr>
<td>Secondary compounds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>15.0</td>
<td>4.27 (2.39)</td>
</tr>
<tr>
<td>2-butanone (MEK)</td>
<td>1.22</td>
<td>2.81 (1.69)</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.17</td>
<td>7.97 (4.69)</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.37(^b)</td>
<td>2.56 (1.43)</td>
</tr>
<tr>
<td>Compounds with mixed or undetermined source</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.94</td>
<td>44.9 (33.4)</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>9.37</td>
<td>3.71 (1.49)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GC-FID Primary compounds</th>
<th>Average mixing ratio ppbv (1 σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.248 300 (169)</td>
</tr>
<tr>
<td>Propane</td>
<td>1.09 140 (78.6)</td>
</tr>
<tr>
<td>n-butane</td>
<td>2.36 48.0 (26.9)</td>
</tr>
<tr>
<td>2-methylpropane</td>
<td>2.12 30.3 (17.1)</td>
</tr>
<tr>
<td>n-pentane</td>
<td>3.80 18.8 (10.5)</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td>3.60 20.9 (11.8)</td>
</tr>
<tr>
<td>2,2-dimethylpropane</td>
<td>0.825 0.306 (0.181)</td>
</tr>
<tr>
<td>n-hexane</td>
<td>5.20 8.32 (4.65)</td>
</tr>
<tr>
<td>Sum of 2- and 3- methylpentane</td>
<td>5.20 6.62 (3.99)</td>
</tr>
<tr>
<td>2,2-dimethylbutane</td>
<td>2.23 0.467 (0.294)</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>6.90 3.65 (2.27)</td>
</tr>
<tr>
<td>n-heptane</td>
<td>6.76 4.00 (2.30)</td>
</tr>
<tr>
<td>Methylocyclohexane</td>
<td>9.64 6.74 (4.17)</td>
</tr>
<tr>
<td>Ethyne</td>
<td>0.88 0.796 (0.40)</td>
</tr>
<tr>
<td>Ethene</td>
<td>8.52 2.05 (1.06)</td>
</tr>
<tr>
<td>Propene</td>
<td>26.3 0.171 (0.0724)</td>
</tr>
</tbody>
</table>

Table 2.1. Compounds analyzed.
\(^a\) Rate constants determined in this work.
\(^b\) Anglada (2004).
All other OH rate constants from Atkinson and Arey (2003).
Chapter 1. Introduction

1. VOCs in the atmosphere

Volatile organic compounds (VOCs) are one of the most fascinating and complex classes of chemicals in Earth’s atmosphere. They are ubiquitous in the troposphere and intrinsically related to life: plants are responsible for three-fifths of the non-methane organic gases emitted to the atmosphere, biological activity in the oceans emits another fifth, and the remaining fifth comes from biomass burning and human activity (Figure 1.1). Chemical transformation of VOCs in the atmosphere can create less volatile species that contribute to the formation and growth of aerosols. Photochemistry involving VOCs and nitrogen oxides leads to the formation of ozone. Aerosols, ozone, and many VOCs are harmful to human health, and ozone and aerosols are radiative forcing agents. In the United States, anthropogenic emission of VOCs is regulated under the Clean Air Act.

In the United States, production and use of fossil fuels have consistently accounted for about half of anthropogenic VOC emissions over the past 45 years (EPA). However, the various contributions to this category, and the total emissions, have changed considerably over time. Since 1970, the total VOC emissions from highway vehicles have decreased by a factor of 10; in 1970, this source accounted for half of anthropogenic VOC emissions, while today it accounts for only 13% (Figure 1.2). Conversely, emissions from petroleum and related industries have been rising substantially since the mid 2000’s.

This thesis describes the development and application of methods to measure VOCs associated with fossil fuel sources. The majority of the work focuses on air quality impacts from oil and natural gas.
extraction. An additional section describes the application of a new measurement technique to on-road vehicle emissions. This chapter provides background information on VOC chemistry from these sources, VOC measurement technology, and a thesis summary.

2. VOC emissions from fossil fuel sources

The recent rise in emissions from petroleum industry reflects a rapid and dramatic increase in domestic production in several regions with “unconventional” reservoirs (tight oil and gas, Figure 1.3). This surge has been largely driven by improvements in extraction technology such as hydraulic fracturing and directional drilling. VOC emissions from oil and natural gas extraction activity can influence global climate, and local and regional air quality.

Replacing coal with natural gas may have climate and air quality benefits: natural gas produces less CO$_2$ and other pollutants (Jackson et al., 2014; de Gouw et al., 2014). However, methane, the main component of natural gas, is a potent greenhouse gas, with a global warming potential 30 times that of CO$_2$ over a 100 year time frame (IPCC, 2013). If a natural gas extraction field leaks a sufficient amount of methane, the climate benefits of using natural gas could be offset. There are different numbers for the “break-even” leak rate, but it is likely around 3% of production (Alvarez et al., 2012). Top-down estimates from aircraft suggest that leak rates in some basins are higher than this, and that regulatory inventories generally underestimate methane emissions (Miller et al., 2013; Karion et al., 2013; Moore et al., 2014; Brandt et al., 2014; Pétron et al., 2014; Peischl et al., 2015).

![Figure 1.3. Oil and gas production from several key unconventional production regions. Data and map from US Energy Information Administration.](image-url)
Regional air quality can be adversely affected by extraction activity. VOCs emitted by oil and gas operations contribute to extremely high ozone episodes in rural areas of Utah and Wyoming in the winter (Schnell et al., 2009; Edwards et al., 2014), and can enhance ozone and possibly fine particulate levels near urban areas in the summer (Kemball-Cook et al., 2010; Olaguer, 2012; McDuffie et al., 2016; Roohani et al., 2017).

Air toxics, including small aromatics (benzene, toluene, ethylbenzene, and xylenes, or “BTEX”), formaldehyde, hydrogen sulfide (H$_2$S), polycyclic aromatic hydrocarbons (PAHs), and methylene chloride, can be emitted from production sites in significant quantities, during the initial drilling phase but also afterwards during the production phase (Colborn et al., 2014; McKenzie et al., 2012; Adgate et al., 2014; Macey et al., 2014; Li et al., 2014; Warneke et al., 2014). Several studies have indicated that air toxic emissions may be important on a very local scale, to people who work on well pads, or whose homes are near production sites (Bunch et al., 2014; Colorado State University, 2016).

Most studies of VOC emissions from oil and gas operations have measured a relatively limited set of non-methane VOCs, typically including BTEX, alkanes, and occasionally small oxygenates such as methanol and formaldehyde. Several studies have achieved much higher VOC chemical detail, including quantification of larger (>C5) alkanes, cyclic alkanes, more highly-alkyl-substituted aromatics, alkenes, halocarbons, and a wide range of photochemically produced species (Simpson et al., 2010; Gilman et al., 2013; Swarthout et al., 2013; Utah Division of Air Quality, 2014). The higher chemical detail has been valuable for modeling studies (Edwards et al., 2014; Ahmadov et al., 2015; McDuffie et al., 2016).

While VOC emissions from the production of fossil fuels have been rising, emissions from one of their end uses – vehicles – have fallen dramatically (Figure 1.2). A corresponding decrease in ambient mixing ratios of many VOCs has been described in Los Angeles (Warneke et al., 2012) and London (von Schneidemesser et al., 2010). The decrease is attributable to more stringent emissions standards, leading to improved emissions reduction technology in both vehicles and fuels (Sawyer et al., 2000; Sandhu and Frey, 2012; McDonald et al., 2013). The VOC composition of vehicle-related emissions has been extensively
characterized from laboratory and tunnel studies (Kean et al., 2001; Schauer et al., 2002; Gentner et al., 2013; May et al., 2014), but up-to-date field measurements of VOCs are still important. They are necessary to know whether regulations are working, which emission sources are the most effective regulatory targets, and to answer current science questions, such as whether gasoline or diesel fuel usage contributes more to ambient secondary organic aerosol formation (Gentner et al., 2012; Bahreini et al., 2012). The recent Volkswagen scandal has also illustrated the importance of having real-world in-situ measurements as well as laboratory and dynamometer studies (Thompson et al., 2014).

What types of VOCs are found in fossil fuels? Both crude and refined fuels are dominated by the same types of compounds – alkanes, alkenes, aromatics, and cyclic alkanes – but the relative distribution of these compounds varies (Figure 1.4). Crude fuels have highly variable composition depending on the source reservoir, and can include relatively high abundances (a few weight %) of nitrogen, oxygen, and sulfur-containing VOCs and related volatile species such as H₂S (Speight, 2006). Extraction activity by the fossil fuel industry can release VOCs, like methanol, that are not found in the crude fuel (Mansfield et al., 2016). Tailpipe exhaust can additionally contain oxygenates such as ethanol and formaldehyde (Gentner et al., 2013).

In the atmosphere, these compounds undergo oxidation reactions and form a wide range of products. Generally speaking, the reactivity of these groups with the OH radical increases in the order: alkanes < cycloalkanes < aromatics < alkenes (Atkinson and Arey, 2003). Alkenes
additionally undergo reaction with O₃ and NO₃. First-generation products of alkanes and cycloalkanes include a range of carbonyls, alkyl nitrates, and (hydro)peroxides (Calvert et al., 2008); aromatics produce glyoxal, phenols, nitrophenols, benzaldehydes, and furanones (Wagner et al., 2003; Wyche et al., 2009); alkenes form carbonyls, hydroxynitrates, furans, oxiranes, and nitrates, among other products (Calvert et al., 2000). First generation products react further to produce more highly oxidized species, fragmentary compounds, peroxy nitrates (PANs), and ultimately CO and CO₂.

3. Measurement of VOCs using Proton-transfer-reaction mass spectrometry

It is clear that comprehensive and precise measurements of VOCs are required to understand the chemistry leading to the formation of ozone and particulates, and to properly assess the need for and effect of regulations. However, VOC measurements are challenging. Goldstein and Galbally (2007) estimate that 10⁴ to 10⁵ individual organic species have been detected in the atmosphere, and many more remain as yet undetected. VOCs are highly chemically diverse, and the composition of the VOC mixture can change dramatically depending on emission sources and chemistry. VOCs in air are typically very dilute, requiring instrumentation with part-per-trillion (ppt) detection level capability.

A number of methods have been developed to address the challenges of measuring VOCs in-situ. One class of techniques is based on gas chromatography (GC). GC techniques can provide very specific VOC identification, measure a wide range of compounds, and have very high sensitivity when used with cryogenic or adsorbent pre-concentration (Nozière et al., 2015). However, GC techniques have several drawbacks. They have limited time resolution, with typical sample periods of 15 minutes to several hours. Several pre-treatment steps such as remote collection with a whole-air-sampler, removal of water and ozone, and cryogenic pre-concentration may be required, which may create sample artifacts or loss of specific classes of VOC (Kuster et al., 2004; Lerner et al., 2017).

Mass spectrometry techniques provide a complementary approach. Although less chemically specific information is provided (only the mass-to-charge ratio of a VOC is measured), mass spectrometry techniques can measure much faster and require less sample pre-treatment. They are better suited to
measurement from a mobile platform, or for other studies such as eddy covariance investigations where very high time resolution is necessary. Combined with co-deployment of a GC technique, highly time resolved and chemically specific VOC information can be obtained.

One especially popular direct mass spectrometry analysis technique in atmospheric chemistry is proton-transfer-reaction mass spectrometry (PTR-MS). PTR-MS was first developed in the mid-1990s by the Lindinger group in Innsbruck, Austria (Lindinger et al., 1998) and has found widespread use not only in atmospheric chemistry, but also in medical diagnostics, the food and flavor industry, and security applications (Blake et al., 2009; Biasioli et al., 2011).

PTR-MS is a chemical ionization method, the goal of which is to create ions with little excess energy. The resulting mass spectrum contains few fragment ions, and may be used to analyze complex sample mixtures, such as VOCs in air. A reagent ion $RH^+$ is created and mixed with analyte molecules $A$. The thermodynamics are described by the “proton affinity” of the neutral molecules, which is the energy released when a neutral molecule is protonated. If the reaction $RH^+ + A \rightarrow R + A^H^+$ is exothermic (in other words, if the proton affinity of $A$ is higher than that of $R$), then the proton transfers from the reagent ion to the analyte molecule, which can then be measured with a mass spectrometer.

Although proton transfer reactions can be accomplished with a number of reagents, most commonly methane, isobutene, or ammonia; in atmospheric applications, “PTR-MS” almost exclusively refers to proton transfer using protonated water ($H_3O^+$) reagent ions. $H_3O^+$ is generated from water vapor in an ion source (in the PTR-MS instruments used in this work, the ion source is an electrical discharge in a hollow cathode). $H_3O^+$ ions are then mixed with VOC-containing air in a drift tube region. A strong electric field is applied along the length of the drift tube to prevent cluster formation and accelerate the ions into the mass analyzer section of the instrument (de Gouw and Warneke, 2007).

In theory, PTR-MS can detect molecules with a proton affinity higher than that of water (PA = 691 kJ mol$^{-1}$); this includes aromatics, alkenes larger than ethene, alkanes larger than hexane, alkyl-substituted
cycloalkanes, and a wide range of oxygenated and other polar molecules, including carbonyls, alcohols, acids, furans, etc.

The PTR-MS response to a particular VOC $A$ can be described relatively simply (de Gouw and Warneke, 2007). As molecules of $A$ travel through the drift tube, they react with $H_3O^+$ with rate $k$ over reaction time $\Delta t$. The number of $AH^+$ ions created is equal and opposite to the $H_3O^+$ lost. If only a small fraction of $H_3O^+$ are lost ([A] is small), then the number of $AH^+$ created is approximately linear with $k$, $[H_3O^+]$, and [A]:

$$[AH^+] = [H_3O^+](1 - e^{-k[A]|\Delta t}) \approx [H_3O^+]k[A]|\Delta t$$

The reaction time $\Delta t$, the time needed to traverse the drift tube, depends on drift tube length $L$, number density $N$, electric field $E$, and ion mobility $\mu$:

$$\Delta t = \frac{L}{\mu E} = \frac{L}{\mu N} \times \left(\frac{E}{N}\right)^{-1}$$

(The ion mobility $\mu$ is usually reported as the mobility under standard conditions, $\mu_0 = \mu \times N_0/N$).

The measured ion signal of $AH^+$ ($I_{AH^+}$), normalized to the primary ion signal ($I_{H_3O^+}$), is then linearly related to the volume mixing ratio of $A$ ($[A]/N$):

$$\frac{I_{AH^+}}{I_{H_3O^+}} = \frac{[AH^+]}{[H_3O^+]T_{AH^+}} = \frac{kL}{\mu} \times \frac{E}{N} \times \frac{[A]}{N}$$

where $T_{AH^+}$ and $T_{H_3O^+}$ are the relative transmissions of the VOC and reagent ions between the drift tube and detector. The volume mixing ratio of VOC $A$ can therefore be determined by measuring the ion signal of $AH^+$, normalizing to the ion signal of $H_3O^+$, and applying a linear calibration factor.

In practice, more reactions than simple proton transfer are possible in a PTR-MS instrument, and factors other than proton affinity and reaction rate constant contribute to the instrument response. Some $H_3O^+$ reactions, such as with alcohols and alkanes, are dissociative, and significant fragmentation occurs. Other reactions involve ligand-switching between a water cluster and VOC molecule. Sensitivities can also be humidity-dependent. Characterization of a PTR-MS instrument response to a wide range of VOCs is described in Chapter 3.
The measurement capability of PTR-MS instruments has improved dramatically over the past two decades. One major advance has been the application of time-of-flight mass analyzers to PTR-MS. Until very recently, PTR-MS most commonly used a quadrupole mass analyzer. (This includes the instrument described in Chapter 2). Typically, quadrupole PTR-MS instruments are operated in selected-ion-scan mode (SIS), where a limited set of ions are chosen, and the quadrupole successively steps from one ion to the next, spending a certain dwell time on each. This limits the overall duty-cycle of the instrument and the de-facto time response. ToF instruments can measure all masses simultaneously, and modern PTR-ToF have high enough sensitivity for this characteristic to be advantageous. Additionally, modern PTR-ToF instruments are capable of high resolution (>4000 m/Δm), which allows the separation of isobaric species, and the determination of the exact elemental composition of many ion masses.

Another advance has been the development of “switchable reagent ion” instruments (Jordan et al., 2009a). These are PTR-MS instruments that have been modified to use reagent ions other than H_3O^+. Alternative reagent ions are used in order to detect trace gases not easily measurable with H_3O^+ and to separate isobaric and isomeric ions. Modifying a PTR-MS instrument can be relatively easy, and has obvious cost benefits over using a separate CIMS instrument. Most commonly, NO^+ and O_2^+ have been investigated as alternate reagent ions; use of NH_4^+, Kr^+, and other ions has also been explored. Prior to this work, only a few applications of NO^+ CIMS had been reported and the application to ambient air measurement was limited. The development of an NO^+ CIMS instrument and its application to VOC measurement are described in Chapter 5.
4. Thesis overview

In this thesis, I describe the development of CIMS techniques, specifically \( \text{H}_3\text{O}^+ \) CIMS (PTR-MS) and NO\(^+\) CIMS, and the application of those techniques to VOC emissions and chemistry related to fossil fuel production and use. The chapters are as follows:

Chapter 2. Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event

The UBWOS 2013 study was conducted at a ground site in the Uintah Basin, Utah, an oil and gas producing region that experiences very high winter ozone. I used quadrupole PTR-MS to investigate photochemical aging of VOCs. Using an OH-chemistry driven box model constrained to measured VOC ratios, I determined ambient OH concentrations, defined the aromatic VOC source composition and emission rate, and inferred significant formation of unquantified secondary species. Co-deployment of a PTR-time-of-flight instrument (PTR-ToF) emphasized the potential for scientific advances using improved PTR-MS technology.

Chapter 3. Development of a high-resolution \( \text{H}_3\text{O}^+ \) time-of-flight chemical ionization mass spectrometer (\( \text{H}_3\text{O}^+ \) ToF-CIMS)

We developed our own PTR-ToF instrument based on the Aerodyne CIMS (the NOAA \( \text{H}_3\text{O}^+ \) ToF-CIMS). This instrument had higher sensitivity than contemporary commercially available instruments and is designed for mobile lab deployment. We extensively characterized the instrument performance. I have included detailed characterization of the effect of the RF-only segmented quadrupole ion guides, which are part of the latest generation of commercial PTR-ToF and Aerodyne CIMS.

Chapter 4. Observations of VOC emissions and chemical products over US oil- and gas-producing regions using high-resolution \( \text{H}_3\text{O}^+ \) ToF-CIMS (PTR-ToF-MS)

The new PTR-ToF instrument was deployed on the NOAA WP-3D Orion aircraft during the SONGNEX 2015 campaign, targeting western US oil and gas fields. Using PTR-ToF, we observed several previously unreported VOCs, including cyclic nitrogen-containing species and cycloalkane oxidation
products. I also compare mixing ratios of aromatics, oxygenated species, and hydrogen sulfide (H\textsubscript{2}S) between production regions. The differences reflect regional sources, chemistry, and regulations. This work includes the first detailed VOC measurements in the Permian Basin, the largest oil and gas field in the United States.

**Chapter 5. Evaluation of NO\textsuperscript{+} reagent ion chemistry for online measurements of atmospheric volatile organic compounds**

The SONGNEX PTR-ToF deployment highlighted several weaknesses of the PTR-MS technique. PTR-MS has difficulty detecting many compounds found in fossil fuels, and provides no isomeric information (e.g. separating aldehydes and ketones). CIMS using NO\textsuperscript{+} has the potential to address these issues, but its application to atmospheric chemistry had not been thoroughly evaluated. Using a modified PTR-ToF instrument and a GC interface, I quantified the selectivity of NO\textsuperscript{+} for a number of aliphatics, created a guide to interpreting NO\textsuperscript{+} CIMS measurements of urban air, and demonstrated separation of carbonyl isomers and fast in-situ measurement of C12-C15 alkanes in ambient air.

**Chapter 6. Direct measurement of on-road VOC emissions from vehicles using NO\textsuperscript{+} ToF-CIMS**

The newly developed NO\textsuperscript{+} ToF-CIMS was deployed on a mobile laboratory in a pilot study to measure real-world highway vehicle emissions. The high time resolution of the NO\textsuperscript{+} ToF-CIMS allows the measurement of emission plumes from individual vehicles. This ability bridges the gap between dynamometer studies, which provide detailed information about specific vehicles but may not reflect fleet averages, and tunnel studies, which provide fleet-averaged emissions. Application of positive matrix factorization clearly identified the important emission sources, their VOC composition, and contribution to total VOC emissions.

**Chapter 7. Summary and conclusions**
Chapter 2. Photochemical aging of volatile organic compounds associated with oil and natural gas extraction in the Uintah Basin, UT, during a wintertime ozone formation event

Abstract

High concentrations of volatile organic compounds (VOCs) associated with oil and natural gas extraction were measured during a strong temperature inversion in winter of 2013 at a rural site in the Uintah Basin, Utah. During this period, photochemistry enhanced by the stagnant meteorological conditions and concentrated VOCs led to high ozone mixing ratios (150 ppbv). An analysis of aromatic VOCs measured by quadrupole proton-transfer-reaction mass-spectrometry (PTR-MS) is used to estimate (1) VOC emission ratios (the ratio of two VOCs at the time of emission) relative to benzene, (2) aromatic VOC emission rates, and (3) ambient OH radical concentrations. These quantities are determined from a best fit to VOC:benzene ratios as a function of time. The main findings are that (1) emission ratios are consistent with contributions from both oil and gas producing wells; (2) the emission rate of methane (27-57×10³ kg methane hr⁻¹), extrapolated from the emission rate of benzene (4.1±0.4×10⁵ molecules cm⁻³ s⁻¹), agrees with an independent estimate of methane emissions from aircraft measurements in 2012; and (3) calculated daily OH concentrations are low, peaking at 1×10⁶ molecules cm⁻³, and are consistent with Master Chemical Mechanism (MCM) modeling. The analysis is extended to photochemical production of oxygenated VOCs measured by PTRMS and is able to explain daytime variability of these species. It is not able to completely reproduce nighttime behavior, possibly due to surface deposition. Using results from this analysis, the formation rate of measured secondary compounds was compared to the oxidation rate of primary species. The oxidation rate of primary species is a factor of two higher than the measured secondary species formation rate. The disparity is likely due to substantial formation of unquantified oxygenated products.


1. Introduction

Natural gas, crude oil, and natural gas liquids are major fuel sources -- accounting for 54% of 2013 US domestic energy production -- and extraction of these resources has been rising substantially since the mid 2000’s (US Energy Information Administration, 2016). This activity is associated with a range of possible environmental issues. Emissions due to extraction can: increase atmospheric concentrations of methane, a greenhouse gas (Miller et al., 2013; Brandt et al., 2014); directly impact local air quality through release of air toxics (Moore et al., 2014; Adgate et al., 2014; Li et al., 2014); and contribute to photochemical ozone formation (Schnell et al., 2009; Carter and Seinfeld, 2012; Edwards et al., 2014). Many scientific aspects of these processes are uncertain. Emissions budgets of methane and VOCs are poorly constrained and frequently do not agree with inventory estimates (Miller et al., 2013; Brandt et al., 2014). Many variables can affect the composition of emissions, including well life-cycle stage, extraction techniques, whether the well is producing oil or gas, and diverse infrastructure/equipment components (Litovitz et al., 2013; Allen et al., 2013; Moore et al., 2014). Wintertime ozone events, while sharing some similarities with ozone formation typically seen in urban areas during the summer, occur in different meteorological and chemical conditions and have attracted several recent measurement and modeling investigations (Kotamarthi and Holdridge, 2007; Schnell et al., 2009; Carter and Seinfeld, 2012; Edwards et al., 2013; Edwards et al., 2014).

The Uintah Basin, located in northeastern Utah, is a region of intense oil and natural gas extraction activity. In 2013, approximately 4000 active oil-producing and 6500 gas-producing wells were located in a 10000 km² area, with an additional 1000 wells added each year for several previous years (State of Utah Division of Oil Gas and Mining, 2017). In January and February of 2012-2014, a suite of chemical and meteorological instrumentation was deployed at Horse Pool, a remote site in the eastern part of the basin. Little active photochemistry was observed in 2012, but in 2013 ground snow cover was accompanied by
several sustained periods of strong temperature inversion. Temperature inversions trap ozone precursors emitted by oil and natural gas activity (VOCs and NOx) and ozone close to the surface. Increased actinic flux from reflective snow cover contributes to heightened ozone-producing photochemistry (Edwards et al., 2014). The gradual buildup of VOCs and ozone during a several day period of these conditions can lead to very high mixing ratios – in this case, up to 5ppmC non-methane hydrocarbon and 150ppb ozone. VOCs are a fundamental component of the photochemistry that occurred during these events, and so it is important to quantify (1) the rate at which VOCs are emitted from primary sources (“emission rate”), (2) the source composition of the VOC mixture (“emission ratios”), and (3) the degree of VOC oxidation.

In this chapter, I analyze the photochemical aging of VOCs during an ozone formation period in 2013 using a box model. I first examine primary, aromatic VOCs with a method that considers reaction with OH and constant primary emission. This analysis provides information on the emission rate and emission ratios of these VOCs, and the typical daily concentration of OH. I next investigate oxygenated VOCs with a method that includes production and loss via OH chemistry and loss to photolysis. This approach identifies oxygenated VOCs with substantial primary sources and suggests rates of carbonyl formation from photochemistry. Finally, I calculate the organic carbon mass balance of primary and product species. This defines overall VOC speciation and determines the fraction of product species measured with the Horse Pool instrumentation.

2. Methods

2.1 Measurement site and instrumentation.

The Horse Pool site is located in the central eastern part of the Uintah basin, approximately 30 km south of Vernal, Utah. Meteorological, gas, and particle-phase measurements were deployed concurrently at the site from 15 Jan. - 29 Feb. 2012, 23 Jan. – 22 Feb. 2013, and 15 Jan. – 13 Feb. 2014. Data referenced in this paper are primarily from a proton-transfer-reaction mass-spectrometer (PTR-MS), deployed in both 2012 and 2013, and a gas chromatograph with flame ionization detection (GC-FID), deployed in 2013. Measurements from 2014 are not discussed in this analysis.
PTR-MS uses chemical ionization with H$_3$O$^+$ ions to selectively detect VOCs (de Gouw and Warneke, 2007). The technique is particularly sensitive to aromatic and small oxygenated VOCs, but cannot detect small alkanes due to their low proton affinity relative to water. The instrument deployed at Horse Pool uses a quadrupole mass filter with unit mass resolution that scanned through a set of selected ions every 38 seconds. Data are averaged to a 1-minute time scale. Calibrated measurement accuracy is generally better than 20%, with a precision of 10%. The instrument is not able to distinguish between isomers; e.g. a measurement of C8 aromatics comprises the sum of ethylbenzene, o-, m-, and p- xylenes. A high-resolution PTR time-of-flight mass spectrometer (PTR-ToF) from Ionicon Analytik owned by the University of Wyoming was also deployed at the site, for a shorter period of time (Warneke et al., 2015). Comparison with this instrument indicates negligible contribution from isobaric compounds (e.g., benzaldehyde contributing to the measurement of C8 aromatics). Some measurements from the Ionicon PTR-ToF instrument are discussed in Chapter 4.

The GC-FID deployed at Horse Pool resolves C2-C7 saturated and unsaturated hydrocarbons. Ambient air passes through water and carbon dioxide traps, then into a liquid nitrogen cryogenic VOC trap. VOCs are captured in the cryogenic trap for five minutes every half hour. After the five-minute sampling period, compounds are injected onto a 50m Al$_2$O$_3$/KCl PLOT column and analyzed using flame ionization detection. The accuracy and precision are dependent on compound and sample flow rate, but are generally <20% and <5%, respectively. The instrument has been previously described in more detail by Kuster et al. (2004).

Other measurements used in this paper include gas-chromatography mass-spectrometry (GC-MS) operated in 2012 (Gilman et al., 2010), methane cavity ring-down spectroscopy (CaRDS, Picarro) operated in 2013 (Crosson, 2008; Peischl et al., 2012), organic aerosol via quartz filter collection/thermal desorption in 2013 (Bates et al., 2004), snow organic carbon using a Shimadzu TOC-VCSH instrument in 2013, and organic peroxy nitrate (PAN) species by chemical ionization mass spectrometry (Slusher et al., 2004). Some sulfur-containing species were measured (Li et al., 2014) but are not discussed in this manuscript. Further

2.2 Data treatment

A stagnation event associated with high levels of ozone formation occurred from 29 Jan. to 10 Feb. 2013. A subset of this period, 31 Jan. 2013 20:48 (LT) through 08 Feb. 2013 05:29, is analyzed here (Figure 2.1). This period captures the majority of the ozone formation event, is characterized by a strong temperature inversion, and avoids periods of higher wind on 31 Jan. and 08 Feb. Selecting these meteorological conditions minimizes changes in VOC concentrations and ratios due to stronger mixing into or out of the basin.

Figure 2.1. Ozone formation event and analysis period selection. The analyzed period (colored) was selected to avoid high wind events on Jan 31 and Feb 8. (center) and include strong temperature inversions (bottom) to minimize mixing of VOCs in or out of the basin. Meteorological data courtesy of NOAA Physical Sciences Division. Temperature data from tethered balloon sondes operated by NOAA Global Monitoring Division.
Primary hydrocarbons and oxygenated compounds investigated are listed in Table 2.1. The majority of analysis was applied to compounds measured by PTR-MS. The fast time resolution of this instrument (1 minute) allows the separation of plumes of VOCs from nearby sources from the more regionally widespread, accumulated emissions in the basin. Additionally, restricting analyzed compounds to a single instrument helps eliminate instrumental variation. Additional compounds from the GC-FID data set were used to investigate the balance of primary and secondary species.

<table>
<thead>
<tr>
<th>PTR-MS</th>
<th>OH rate constant 10^{12} cm^3 molecule^{-1} s^{-1}</th>
<th>Average mixing ratio ppbv (1 σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Primary compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td>1.22</td>
<td>3.30 (1.92)</td>
</tr>
<tr>
<td>Toluene</td>
<td>5.63</td>
<td>4.00 (2.76)</td>
</tr>
<tr>
<td>C8 aromatics</td>
<td>16.4a</td>
<td>1.74 (1.36)</td>
</tr>
<tr>
<td>C9 aromatics</td>
<td>16.9a</td>
<td>0.365 (0.271)</td>
</tr>
<tr>
<td>C10 aromatics</td>
<td>24.2a</td>
<td>0.071 (0.055)</td>
</tr>
<tr>
<td><strong>Secondary compounds</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>15.0</td>
<td>4.27 (2.39)</td>
</tr>
<tr>
<td>2-butanone (MEK)</td>
<td>1.22</td>
<td>2.81 (1.69)</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.17</td>
<td>7.97 (4.69)</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.37b</td>
<td>2.56 (1.43)</td>
</tr>
<tr>
<td><strong>Compounds with mixed or undetermined source</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>0.94</td>
<td>44.9 (33.4)</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>9.37</td>
<td>3.71 (1.49)</td>
</tr>
</tbody>
</table>

| GC-FID                       |                                                     |                                 |
|------------------------------|                                                     |                                 |
| **Primary compounds**        |                                                     |                                 |
| Ethane                       | 0.248                                               | 300 (169)                       |
| Propane                      | 1.09                                                | 140 (78.6)                      |
| n-butane                     | 2.36                                                | 48.0 (26.9)                     |
| 2-methylpropane              | 2.12                                                | 30.3 (17.1)                     |
| n-pentane                    | 3.80                                                | 18.8 (10.5)                     |
| 2-methylbutane               | 3.60                                                | 20.9 (11.8)                     |
| 2,2-dimethylpropane          | 0.825                                               | 0.306 (0.181)                   |
| n-hexane                     | 5.20                                                | 8.32 (4.65)                     |
| Sum of 2- and 3- methylpentane | 5.20                                              | 6.62 (3.99)                     |
| 2,2-dimethylbutane           | 2.23                                                | 0.467 (0.294)                   |
| Methylcyclopentane           | 6.90                                                | 3.65 (2.27)                     |
| n-heptane                    | 6.76                                                | 4.00 (2.30)                     |
| Methyloxyhexane              | 9.64                                                | 6.74 (4.17)                     |
| Ethyne                       | 0.88                                                | 0.796 (0.40)                    |
| Ethene                       | 8.52                                                | 2.05 (1.06)                     |
| Propene                      | 26.3                                                | 0.171 (0.0724)                  |

Table 2.1. Compounds analyzed.

a Rate constants determined in this work.
b Anglada (2004).
All other OH rate constants from Atkinson and Arey (2003).
Concentrations of VOCs during an inversion event displayed rapid, diurnal, and multi-day variability (Figure 2.2). Some of this variability is attributable to meteorology (such as changes in boundary layer height during the day, or temporary shifts in wind direction bringing pollution from nearby sources), and some to chemistry, but the relative contributions can be difficult to separate. Analysis of ratios of VOCs provides a way to isolate the effects of chemistry from meteorology. This is a common and flexible approach: applications have included determining the photochemical age of urban emissions (Roberts et al., 1984; de Gouw et al., 2005), quantifying halogen chemistry in arctic air (Jobson et al., 1994), and identifying contributions from oil and natural gas operations to ambient pollution (Gilman et al., 2013).

Figure 2.2. Description of trends in VOC concentrations and ratios.
(A) Mixing ratios of benzene, C9 aromatics, and acetone (black), and a one hour running median to isolate spikes (red). (B) Ratios of C9 aromatics (top) and acetone (center) to benzene. Sunlight intensity is shown beneath. The spikes visible in panel (A) have been removed to isolate longer-term trends in VOC behavior (discussed in text).

Measurements of primary compounds by PTR-MS showed frequent 1-3 minute duration episodes with very high mixing ratios, at least 50% higher than short-term average concentration. These spikes
signify interception of plumes of un-aged emissions and are not representative of the bulk air composition at the Horse Pool site. An hourly running median was applied to separate longer-term variability from transitory primary emissions (Figure 2.2). For consistency, an hourly running median was also applied to oxygenated compounds. The ratio of each VOC to benzene was then determined. Benzene is a well-calibrated compound with few interferences on the PTR-MS; additionally, good agreement with other instrumentation (GC-FID and PTR-ToF) at the site affords a high level of confidence in this measurement (Warneke et al., 2015).

3. Results and Discussion

3.1 Primary compounds

Primary compounds are defined as those species that are directly emitted and not formed by photochemistry. The rate of change with time of a single, primary VOC can be written as

$$\frac{d[VOC]}{dt} = P_{VOC} - k_{VOC}[OH][VOC] - \sum D_i[VOC]$$  \hspace{1cm} (2.1)

where $P_{VOC}$ is the emission rate of the VOC and $k_{VOC}$ is the rate constant for the reaction of the VOC with OH. $P_{VOC}$ is a volumetric input with units of molecule cm$^{-3}$ s$^{-1}$ and describes how direct emission increases observed VOC concentrations. The only chemical loss term included is reaction with OH, the major oxidizing radical in this environment. Previous modeling has suggested that VOC reactions with other radicals, such as Cl•, were negligible in comparison to reaction with OH (Edwards et al., 2014). Additionally, reaction rates of the primary species considered here (C6-C10 aromatics) with O$_3$ and NO$_3$ are at least several orders of magnitude lower than reaction rates with OH (Atkinson and Arey, 2003). $D_i$ are rate constants for first-order loss processes; e.g. deposition, dilution, photolysis, etc.

If two VOCs, “A” and “B”, behave according to Equation (1), the rate of change of their ratio ($[A]/[B]$) can be derived as follows:

$$\text{ratio}(t) = \frac{[A](t)}{[B](t)}$$

Using the partial derivatives of $\text{ratio}(t)$ with respect to [A] and [B], the rate of change of the ratio is:

$$\frac{d\text{ratio}(t)}{dt} = \frac{[A](t)\frac{d[A]}{dt} - [B](t)\frac{d[B]}{dt}}{[B](t)^2}$$
\[
\frac{d(\text{ratio})}{dt} = \frac{1}{[B]} \frac{d[A]}{dt} - \frac{[A]}{[B]} \frac{d[B]}{dt} \tag{2.2b}
\]

Then, substituting Equation (1) for \(dA/dt\) and \(dB/dt\), we arrive at:

\[
\frac{d(\text{ratio})}{dt} = \frac{P_B}{[B]} (ER - \text{ratio}) + (\text{ratio})[OH](k_B - K_A) + \sum(\text{ratio})(D_{iB} - D_{iA}) \tag{2.2c}
\]

The primary emission rate \((P_B)\), emission ratio \((ER)\), and the concentration of OH are unknown. The emission ratio \((ER=P_A/P_B)\) is the ratio of two VOCs in fresh emissions (time \(t = 0\)) and is a measure of source composition. I consistently used benzene as the denominator in the ratio, so that \([B] = [\text{benzene}], \ P_B\) is the emission rate of benzene, \(ER\) is the emission ratio of a VOC to benzene, and so on. Meteorological data and the measured ambient mixing ratio of benzene were used to determine the number density of benzene \(([B])\) as a function of time. These values were referenced directly when applying Equation (2.2c).

C6-C10 aromatic VOCs were selected for analysis of primary compounds because they have readily identifiable parent masses, they are sensitively detected by PTR-MS, and have a relatively wide range of reactivity with OH \((k_{OH} = 1.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ to } 56 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})\). Application of this analysis to VOCs measured by PTR-MS using Equation (2.2c) includes the following assumptions.

(1) For each first-order loss process, loss rates are identical for aromatic compounds \((D_{iA}=D_{iB}=D_{i})\). These loss processes include mixing out of the basin, photolysis, and deposition. Mixing is dependent on dynamics and not on chemical characteristics, so mixing loss rates should be identical for all VOCs with the same vertical concentration profile \((D_{\text{mixing},B} - D_{\text{mixing},A} = 0)\). Vertical gradients were similar for most non-methane hydrocarbons measured by balloonsonde at the Horsepool site (Helmig et al., 2014). As concentrations of VOCs in the background atmosphere were considerably smaller than VOC concentrations inside the basin, changes in VOC ratios due to mixing in of background air are negligible. Integrated UV absorption cross-sections of C5-C10 aromatic hydrocarbons are small and similar to one another (Etzkorn et al., 1999), so \((D_{\text{photolysis},B} - D_{\text{photolysis},A})\) is negligible compared to primary emission and reaction with OH. The same argument can be made for wet or dry deposition \((D_{\text{deposition},B} - D_{\text{deposition},A} \cong 0)\) as monocyclic aromatic compounds are structurally similar and have small solubilities in water. The terms
(2) Primary VOC emission rate and emission ratios are constant in time and similar in composition across the basin – I cannot confidently parameterize a more complicated emissions scenario with available data, nor is there any evidence supporting or reason to assume a change in emissions with time of day. The ability of the box model to describe VOC behavior (see below) suggests that this assumption is reasonable.

(3) Finally, on an hourly scale, I assume that compounds are well mixed inside the basin. The latter assumptions are supported by aircraft measurements in Jan-Feb. 2013, which found elevated VOC concentrations with similar ratios in all parts of the basin, including regions with varying intensities and types of fossil fuel extraction activity (Oltmans et al., 2016). The time period analyzed, characterized by a strong temperature inversion and light winds (Figure 2.1), was specifically selected to support these assumptions.

3.1.1 Emission rates and ratios

The analysis is first applied to night-time data only (any points where solar radiation is zero), to estimate \( P_b \) and \( ER \). During the night, \( OH \) is close to zero and Eq. (2.2c) reduces to:

\[
\frac{d(ratio)}{dt} = \frac{P_b}{[B]} (ER - ratio)
\]  

(2.3)

This method, using only night-time data, reduces the number of free variables. It completely separates primary emission from \( OH \) chemistry. Additionally, it allows the use of C9 and C10 aromatics measurements, as the \( OH \) rate constants for these groups are not well constrained.

The measured ratios of C7, C8, C9, and C10 aromatics to benzene were described using a best fit of Eq. (2.3) to the data. The free parameters in this fit are \( P_b \) and \( ER \). A best fit was determined separately for each of the four aromatic ratios, providing four, similar, independent estimates of \( P_b \) (Figure 2.3) and four emission ratios to benzene (Table 2.2). I evaluated the fit by comparing emission ratios to literature values and the composition of plumes from nearby sources, and, second, by comparing emission rate to an independent estimate.
Figure 2.3. Aromatic compound ratios and best fit to night time data (blue) and both night and day data (red). The background is colored by sunlight intensity to distinguish day and night. For reproducibility, the initial ratio for each night was chosen from the 10th percentile of points during the first two hours of evening. In practice, best-fit parameters were largely insensitive to initial ratio, so long as the selected initial ratio was close to measurements during the early part of the night. A diurnal average is shown to the right.
The derived emission ratios from this analysis represent an averaged source composition of all point sources contributing VOCs to well-mixed air. In Figure 2.4, the derived emission ratios are compared to three other measurements of source composition in the Uintah basin: (1) Mobile laboratory measurements taken at individual well pads in 2012 (Warneke et al., 2014); (2) ambient measurements taken at Horsepool in 2012 (Warneke et al., 2014); and (3) 2013 VOC enhancement ratios in spikes above a 1-hour running median (discussed above). These spikes are likely plumes of fresh emissions from nearby well pads. The fastest-reacting C10 aromatic (1,2,4-trimethylbenzene) had a peak daytime chemical lifetime against OH of about 30 min. Seven other well pads were within 500 m of the Horsepool site; given average wind speed (1.6 m s\(^{-1}\)), this corresponds to a 5-minute transport time – much shorter than the chemical lifetime of any of the analyzed aromatic species. All three measurements are separated into gas-producing and oil-producing well contributions; in mobile lab data, by type of well pad sampled; in Horsepool data, by correlation with wind direction (Warneke et al., 2014).

There is a clear distinction between oil and gas sources. The difference grows with carbon number; i.e. gas producing-wells emit a lighter mixture of VOCs. Average emission ratios suggested by our analysis suggest significant contribution from both oil and gas sources. In addition to the oil/gas distinction, there is a large range of variability in source composition of aromatic species. This variability is difficult to represent in bulk emissions estimates and models. Together with supporting evidence from aircraft that the composition of aromatics was relatively similar across the basin (Oltmans et al., 2016), my analysis provides an independent measure of average emissions composition.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Emission ratio to benzene by mol</th>
<th>Benzene emission rate (10^{5}) molecule cm(^{-3}) s(^{-1})</th>
<th>([\text{OH}]) avg. (10^{5}) molecule cm(^{-3})</th>
<th>OH rate constant (10^{12}) cm(^{3}) molecule(^{-1}) s(^{-1})</th>
<th>(R^2) full time series best fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>1.5</td>
<td>4.5</td>
<td>2.66</td>
<td>5.63</td>
<td>0.242</td>
</tr>
<tr>
<td>C8 aromatics</td>
<td>0.82</td>
<td>4.1</td>
<td>1.86</td>
<td>16.4</td>
<td>0.421</td>
</tr>
<tr>
<td>C9 aromatics</td>
<td>0.18</td>
<td>3.9</td>
<td>16.9</td>
<td>24.2</td>
<td>0.614</td>
</tr>
<tr>
<td>C10 aromatics</td>
<td>0.042</td>
<td>3.8</td>
<td>24.2</td>
<td>0.273</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2. Primary compound results.
This table includes results from the night-data only best fit (emission ratios, benzene emission rate), and the full time series (including both day and night) best fit ([OH], \(k_{\text{OH}}\), and \(R^2\)).
The average benzene emission rate determined from the fit was \((4.1 \pm 0.4) \times 10^5\) molecules cm\(^{-3}\) s\(^{-1}\).

To evaluate this emission rate estimate, I compare to basin-wide methane emission measurements conducted by aircraft in 2012 (Karion et al., 2013). Karion et al. (2013) determined that basin-wide methane emissions were \((55 \pm 15) \times 10^3\) kg hr\(^{-1}\). To compare a volume-normalized estimate (molecules benzene cm\(^{-3}\) s\(^{-1}\)) to the whole-basin estimate (kg methane hr\(^{-1}\)), it is necessary to have (1) the emission ratio of methane to benzene and (2) the total volume of the polluted layer during the 2013 ozone episode.

A strong correlation between methane and benzene is apparent from ground site measurements at Horse Pool in 2012 and 2013 (Figure 2.5). Aircraft flask samples taken in 2013 suggest that the methane:benzene ratio is independent of location in the basin – it was similar in both the eastern gas field and western oil field (Oltmans et al., 2016). The methane:benzene emission ratio was approximated from
2012 measurements and 2013 plumes (ER=1330±80 ppbv/ppbv).

The polluted volume of the basin was determined using a digital elevation model of the region, frequent ozonesonde measurements at a number of locations in the basin, as well as aircraft profiles. They showed well mixed ozone concentrations up 1600–1700 meters above sea level (100-200 meter above ground level at Horsepool), above which mixing ratios decreased sharply (Oltmans et al., 2016). Taking the terrain of the basin into account, the volume of the basin was then integrated from the surface to the mixing height (Figure 2.6). The uncertainty in the basin wide methane emission estimate is dominated by the uncertainty in this volume, and values determined from minimum and maximum polluted layer altitude (1600m – 1700m) are reported.

Using the methane:benzene ratio and the mixing volume of the basin, an emission rate of (14-39)×10³ kg methane hr⁻¹ is derived. This is lower than the Karion et al. (2013) estimate, but of the same magnitude. An inspection of well locations in the basin shows that a significant fraction (40-50%) of wells lie outside the polluted layer (Figure 2.6). An aircraft flux measurement would have likely included contributions from these wells, whereas our analysis only included wells emitting inside the isolated polluted volume. A linear extrapolation based on the number of wells inside and outside the polluted volume suggests an emission rate of (27-57)×10³ kg methane hr⁻¹, which now overlaps with the Karion et al. (2013) value. Although this estimate is considerably less precise than the aircraft flux measurement, it does confirm that the best-fit values of benzene emission rate are plausible.
Figure 2.6. Topographical map of the Uintah Basin showing polluted region and well locations. Total relief is from 1398 meters above sea level to 3627m. The bright (tan) region shows the area of the polluted region assuming the polluted layer extends to 1600 meters above sea level (a) or 1700m (b). Locations of producing oil and gas wells are marked in red.
3.1.2 Concentration of OH radical

The full time series (both day and night) was analyzed over the buildup period, using Eq. (2.2c). The primary emission term \( P_b \) and the emission ratio were fixed as determined from the night best fits. The only remaining free variable is the concentration of OH.

The calculation requires the OH rate constant \( k_{OH} \) for the aromatics. Measurements of C8 aromatics in 2013 were not isomerically resolved by PTR-MS and represent the sum of ethylbenzene and \( o-, m-, \) and \( p- \)-xylenes. Speciated measurements of C8 aromatics by GC-MS were made in 2012, when photochemical aging of VOCs was less active and the bulk air composition more closely resembled primary emissions. The 2012 GC-MS measurements were used to compute a weighted average OH rate constant for the C8 aromatics group. The OH rate constants for individual species in this group are within a factor of 2.1 of the mean. The groups C9 and C10 aromatics contain a much larger number of isomers, with a wider variance in OH rate constants. Not all these isomers were measured by GC-MS in 2012, and some of the OH rate constants are unknown. Therefore, the group average rate constant could not be similarly constrained.

To parameterize the diurnal variation in OH, OH was constrained to be proportional to solar actinic flux. It is well established that [OH] is strongly linearly correlated with UV light intensity (Hard et al., 1986; Rohrer and Berresheim, 2006). A best fit and an average value of OH was computed separately for both toluene and C8 aromatics according to Eq. (2.3) (shown in Figure 2.3). Results are included in Table 2.2. The average of these two values was used as the concentration of OH in further analysis.

Using this [OH], the \( k_{OH} \) for C9 and C10 aromatics were allowed to vary. Best fits for the C9 and C10 aromatics were calculated and are shown in Figure 2.3. The group average rate constants (Table 2.2) are within the range of values known for isomers of C9 and C10 aromatics. For C9 aromatics, the group average rate constant was determined to be \( 16.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \); known values range from \( 5.3 \times 10^{-12} \) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (n-propylbenzene) to \( 56.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) (1,3,5-trimethylbenzene) (Atkinson and Arey, 2003). For C10 aromatics, the group average rate constant was determined to be \( 24.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \);
known values range from $4.5 \times 10^{-12}$ (t-butylbenzene) (Atkinson and Arey, 2003) to $55.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (1,2,4,5-tetramethylbenzene) (Aschmann et al., 2013). The average rate constant constrains group composition, and could be useful in future investigations of photochemical processing. The average rate constant could change over time as the more reactive species within a group are oxidized. How much might the average rate constant be expected to change? Consider an end-case scenario in which the C10 aromatic emissions consist of an equal mixture of t-butylbenzene ($k_{OH} = 4.5 \times 10^{-12}$) and 1,2,4,5-tetramethylbenzene ($k_{OH} = 55.5 \times 10^{-12}$). Over the course of the ozone event, more 1,2,4,5-tetramethylbenzene reacts away and the final ambient mixture consists of 80% t-butylbenzene. The average rate constant decreases from $30 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ to about $15 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. In this scenario, the box model will underpredict the daytime decrease in the C10:benzene ratio at the beginning of the ozone event, and overpredict the decrease towards the end of the event. In reality, C10 aromatics (and C8 and C9 aromatics) likely do not consist of such an extreme mixture and the average rate constant changes by less than 50%. No strong evidence is seen for a time-dependent error in the box model (Figure 2.3).

Knowledge of typical daily OH concentrations is crucial to understand photochemical processing of VOCs and ozone production. OH was not measured directly in 2013, but my analysis provides an estimate of OH exposure, constrained by solar actinic flux and VOC measurements. OH peaked daily at $1 \times 10^6$ (±21%) molecule cm$^{-3}$, which is low compared to urban areas affected by photochemical smog with typical OH concentrations between $(5-10) \times 10^6$ molecule cm$^{-3}$ (Shirley et al., 2006). I compare to an independent estimate of [OH] in 2013 using the Master Chemical Mechanism v.3.2 (MCM) framework (Edwards et al., 2014). The MCM OH estimate is generated using more than 12000 explicit reactions comprising degradation schemes for nearly all hydrocarbons measured at the Horse Pool site and has been applied previously to photochemistry in the Uintah Basin (Edwards et al., 2013; Edwards et al., 2014). The agreement between our model and the MCM estimate in peak daytime concentration is within a factor of 1.7 overall and differs by only 2% on 5 Feb. 2013 (Figure 2.7, next page). The agreement is especially good considering that OH values in my analysis are constrained by measured photolysis rates and a single scaling
factor, and so cannot generate the multi-day trend seen in the MCM calculation. This excellent agreement substantiates the chemistry described by the MCM model.

![Figure 2.7](image)

Figure 2.7. Comparison of OH with the Master Chemical Mechanism prediction (Edwards et al., 2014).

There is good agreement between the MCM OH and OH determined from my analysis.

### 3.2 Oxygenated compounds

Oxygenated compounds can be directly emitted and have photochemical sources. For oxygenated species without direct emissions, the change in concentration with time is controlled by the production rate via photochemistry, loss to reaction with OH, and first-order loss processes such as mixing, photolysis and deposition. The rate of change can be written similarly to Eq. (2.1):

\[
\frac{d[VOC]}{dt} = \text{Yield} \times k_{\text{precursors}}[OH][\text{precursors}] - k_{\text{VOC}}[OH][VOC] - D[VOC]
\]  

(2.4)

Here [precursors] is the sum concentration of all precursor species, \text{Yield} is the fraction of reactions with OH that form the product compound, and \(k_{\text{precursors}}\) is the weighted average OH rate constant of precursor species. Again, \(D\) represents first-order loss processes. The oxygenated species considered here are acetaldehyde, acetone, 2-butanone (MEK), formic acid, methanol, and formaldehyde.
As with Eq. (2.2c), the rate of change of the ratio of a photochemically produced compound to benzene is:

\[
\frac{d\text{ratio}}{dt} = \text{Yield} \times k_{\text{precursors}}[OH] \times R_{PB} - (\text{ratio}) \times \left( [OH] \left( k_{prod} - k_B \right) + f + \frac{P_B}{[B]} \right) \tag{2.5a}
\]

\[
= \lambda_f \times [OH] - (\text{ratio}) \times \left( [OH] \left( k_{prod} - k_B \right) + f + \frac{P_B}{[B]} \right) \tag{2.5b}
\]

\(R_{PB}\) is the ambient ratio of precursor species to benzene, \(k_{prod}\) and \(k_B\) are the OH rate constants of the product species and benzene, and \(J\) is the photolysis rate constant of the product species. Here I again assume that other first-order processes, mixing and deposition, are not significantly different between the oxygenated VOCs and benzene. On the other hand, most of these compounds contain a carbonyl functional group, and photolysis rates could be significant. \(J\) was set proportional to solar actinic flux and scaled to photolysis constants from the literature (values and literature sources are given in Table 2.3). I also assume that the only source of these species is photochemistry; i.e. they are not emitted directly from primary sources. Methanol and formaldehyde are included in this section as they are oxygenated species. However, the high observed mixing ratios of methanol and formaldehyde (Table 2.1), previous modeling work (Edwards et al., 2014), and knowledge of industry practices indicates that these two species also have direct (primary) sources. I first analyzed methanol and formaldehyde assuming solely photochemical sources, to investigate the extent to which secondary formation can explain their behavior. I then modified the analysis to consider primary emission of these species. Methanol and formaldehyde are discussed separately in the analysis (below).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Benzene emission rate (10^5) molecule cm(^{-3}) s(^{-1})</th>
<th>Formation rate constant (10^{-11}) cm(^3) molecule(^{-1}) s(^{-1})</th>
<th>(R^2) (daytime data)</th>
<th>Photolysis rate constant (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>4.91</td>
<td>7.36</td>
<td>0.667</td>
<td>1.2\times10^{-6} (Martinez et al., 1992)</td>
</tr>
<tr>
<td>Formic acid</td>
<td>6.04</td>
<td>3.30</td>
<td>0.414</td>
<td>1.0\times10^{-6} (estimated)</td>
</tr>
<tr>
<td>Acetone</td>
<td>4.46</td>
<td>8.72</td>
<td>0.775</td>
<td>5.0\times10^{-8} (McKeen et al., 1997)</td>
</tr>
<tr>
<td>MEK</td>
<td>4.97</td>
<td>3.42</td>
<td>0.787</td>
<td>3.6\times10^{-8} (Martinez et al., 1992)</td>
</tr>
<tr>
<td>Methanol</td>
<td>1.34</td>
<td>(day analysis not performed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>0.90</td>
<td>(day analysis not performed)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.3. Oxygenated compound results.
As the relative amounts of precursor species and their product yields were unknown, yield, $k_{\text{precursors}}$, and $R_{PB}$ were bundled into a single free variable, $\lambda_f$ (formation rate constant). The term $R_{PB}$ requires further discussion. The analysis of primary compounds (above) shows that the ratios of C7-C10 aromatics to benzene are highly variable and depend on photochemical exposure. $R_{PB}$, the ratio of precursor species to benzene, should also change over time. However, in applying Equation (2.5b), I have simplified analysis by treating $R_{PB}$ as approximately constant. By volume, the dominant VOCs measured at Horse Pool were C1-C5 alkanes. These compounds react more slowly with OH than C7-C10 aromatics. Reaction with OH has a proportionally smaller effect on their concentrations, and indeed, ratios of these compounds to benzene show less diurnal variability (Figure 2.8a). Despite how slowly these compounds react with OH, the very large concentration of these compounds means that C2-C5 alkanes account for most of the reactions between OH and VOCs, and are the most important precursor compounds (Figure 2.8b). I therefore used the simplifying approximation of constant precursor:benzene ratio.

![Figure 2.8. Alkane variability and reactivity.](image)

(a) Because of their slow reaction rates with OH, the ratios of C2-C5 alkanes to benzene did not have high diurnal variability and did not change substantially from beginning to end of the stagnation event (propane and n-pentane measured by GC-FID are shown as representatives). (b) However, because of their high mixing ratios, these species account for a large fraction (~70%) of primary hydrocarbon-OH reactions.
As with the aromatic VOCs box model, the analysis was first applied to night data only. During the night, photolysis and [OH] are negligible, so (2.5b) reduces to:

\[
\frac{d(ratio)}{dt} = -(ratio) \left( \frac{P_B}{1} \right) \quad (2.6)
\]

Using Equation (2.6), a best fit was calculated for acetaldehyde, formic acid, acetone, MEK, methanol, and formaldehyde (Figure 2.9, next page), providing six values of the primary benzene emission rate \(P_B\) (Table 2.3).

The best fit functions to acetone, acetaldehyde, formic acid, and MEK for nighttime data only were able to describe a decreasing trend in the ratio of VOC:benzene, but did not replicate the strong decrease in ratio towards the end of the night. Primary emission of benzene during the night could only account for a portion of the decrease, signifying an additional oxygenate removal process not included in Equation (2.6). A possible candidate is increased deposition of oxygenates. Including a free first-order deposition variable did not significantly affect model output, suggesting a complex process increasing in strength during the night. One possibility is deposition on ice crystals. Surfaces, including the sampling inlet, typically gained a thick coating of ice rime during the night, creating additional surface area available for deposition (Figure 2.10). This process would also affect polar oxygenated species much more than primary hydrocarbons, consistent with the additional decrease in oxygenates not observed with aromatics. Because this process affected our sampling inlet, it is possible that oxygenate behavior during early morning is an inlet artifact rather than a significant basin-wide process. We removed rime ice from the sampling inlet early each morning, and other
surfaces were typically free of rime by mid-morning (snow cover remained during the day). There were no obvious immediate changes in the VOC data when the rime ice was removed from the inlet.

Figure 2.9. Analysis results for oxygenated compounds. Measured ratio is in black, night best fit in blue, and day best fit in red. A. The best fit is able to reproduce VOC trends during the day for acetone, MEK, acetaldehyde, and formic acid. B. The best fit does not reproduce night time variability or trends in methanol and formaldehyde, which may have substantial primary sources uncorrelated with benzene.
The values of benzene emission rate derived from night-only best fit to acetone, acetaldehyde, formic acid, and MEK were slightly higher than estimates from primary compounds: $5 \times 10^5$ as opposed to $4 \times 10^5$ molecule cm$^{-3}$ s$^{-1}$. This is consistent with an undetermined additional removal process. In the absence of an appropriate loss term, a best fit using Equation (2.6) would artificially increase the benzene emission rate to reproduce the stronger downwards trend in ratio.

The diurnal behaviors of methanol and formaldehyde differ significantly from other species. The ratios of methanol and formaldehyde to benzene do not increase steadily during the day and do not decrease at night. Additionally, the values of primary benzene emission rate determined from methanol and formaldehyde are at least a factor of two smaller than values determined from any other compound. For methanol, this behavior is almost certainly due to large primary sources. Methanol is used by the oil and natural gas industry in a variety of applications in the basin (Lyman, 2014; Mansfield et al., 2016), including storage of methanol containers on wellpads, and direct emissions of methanol associated with this use are very high as witnessed by hourly average mixing ratios in the basin, which can build up to more than 200 ppbv. It is therefore unsurprising that methanol variation is poorly described by Equation (2.6). Primary sources of formaldehyde are less clear. Incomplete combustion and emission from dehydrators, separators, compressors, flares, oil pumps and processing plants have been suggested as sources, but are not well quantified in the Uintah basin. Additionally, there is no easily distinguishable correlation between formaldehyde and NO$_x$, so it is not clear that combustion is a significant source of formaldehyde. In accordance with our findings, Edwards et al. (2014) left the option open for primary emissions of formaldehyde due to the inability of the MCM model to reproduce the ambient mixing ratios.

To investigate primary emission of methanol and formaldehyde I modified Equation (2.6) in several ways. First, a term representing primary emission of oxygenates was added, and best-fit values of benzene emission rate and oxygenate:benzene emission ratio were determined. $\chi^2$ values decreased insignificantly (-5%, methanol) and slightly (-22%, formaldehyde) and calculated values of primary benzene emission rate were unreasonable ($8 \times 10^5$ and $1 \times 10^6$ molecules cm$^{-3}$ s$^{-1}$ from the methanol and formaldehyde analysis,
respectively). Next, the primary benzene emission rate was fixed to the value determined from the primary compounds analysis, and I used the box model to determine only the emission ratios for methanol and formaldehyde. Emission ratios of formaldehyde:benzene and methanol:benzene were 1.01 and 10.3. These values are slightly less than the ambient ratios, consistent with accumulation from both photochemistry and primary emission. However, the best fit still did not capture the majority of measurement variability and may not be accurately characterizing physical processes affecting methanol or formaldehyde. For instance, an emission source poorly correlated with benzene would not be well represented by Equation (2.6).

Because of possible complex deposition of oxygenated species during the night, and primary emission of methanol and formaldehyde, emission rates derived from the analysis of these oxygenates are less likely to be accurate than those derived from analysis of primary species. I elected to exclude night data from further analysis, and retain the primary benzene emission rate (\(P_B\)) determined from the primary compounds model. The fit of Equation (2.5b) was then calculated for acetone, MEK, acetaldehyde, and formic acid, using daytime data (Figure 2.9), to determine values of the formation rate constant (\(\lambda_f\)) for each compound (Table 2.3).

The best-fit of daytime oxygenate ratios is better able to explain the measurements, with \(R^2\) values of 0.4 to 0.8 (Table 2.3). Values of the formation rate constant (\(\lambda_f\)) are plausible. For instance, the best-fit value of \(\lambda_f\) for acetone is \(8.72\times10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). The main precursors of acetone present in the Uintah Basin were iso-butane and propane. The weighted average rate constant for reaction of iso-butane and propane with OH is \(1.3\times10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) and the mol ratio of these compounds to benzene was approximately 70. Assuming that all propane-OH and iso-butane-OH reactions formed acetone, the calculated \(\lambda_f\) for acetone is \(9.1\times10^{-11}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), which is very close to the best-fit calculated value. The high \(R^2\) values and reasonable \(\lambda_f\) suggest that Equation (2.5b) captures the most important daytime processes affecting acetone, acetaldehyde, MEK, and formic acid.
4. Organic carbon budget

In this section, I categorize VOCs as either primary (directly emitted) or secondary (enhanced by oxidative chemistry), and quantify the total organic carbon mass in each category. Using two complementary mass balance approaches, I show that one might expect to see more oxygenated species than were measured. Both approaches rely on conservation of organic carbon mass: when a primary compound is oxidized, the total mass of organic carbon does not change. This is true regardless if the molecule’s structure changes, if it fragments into several smaller molecules, if subsequent reactions form higher generation products, or if it moves into a different reservoir (e.g. aerosol or snowpack).

First, carbon mass concentration is conserved. The total organic carbon mass of primary compounds lost to oxidation must be equal to the total organic carbon mass gained by secondary compounds. To quantify this mass, the loss rate of a primary compound to oxidation is used:

\[
\frac{d(\text{primary VOC})}{dt}_{\text{oxidation}} = -k_{\text{primary VOC}}[\text{OH}][\text{primary VOC}] \tag{2.7}
\]

To be clear, this is only the loss rate to oxidation, and not the total loss rate, which includes physical losses. Equation 2.7 was used to find the total amount of organic carbon lost to oxidation from all primary species. This was done by multiplying each individual primary VOC listed in Table 2.1 by its OH rate constant and the instantaneous [OH], integrating from beginning to end of the stagnation event, then summing the results from all primary VOCs. For completeness, methane (from CaRDS) was also included. [OH] was set to the values calculated above (Table 2.2). OH rate constants for C8, C9, and C10 aromatics were taken from Table 2.2, and OH rate constants for all other species were taken from Atkinson and Arey (2003).

Because total carbon mass is conserved, at the end of the stagnation event, the total carbon mass lost from primary species is equal to the total carbon mass gained by all secondary species. This value, about 3.7×10^{-10} gram C cm^{-3} on day 6 of the stagnation event, is the calculated or expected mass of secondary species, not including physical loss of the secondary species. Measured oxygenates and secondary species, including methanol, formaldehyde, formic acid, acetone, acetaldehyde, MEK, PAN
species (peroxyacrylic nitric anhydride (APAN), peroxymethacrylic nitric anhydride (MPAN), peroxyacetic nitric anhydride (PAN), and peroxypropionic nitric anhydride (PPN)), organic carbon in snow, and PM2.5 organic aerosol, only sum to $0.64 \times 10^{-10}$ gram C cm$^{-3}$, or 17% of calculated secondary carbon mass.

Methanol and formaldehyde have substantial primary sources, so including them in this calculation artificially increases the percentage of secondary species accounted for: $0.64 \times 10^{-10}$ gram C cm$^{-3}$ is an upper bound to the mass of measured secondary species. If methanol is assumed to be entirely primary, measured secondary species only sum to $0.48 \times 10^{-10}$ gram C cm$^{-3}$, or 12.9% of calculated secondary carbon mass. If both methanol and formaldehyde are assumed have no photochemical sources, measured secondary species sum to $0.46 \times 10^{-10}$ gram C cm$^{-3}$, or 12.5% of calculated secondary carbon mass. Figure 2.11 shows the upper bound to measured secondary species (including both methanol and formaldehyde).

This gap between the calculated (expected) mass of secondary species and the measured mass of secondary species is a factor of 5.8 (Figure 2.11). Other measurement and modeling studies of the Uintah Basin have shown that unquantified secondary species must be responsible for at least part of this gap: many additional oxygenated VOCs were detected, but not quantified, by PTR-time-of-flight (PTR-ToF) mass spectrometry (Warneke et al., 2015), and MCM modeling indicates that carbonyl groups formed from higher-weight species (e.g. aromatics) were not only abundant but major drivers of ozone formation.

Oxidation of quantified secondary species to CO and CO$_2$, or loss to mixing out of the basin are alternate explanations that could account for some of the disparity. Loss to mixing could certainly be an important factor. Based on methane measurements, Edwards et al. (2014) estimated the physical loss rate from boundary layer dilution to be between $0.2-1.8 \times 10^{-5}$ s$^{-1}$. This could account for anywhere from 20% to 200% of the calculated “missing” carbon, which is not precise enough to be helpful.
Using a second carbon mass balance technique, I show that unquantified secondary species are an important factor. The second technique compares oxidation rates: the oxidation loss rate of primary species must be equal to the photochemical formation rate of secondary species. The rate of these low-generation oxidation reactions is not affected by higher-generation oxidation reactions or loss to mixing or deposition. A disparity between the carbon mass loss rate to oxidation of primary species and the formation rate of measured secondary species means that there must be other, unquantified, secondary species forming.

Figure 2.11. Organic carbon mass of oxygenated and secondary species. The leftmost two bars show the carbon mass of secondary species at the beginning (average of first 12 hours) and end (average of last 12 hours) of the ozone event; speciation is detailed in the two insets. Although methanol and formaldehyde likely have primary sources, they are included here in the “product compounds” category to show the maximum contribution of these species to measured products. The rightmost bar shows the calculated mass of secondary compounds at the end of the ozone event; within this bar, the contribution from each precursor is delineated.

Using a second carbon mass balance technique, I show that unquantified secondary species are an important factor. The second technique compares oxidation rates: the oxidation loss rate of primary species must be equal to the photochemical formation rate of secondary species. The rate of these low-generation oxidation reactions is not affected by higher-generation oxidation reactions or loss to mixing or deposition. A disparity between the carbon mass loss rate to oxidation of primary species and the formation rate of measured secondary species means that there must be other, unquantified, secondary species forming.
Therefore, comparing oxidation and formation rates provides a way to determine if the mass disparity between calculated and measured secondary species is at least partly due to unquantified compounds.

The loss rate to oxidation of each primary species was determined by multiplying the number concentration of the species by its rate constant with OH, and the OH concentration:

\[
\frac{d(\text{primary VOC})}{dt} \biggr|_{\text{oxidation}} = -k_{\text{primary VOC}}[OH][\text{primary VOC}] \tag{2.7}
\]

This rate is not dependent on physical loss. The total oxidation rate of all primary species was found by summing the loss rates of each individual species. The formation rate of quantified secondary species was determined using Equation (2.4):

\[
\frac{d[\text{VOC}]}{dt} = \text{Yield} \cdot k_{\text{precursors}}[OH][\text{precursors}] - k_{\text{VOC}}[OH][\text{VOC}] - D[\text{VOC}] \tag{2.4}
\]

The first term in Equation (2.4), \( \text{Yield} \cdot k_{\text{precursors}}[OH][\text{precursors}] \), which has been highlighted, is the formation rate of a secondary VOC. To clarify, this is the rate at which a secondary VOC is produced by oxidation chemistry, not the rate of net increase in concentration (net = \( \frac{d[\text{VOC}]}{dt} = \text{formation} - \text{loss} \)). Loss terms to OH chemistry and physical processes are also shown in Eq. 2.4, but I am concerned only with the formation rate here).

I simplified this formation rate term, and avoided the need to know the exact values of \( \text{Yield}, k_{\text{precursors}}, \) and \( [\text{precursors}] \), by making several substitutions similar to those used in Equation 2.5b. The concentration of precursors can be replaced with:

\[
[\text{precursors}] = R_{PB}[\text{benzene}] \tag{2.8}
\]

where \( R_{PB} \) is the ratio of precursor species to benzene (see section 3.2). Then, \( \text{Yield}, k_{\text{precursors}}, \) and \( R_{PB} \), can be bundled into a single constant \( \lambda_f \):

\[
\lambda_f = \text{Yield} \cdot k_{\text{precursors}} \cdot R_{PB} \tag{2.9}
\]

Using these substitutions, the formation rate term simplifies to:

\[
\text{Yield} \cdot k_{\text{precursors}}[OH][\text{precursors}] = \lambda_f [OH][\text{benzene}] \tag{2.10}
\]
The simplification is useful, because benzene is a known, measured quantity; [OH] is known (section 3.1.2); and \( \lambda_f \), the formation rate constant, was determined for several species in section 3.2. \( \lambda_f \) was determined for acetone, acetaldehyde, formic acid, and MEK (Table 2.3). The oxidation rate of primary compounds is a factor of two higher than the total formation rate of acetaldehyde, acetone, formic acid, and MEK combined (Figure 2.12). This large disparity indicates a substantial formation rate of unquantified secondary species. The formation rate of these unquantified species is \( 3.2(\pm1.2) \times 10^{-16} \text{ g C cm}^{-3} \text{s}^{-1} \) on average or \( 60(\pm23) \text{ ppbv C day}^{-1} \).

Separately from the work described in this chapter, a highly chemically detailed investigation of formic acid formation during UBWOS 2013 was conducted using MCM modeling (Yuan et al., 2015). The MCM model was not able to explain approximately 50% of the measured formic acid production, even including several updates to the gas-phase chemistry included in the model. The Yuan et al. (2015) study highlighted the complexity of the chemistry involved in the production of formic acid, and the difficulty of measuring and understanding its formation rate from measured precursors. The disagreements between measurements and model in this work and in Yuan et al. (2015) are due to unmeasured species, and unknown reaction pathways. In Chapter 4, I discuss observations of additional oxygenated species made with a separate \( \text{H}_3\text{O}^+ \) ToF-CIMS (PTR-ToF) instrument during the SONGNEX 2015 aircraft campaign.
5. Conclusions

High concentrations of organic carbon species (up to 5 ppm non-methane carbon) associated with oil and natural gas extraction were measured at a rural site in the Uintah Basin, Utah, during the winter of 2013. A relatively simple box model analysis was applied to measurements of aromatic species by PTRMS to explain variation in their ratios due to reaction with OH and primary emission. The analysis was extended to measurements of small oxygenated compounds by PTRMS, with the goal of explaining ratios of these compounds to benzene in terms of production and loss via OH chemistry, photolysis, and primary emission. Results of both analyses were used to develop a carbon mass budget, to determine the relative fractions of carbon in primary and secondary species.

The analysis of primary aromatic species provided plausible estimates of [OH], aromatic VOC emission ratios, and benzene emission rate. The daily peak of [OH] was low (1×10^6 molecule cm^{-3}), consistent with MCM modeling, which highlights the unusual oxidation chemistry occurring in this region. Emission ratios indicate source contributions from both oil and gas wells. Using measured correlation between benzene and methane, the benzene emission rate ((4.1±0.4)×10^5 molecule cm^{-3} s^{-1}) was extrapolated to a basin-wide methane emission rate ((27-57)×10^3 kg methane hr^{-1}) in order to compare with an independent top-down estimate from aircraft. Although the large uncertainties associated with the extrapolation of the benzene emission rate to a basin-wide methane emission rate preclude the use of our estimate as an assessment of regulatory inventories, the agreement with the 2012 aircraft methane flux value supports the plausibility of our analysis. My analysis was not able to completely explain night time variability of small oxygenated VOCs, whose behavior may be affected by primary emission (methanol and formaldehyde) and deposition to ice surfaces. However, a best fit to day time data provided values of carbonyl formation rate consistent with expected formation rates from known precursors. The calculated carbon budget indicated that a large fraction of secondary carbon mass (83%, or 3×10^{-10} gC cm^{-3}) is unaccounted for. Physical loss could account for some of the gap, but unquantified secondary species almost
certainly are also a contribution. A comparison of measured carbonyl formation rates to primary compound oxidation rates indicated substantial formation of unquantified secondary species.

The analysis method outlined here is relatively simple, including just a few terms for basic chemistry and primary emission. It uses little computer processing power and references only measurements that can be made with standard VOC instrumentation. Despite its simplicity, this method is able to provide considerable information on VOC chemistry, including source composition and emission rates, the concentration of OH, and the importance of unmeasured secondary species. Best-fit values of [OH], emission ratios to benzene, and VOC primary emission rate, are very reasonable and support findings from more complicated chemical models. A similar analysis could be applied to investigations of other regions where VOC pollutants are geographically or meteorologically contained, especially where detailed chemical measurements are unavailable or not possible. That said, this study also suggests the additional potential for scientific discoveries with a VOC instrument capable of detecting a much larger number of oxygenates and primary compounds. In the next chapter, I describe the development of a PTR-MS instrument capable of faster measurement of a larger number of species.
Chapter 3. Development of a high-resolution H\textsubscript{3}O\textsuperscript{+} time-of-flight chemical ionization mass spectrometer (H\textsubscript{3}O\textsuperscript{+} ToF-CIMS)

Abstract

Proton-transfer-reaction mass spectrometry (PTR-MS) is a fast and sensitive technique to measure VOCs in the atmosphere. Use of time-of-flight (ToF) mass analyzers is a recent development that has greatly improved the measurement capability of PTR-MS. This chapter describes the development and characterization of a high-resolution PTR-ToF instrument based on the Aerodyne ToF-CIMS instrument (“NOAA H\textsubscript{3}O\textsuperscript{+} ToF-CIMS”). Trace gas limits of detection for a 1-sec measurement range from 20 ppt (acrylonitrile, furfural) to 2 ppb (H\textsubscript{2}S) and are below 100 ppt for most polar and aromatic VOCs. Product ion count rates are approximately an order of magnitude higher than commercial instruments available at the time. Improved sensitivity is partly due to the use of RF-only segmented quadrupole ion guides, which are now included in the latest generation of commercial PTR-ToF. We have characterized the settings of the quadrupole ion guides and their effect on VOC sensitivity and primary ion distribution. Transmission effects, especially low-mass cutoff, strongly affect the primary ion distribution, which complicates normalization and determining humidity dependence of VOC sensitivities. This instrument was deployed during the Shale Oil and Natural Gas Nexus (SONGNEX) 2015 mission (Chapter 4) and used in the development and field demonstration of NO\textsuperscript{+} CIMS (Chapter 5).

Some of the content of this chapter has been published in Yuan et al. (2016a): A high-resolution time-of-flight chemical ionization mass spectrometer utilizing hydronium ions (H\textsubscript{3}O\textsuperscript{+} ToF-CIMS) for measurements of volatile organic compounds in the atmosphere, Atmospheric Measurement Techniques, 9 (6). In addition to the instrument characterization presented by Yuan et al. (2016a), this chapter contains additional information on VOC sensitivity, characterization of the instrument after the removal of a quadrupole ion guide, and discussion of high-resolution peak fitting.
1. Introduction

Volatile organic compounds (VOCs) are important trace gases in the atmosphere. Measurement of these species is crucial in order to understand oxidation chemistry and the formation of ozone and secondary organic aerosol. VOCs have many different sources and often exist in a quickly changing, complex mixture. Analytical techniques that can measure part-per-trillion (ppt) level concentrations of many different VOCs with high time resolution are especially valuable. PTR-MS is such a technique and has gained widespread use in atmospheric chemistry. The operating principle is based on proton transfer from $\text{H}_3\text{O}^+$ to VOCs. The VOC product ions are then detected with a mass spectrometer.

The original and historically most widely used PTR-MS configurations used a quadrupole mass analyzer (Lindinger et al., 1998; de Gouw and Warneke, 2007). Other types of mass analysis have also been explored, including ion traps and time-of-flight (Blake et al., 2009). Time-of-flight PTR-MS instruments (PTR-ToF) have several advantages over quadrupole PTR-MS (PTR-qMS) (Blake et al., 2004). For one, they measure all masses simultaneously. Simultaneous mass measurement allows measurement of more species and is useful when investigating correlations between VOC species. The simultaneous mass measurement can provide better time resolution, which translates to better spatial resolution when measuring from a mobile platform. Modern PTR-ToF instruments can also have much higher mass resolution ($m/\Delta m > 5000$), which allows separation of many isobaric compounds, and the determination of the elemental formula of a VOC. Beginning in the early 2000s a number of PTR-time-of-flight (PTR-ToF) instruments were developed. Early PTR-ToF instruments suffered from sensitivity much lower than contemporary quadrupole instruments, with detection limits on the order of 0.5-1 ppb for minute averaging times (Blake et al., 2004; Ennis et al., 2005; Tanimoto et al., 2007). The lower sensitivity was due to the low duty cycle of the orthogonal extraction of the ion beam in to the ToF region (Blake et al., 2004), technical difficulties related to back-diffusion of air into the ion source (Ennis et al., 2005), and (possibly) relatively low primary ion count rates (Tanimoto et al., 2007). The low sensitivity offset the advantages of simultaneous mass measurement and higher resolution.
Ionicon Analytik reported a greatly improved PTR-ToF instrument, with resolution of >6000 m/Δm and detection limits of around 20 pptv for 1-minute averaging time (Jordan et al., 2009b; Graus et al., 2010). The higher sensitivity and resolution were achieved with improved orthogonal extraction at a higher duty cycle, ion guides, and multi-channel plate detector. The Ionicon instrument has since been used extensively in atmospheric chemistry; examples of applications have included eddy covariance measurements (Müller et al., 2010), biomass burning emissions (Brilli et al., 2014; Stockwell et al., 2015), biogenic emissions (Kim et al., 2010), and aerosol composition (Holzinger et al., 2013).

Recently, improved versions of PTR-MS have been presented that have shown improved sensitivity due to the use of quadrupole ion guides (Sulzer et al., 2014) and RF ion funnel ion guides (Barber et al., 2012; Brown et al., 2017). Compared to conventional ion lens systems, the quadrupole ion guides improve the transmission of ions from the drift tube to the mass analyzer, resulting in higher sensitivity.

The PTR-ToF instrument described in this chapter, the NOAA H$_3$O$^+$ ToF-CIMS, is based on the Aerodyne CIMS, which has two quadrupole ion guides. The H$_3$O$^+$ ToF-CIMS was deployed on the SONGNEX 2015 aircraft mission, some results of which are discussed in Chapter 4. After the SONGNEX campaign, we removed one of the quadrupole ion guides to improve transmission of the reagent ion. This chapter first describes the instrument configuration and data work-up procedure. Then, I discuss the characterization of the reagent ion distribution and VOC sensitivities, paying particular attention to the effect of the quadrupole ion guide. I also discuss some simple laboratory experiments to evaluate the high-resolution peak fitting algorithms used to retrieve ion intensity from high-resolution ToF data. Finally, I share a few examples of improved VOC measurement enabled by the development of the H$_3$O$^+$ ToF-CIMS.

2. Instrument Description

The mass analyzer section of the Ionicon instrument described by Jordan et al. (2009b) was produced by Tofwerk AG, which also supplies ToF mass analyzers to Aerodyne Research Inc. for use in AMS and ToF-CIMS instruments. Aerodyne ToF-CIMS consist of a high pressure (~100 mbar) ion-molecule-reaction (IMR) chamber, a set of ion guides, and the ToF unit (Bertram et al., 2011).
To develop the NOAA H$_2$O$^+$ Tof-CIMS (=PTR-ToF), we replaced the Aerodyne IMR unit with a homebuilt hollow cathode ion source and drift tube assembly, and reconfigured the instrument to be aircraft deployable. The NOAA H$_2$O$^+$ Tof-CIMS uses the same operating principle and mass analyzer as the Ionicon instrument, but uses a home-built ion source and drift tube, used both quadrupole ion guides in its first version, and uses different data analysis software. This section describes the instrument set-up and provides basic information about data work-up.

2.1 Configuration

The instrument consists of the following sections (Figure 3.1): (a) hollow cathode ion source; (b) drift tube; (c) small segmented RF-only quadrupole ion guide (SSQ); (d) big segmented RF-only quadrupole ion guide (BSQ); (e) DC optics that focus and accelerate the ion beam into the ToF (PB); (f) ToF mass analyzer; (g) multi-channel plate detector (MCP).

![Figure 3.1. Instrument diagram.](image)

(a) hollow cathode ion source; (b) drift tube; (c) small segmented RF-only quadrupole ion guide (SSQ); (d) big segmented RF-only quadrupole ion guide (BSQ); (e) DC optics that focus and accelerate the ion beam into the ToF (PB); (f) ToF mass analyzer; (g) multi-channel plate detector (MCP). The light gray section shows the configuration with SSQ removed. The ion source is shown using either H$_2$O vapor to produce H$_3$O$^+$ ions, or UHP air to produce NO$^+$ ions. NO$^+$ ToF-CIMS is discussed in Chapter 5.
The inlet consists of 1/8 Teflon tubing (for SONGNEX mission) or 1/16 PEEK tubing (for missions after SONGNEX) heated to 40 °C (Figure A3.1). The inlet can sample either through an “ambient” air channel or a catalyst channel to provide VOC-free air. The catalyst consists of a 1/4” stainless tube filled with Shimadzu high-sensitivity platinum wool catalyst and held at 350 °C, which removes VOCs but maintains ambient humidity. A 10-component calibration gas standard can be added to either ambient or catalyst air. A diffusion cell continuously adds a small amount of 1,3,5-trichlorobenzene, to help convert ion time-of-flight to m/z. A pressure controller maintains 180 mbar pressure at the end of the inlet, and a PEEK flow restriction drops the pressure to 2.4 mbar in the drift tube. During field operation, instrument background was determined by sampling the catalyst channel for 1.5 minutes every 20-40 minutes. During field operation, the 10-component calibration gas was added for 1.5 minutes every 1-2 hours, and frequent multi-step calibrations (e.g. at the beginning and end of every SONGNEX flight) were performed.

The ion source is a hollow-cathode discharge in water vapor (Figure 3.1 a). Water flow through the ion source is controlled at 4-7 sccm. The ion source is identical to that used on the NOAA PTR-qMS and has been described previously (de Gouw and Warneke, 2007). The source produces a relatively pure stream of H$_3$O$^+$ reagent ions. Figure 3.1 also shows the possibility of replacing water with air to produce NO$^+$ ions; this instrument adaptation is described in Chapter 5.

H$_3$O$^+$ reagent ions and ambient air containing VOCs are mixed together in the drift tube region (Figure 3.1 b). The drift tube consists of a set of alternating stainless steel and Teflon rings, connected by a series of resistors. The drift tube is 11 cm long, pressure controlled at 2.4 mbar, and temperature controlled at 50 °C. The operating E/N (electric field/gas number density) is approximately 120 Td (1Td = 10$^{-17}$ V cm$^{-2}$), which is similar to the E/N of most other PTR-MS instruments reported in the literature.

Two RF-only segmented quadrupoles are used as ion guides: a small segmented quadrupole (SSQ, Figure 3.1 c) and a big segmented quadrupole (BSQ, Figure 3.1 d). The low end of the mass range transmitted by RF-only quadrupoles is limited by the RF amplitude voltage; transmission decreases at high masses due to poorer focusing. The SSQ pressure is controlled at 1.3 mbar using a Pfeiffer D-35614 Asslar
turbo pump and MKS T3Bi throttle valve. After the SONGNEX mission, we elected to remove the SSQ to simplify the detection of reagent ions and increase the transmission of low masses. The two quadrupoles were originally intended to help decrease pressure from ambient, in the IMR, to ToF pressures (10^-7 mbar); in our instrument, the drift tube operates at 2.4 mbar and the additional differential pumping on the SSQ chamber is not necessary. In the modified H_3O^+ ToF-CIMS instrument, the drift tube sits immediately upstream of the skimmer plate in front of the BSQ. The turbo pump was retained but SSQ chamber/BSQ pressure is no longer actively controlled. The removal of the SSQ provided an opportunity to assess the effects of the SSQ on primary ion and VOC ion behavior, and several comparisons with and without SSQ are given later in this chapter.

The mass analyzer is a high-resolution ToF detector (HTOF, Tofwerk AG, Thule, Switzerland). The typical mass resolution of the instrument in the range where most VOCs are detected (m/z 30-200) is 4000-6000 FWHM m/Δm (Figure 3.2).

The pulse occurs at 25kHz frequency to allow measurement of mass range 0-500 m/z.

The MCP detector is operated in high gain mode and increased when necessary to maintain the single ion signal around 1.8 mV ns^-1. This prevents mass discrimination caused by MCP aging (Müller et al., 2014). The necessary MCP voltage has linearly increased at a steady rate over time and does not seem to be affected by instrument transportation or bringing the ToF to ambient pressure (Figure A3.2).
2.2 Data treatment

A simplified flow chart of the data workup process is shown in Figure 3.3. ToF-CIMS data were analyzed using Tofware high-resolution peak-fitting software (Aerodyne Research Inc/ Tofwerk AG). A description of the algorithm is given in DeCarlo et al. (2006). Tofware and high-resolution peak fitting are discussed further in section 6. High resolution-peak fitting in Tofware produces raw ion counts per second (cps) per high-resolution peak. The cps reflects the fundamental counting statistics and sensitivity of the instrument, and is used in this chapter in discussions of sensitivity and statistics. A duty-cycle correction is then applied:

\[ I_{corr} = cps \times \sqrt{\frac{m/z_{reference}}{m/z}} \]

where \( I_{corr} \) is the duty-cycle corrected ion count rate and \( m/z_{reference} \) is an arbitrary reference mass (in this work \( m/z_{reference} \equiv 55 \)). The duty-cycle correction accounts for differences in ion residence time in the extraction region of the ToF and accounts for a mass-dependent sensitivity bias (Chernushevich et al., 2001). Then, measurements were normalized to the duty-cycle corrected \( \text{H}_2\text{O}^+ \) (primary ion) measurement, which typically has count rates on the order \( \sim 10^6 \):

\[ n_{cps} = 1 \times 10^6 \frac{I_{corr}}{H_2O^+_{corr}} \]

The normalization removes variability due to fluctuations in the ion source and detector.

The next step is to correct the normalized-counts-per-second (ncps) for the humidity dependence of VOC sensitivity (section 4.2). Then, background is subtracted by interpolating between instrument zeros. The interpolation is not necessarily linear. The background of some species decreases exponentially after the instrument is turned on; other backgrounds are humidity dependent. The type of background interpolation is chosen based on correlation (or lack thereof) with an exponential curve or humidity-
dependent tracers (e.g. CO$_2$H$^+$). Finally, an experimentally-determined calibration factor (ncps/ppb) is applied to convert humidity-corrected, background-subtracted ncps to ambient mixing ratio.

3. Reagent ion distribution

Several reactive and contaminant ions are produced by the ion source. The most important are m/z 19 H$_3$O$^+$ and the water cluster m/z 37 H$_2$O H$_3$O$^+$. M/z 30 NO$^+$ and m/z 32 O$_2^+$ exist in small amounts, typically <1% and <8% of the measured m/z 19 intensity. It is desirable to minimize NO$^+$ and O$_2^+$ because these contaminant ions also react with VOCs, which can complicate interpretation of mass spectra and calibration. VOC sensitivities mainly depend on the reagent ion distribution in the drift tube, which has been modeled and is well understood (de Gouw and Warneke, 2007). However, the distribution can be changed by different E/N conditions that are encountered as the ions travel through the ion guides and into the ToF. This means that the measured distribution of primary ions is not necessarily the same as it was in drift tube. In order to properly normalize data, understand the effect of humidity on VOC measurements, and minimize non-H$_3$O$^+$ reactions, it is important to understand the distribution of various primary and contaminant ions, and the differences between the measured and drift-tube distributions. This section describes the effect of humidity and the RF-only segmented quadrupoles on the measured ion distribution.

3.1 Effect of humidity

H$_3$O$^+$ reagent ions can cluster with neutral water molecules in the air:

$$H_3O^+ + nH_2O \leftrightarrow H_3O^+(H_2O)_n$$

As ambient humidity increases, we would expect the concentration, and therefore ion count rate, of H$_3$O$^+$ to decrease, and the concentrations of various water clusters H$_3$O$^+(H_2O)_n$ to increase. It is generally desirable to have most reagent ions as H$_3$O$^+$ and not as water clusters, because the water clusters can complicate the mass spectra and affect VOC sensitivity.

The relative abundances of H$_3$O$^+$ and water clusters can be controlled with the E/N settings of the instrument (de Gouw and Warneke, 2007). In the PTR-qMS, the measured m/z 19 H$_3$O$^+$ decreases and m/z 37 H$_2$O H$_3$O$^+$ increases with increasing water mixing ratio, as expected (Figure 3.4). However, in the H$_3$O$^+$
Tof-CIMS with SSQ, both the m/z 19 and m/z 37 signals increase with humidity, and the signal intensity of m/z 37 is of the same magnitude as m/z 19. With the SSQ removed, m/z 19 still increases with humidity, but only slightly, and m/z 37 is much smaller than m/z 19. The ratio of m/z 37:m/z 19 increases with increasing humidity and is used to correct humidity-dependence of VOC sensitivity (section 4.2). All three instruments have the same drift tube and drift tube operating conditions, so these differences in behavior must be due to the different ion guides. The effects of the RF-only quadrupole ion guides are explored further in the next two sections.

3.2 Effect of segmented quadrupole settings

The two segmented RF-only quadrupoles, especially the SSQ, can change the measured primary ion distribution from what exists in the drift tube, and can also affect the detection of VOC ions. The E/N conditions in the quadrupoles are different from the drift tube, which can change the distribution of water clusters. Quadrupole settings can affect the relative transmission of various ions. Finally, some additional reactions may occur in the quadrupoles. In this section, I explore the effects of quadrupole settings, focusing mainly on the SSQ, which has the greatest effects.

Ions in the drift tube and SSQ experience acceleration from the electric field, and decelerating drag from collisions with neutral molecules. The axial drift velocity in the drift tube and SSQ is given as:

$$v_d = \mu \times E \quad (de\ Gouw\ and\ Warneke,\ 2007)$$
The drift velocity depends on the ion mobility $\mu$, and the electric field $E$. Given the length (~4cm), axial voltage (75V), and pressure (1.3 mbar) in the SSQ, it can be calculated that the mean free path and residence time of ions in the SSQ are of the same magnitude as that in the drift tube (Figure 3.1). We can expect that ion-molecule chemistry continues, to some extent, in the SSQ. In the BSQ, the pressure is significantly lower and there are very few interactions between ions and neutral molecules.

Figure 3.5 shows the measured intensities of reagent and VOC ions as a function of SSQ pressure, and of SSQ RF amplitude voltage. The pressure and voltage selected for operation are shown by the gray dashed lines. At low SSQ pressures (1-1.5 mbar), transmission of all ions increases with pressure. At higher pressures, the E/N in the quadrupole is lowered, which favors cluster formation. It can be seen that above

![Graphs showing ion signals vs SSQ pressure and RF amplitude](image-url)

**Figure 3.5.** Dependence of primary ion signals (top two panels) and VOC ion signals (bottom two panels) on SSQ pressure (left) and SSQ RF amplitude (right).
1.5 mbar, m/z 19 H₃O⁺ decreases slightly while water clusters continue to rise. VOC ion signals also increase with increasing SSQ pressure, although only slightly. We selected an SSQ pressure of 1.3 mbar as a compromise between high VOC ion transmission and low measured water clusters.

SSQ RF amplitude strongly affects reagent and VOC ion distributions. Low SSQ RF amplitudes (<40 V) cause poor ion transmission and focusing. At higher amplitudes (>80V), m/z 19 H₃O⁺ and clusters decrease. This is consistent with the expectations that increasing the RF amplitude increases the m/z of the low-mass cutoff (m/z 19 is not transmitted as well at high RF amplitude), and increases overall energy of ions (favoring declustering). We also observed a large increase in O₂⁺, and VOC+O₂⁺ reaction products, as SSQ RF amplitude increased. This could be due to a discharge inside the SSQ creating O₂⁺ primary ions. We selected an RF amplitude of 50 V as a compromise between high VOC ion signal and low O₂⁺.

The pressure in the BSQ cannot be controlled independently, but the behavior of primary ions and VOC ions as a function of BSQ RF amplitude was characterized (Figure A3.3). We selected an RF amplitude of 350 V to compromise between high VOC ion signal, and low O₂⁺ and H₂O₂⁺ relative to H₃O⁺.

The RF frequency of the quadrupoles is set to an optimum resonance frequency determined by the circuit design. We set the SSQ and BSQ to Tofwerk recommendations at 2.6MHz (medium mass coil) and 4.5 MHz (low mass coil), respectively.

3.3 Transmission of H₃O⁺ relative to H₂O₂⁺

For masses between m/z 33 and 400, VOC ions are transmitted with approximately equal efficiency through the ion guides. However, the low-mass RF cut-off of the quadrupole ion guides significantly decreases the efficiency of detecting m/z 19 H₃O⁺. At dry conditions, in the instrument with SSQ, ions in the m/z 33-400 mass range were transmitted approximately 7 times as efficiently as m/z 19, and in the instrument without SSQ, ions were transmitted approximately 2.5 times as efficiently (Figure 3.6). The decrease in the ratio (7x to 2.5x) is because H₃O⁺ is now detected more efficiently, not because VOC sensitivity has decreased.
The more efficient transmission of m/z 37 relative to m/z 19 can help explain why the intensity of 
\( \text{H}_3\text{O}^+ \) increases with increasing humidity, which is a surprising result (section 3.1). \( \text{H}_3\text{O}^+ \) and \( \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \) exist in equilibrium and can interconvert in the drift tube or in the SSQ. After the SSQ, clusters can fragment, but cluster formation is likely slow due to the low pressures and infrequent collisions. At higher humidity, an individual ion spends more time as \( \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \) and is transmitted with higher average efficiency through the quadrupoles. The resulting detected \( \text{H}_3\text{O}^+ \) is higher. To assess this effect, we quantified the transmission efficiency of m/z 37 \( \text{H}_2\text{O} \cdot \text{H}_3\text{O}^+ \) relative to m/z 19 \( \text{H}_3\text{O}^+ \) at several humidity levels. Large amounts of methanol (m/z 33) and acetonitrile (m/z 42) were introduced into the instrument, at concentrations high enough to significantly deplete the reagent ions. The number of VOC product ions (\( \text{VOC}^+ \)) should be equal and opposite to the number of product ions depleted, scaled by the relative transmission \( (T_m) \) of each ion:

![Figure 3.6. Measured transmission ratios of VOC ions relative to m/z 19 \( \text{H}_3\text{O}^+ \). The transmission is measured by introducing large amounts of VOC, such that m/z 19 \( \text{H}_3\text{O}^+ \) is significantly depleted. The transmission is measured by comparing the increase in VOC ions to the decrease in \( \text{H}_3\text{O}^+ \). For the instrument without SSQ, transmissions of a number of additional m/z were calculated from fragment ions using a matrix technique; these points have larger uncertainty. The experiment is performed at dry conditions. The values shown are duty-cycle-corrected counts-per-second, to show mass discrimination caused by the quadrupoles rather than by the ToF pulser. The averages for the instrument with SSQ (7.2±1.1) and without SSQ (2.5±0.2) are shown.](image-url)
Methanol and acetonitrile have product ion masses that bracket m/z 37, and the calculated \( \frac{T_{\text{H}_3\text{O}^+}}{T_{\text{H}_2\text{O}\cdot\text{H}_3\text{O}^+}} \) should bracket the actual value. The calculated values have some error due to the differences in transmission between m/z 33 and 37, and between m/z 42 and 37. In the instrument with SSQ, \( \frac{T_{\text{H}_3\text{O}^+}}{T_{\text{H}_2\text{O}\cdot\text{H}_3\text{O}^+}} \) was calculated to be in the range of 0.14-0.21 at dry conditions, and increased with increasing humidity (Figure 3.7). In the instrument without SSQ, \( \frac{T_{\text{H}_3\text{O}^+}}{T_{\text{H}_2\text{O}\cdot\text{H}_3\text{O}^+}} \) is higher overall (about 0.45 at dry conditions), and the transmission depends less strongly on humidity. This reflects the better transmission of low masses. There is also essentially no difference in the estimates from methanol and acetonitrile experiments, which suggests that m/z 33, m/z 37, and m/z 42 have nearly identical transmission efficiency. I also note that while the removal of the SSQ increased the detected m/z 19 H\(_3\)O\(^+\) cps by a factor of three (due to better low-mass transmission), the detected m/z 37 H\(_2\)O H\(_3\)O\(^+\) at high humidity decreased by about a factor of six. This demonstrates that the E/N conditions in the SSQ were promoting water cluster formation.

If the humidity-dependence of the transmission of m/z 19 relative to m/z 37 is accounted for, the surprising total reagent ion increase seen in figure 3.4b can be explained. It is also clear that the behavior of reagent ions with humidity is highly dependent on instrument settings, and should be carefully considered when normalization is performed. Finally, I reiterate that the ratio of m37:m19 is a reliable proxy for humidity (for a particular instrument setting).
4. VOC sensitivities

4.1 Sensitivities and detection limits

Sensitivities in terms of raw counts-per-second (cps) per ppb, normalized counts-per-second per ppb, and limit of detection are listed in Table 3.1. Raw cps/ppb are not duty-cycle-corrected and reflect the fundamental counting statistics of the instrument. Ncps/ppb gives the calibration factor used to convert from humidity and background corrected ncps to ambient mixing ratio.

<table>
<thead>
<tr>
<th>VOC</th>
<th>m/z</th>
<th>Ion formula</th>
<th>Sensitivity† ncps/ppb</th>
<th>Sensitivity‡ cps/ppb</th>
<th>Background (cps)‡</th>
<th>α scaling factor</th>
<th>1s detection limit (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>33</td>
<td>CH₃OH⁺</td>
<td>81</td>
<td>158</td>
<td>128</td>
<td>1.34</td>
<td>397</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>35</td>
<td>H₂S⁺</td>
<td>7</td>
<td>21</td>
<td>34</td>
<td>1.51</td>
<td>2300</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>42</td>
<td>C₂H₃NH⁺</td>
<td>376</td>
<td>822</td>
<td>26</td>
<td>1.33</td>
<td>45</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>45</td>
<td>C₂H₅OH⁺</td>
<td>289</td>
<td>654</td>
<td>499</td>
<td>1.36</td>
<td>195</td>
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<tr>
<td>Formic acid</td>
<td>47</td>
<td>C₂H₄O⁺</td>
<td>68</td>
<td>159</td>
<td>497</td>
<td>1.32</td>
<td>838</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>54</td>
<td>C₃H₅NH⁺</td>
<td>445</td>
<td>889</td>
<td>1</td>
<td>1.20</td>
<td>17</td>
</tr>
<tr>
<td>Acetone</td>
<td>59</td>
<td>C₃H₆OH⁺</td>
<td>354</td>
<td>916</td>
<td>261</td>
<td>1.28</td>
<td>97</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>61</td>
<td>C₂H₅O₂H⁺</td>
<td>209</td>
<td>551</td>
<td>660</td>
<td>1.40</td>
<td>283</td>
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<tr>
<td>Furan</td>
<td>69</td>
<td>C₃H₄OH⁺</td>
<td>168</td>
<td>470</td>
<td>11</td>
<td>1.26</td>
<td>58</td>
</tr>
<tr>
<td>Isoprene</td>
<td>69</td>
<td>C₃H₆⁺</td>
<td>73</td>
<td>206</td>
<td>26</td>
<td>1.21</td>
<td>162</td>
</tr>
<tr>
<td>MVK</td>
<td>71</td>
<td>C₄H₆OH⁺</td>
<td>160</td>
<td>454</td>
<td>46</td>
<td>1.24</td>
<td>85</td>
</tr>
<tr>
<td>MEK</td>
<td>73</td>
<td>C₄H₆OH⁺</td>
<td>308</td>
<td>886</td>
<td>48</td>
<td>1.21</td>
<td>45</td>
</tr>
<tr>
<td>Benzene</td>
<td>79</td>
<td>C₆H₆⁺</td>
<td>165</td>
<td>493</td>
<td>22</td>
<td>1.48</td>
<td>96</td>
</tr>
<tr>
<td>Toluene</td>
<td>93</td>
<td>C₆H₅⁺</td>
<td>178</td>
<td>579</td>
<td>6</td>
<td>1.39</td>
<td>47</td>
</tr>
<tr>
<td>Furfural</td>
<td>97</td>
<td>C₆H₆O₂H⁺</td>
<td>227</td>
<td>810</td>
<td>4</td>
<td>1.20</td>
<td>22</td>
</tr>
<tr>
<td>Me-cyclohexane</td>
<td>97</td>
<td>C₇H₁₃⁺</td>
<td>9</td>
<td>20</td>
<td>5</td>
<td>1.24</td>
<td>1020</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>107</td>
<td>C₈H₁₀H⁺</td>
<td>193</td>
<td>673</td>
<td>4</td>
<td>1.49</td>
<td>40</td>
</tr>
<tr>
<td>α-Methylstyrene</td>
<td>119</td>
<td>C₉H₁₀H⁺</td>
<td>161</td>
<td>547</td>
<td>0.5</td>
<td>2.25</td>
<td>85</td>
</tr>
<tr>
<td>1,2,4-trimethylbenzene</td>
<td>121</td>
<td>C₉H₁₂H⁺</td>
<td>185</td>
<td>686</td>
<td>3</td>
<td>1.69</td>
<td>45</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>137</td>
<td>C₁₀H₁₆H⁺</td>
<td>67</td>
<td>263</td>
<td>2</td>
<td>1.24</td>
<td>67</td>
</tr>
</tbody>
</table>

Table 3.1. Sensitivities and detection limits of VOCs measured by H₃O⁺ ToF-CIMS during SONGNEX campaign (with SSQ).

† Sensitivity under dry conditions. ‡ cps not corrected for ToF duty cycle.

Limits of detection at 1Hz measurement frequency were calculated by finding the mixing ratio at which the signal-to-noise ratio (S/N) is equal to 3. The calculation can be expressed by (Bertram et al., 2011; Yuan et al., 2016a):

\[
\frac{S}{N} = 3 = \frac{G_f[X]_{lod}t}{\alpha \times \sqrt{G_f[X]_{lod}t + 2Bt}}
\]
where $C_f$ is the instrument response factor, in cps per ppb; $[X]_{lod}$ is the limit-of-detection mixing ratio of species X in ppb; $t$ is the sampling period of 1 second; $\alpha$ is the scaling factor of noise compared to expected Poissonian counting statistics; and $B$ is the background count rate in cps. The scaling factor $\alpha$ is generally greater than 1 because high-resolution peak fitting creates additional noise (Cubison and Jimenez, 2015). Factors $\alpha$ for individual VOCs were determined experimentally using the measured signal $N$ and standard deviations during calibrations (Figure A3.4). The standard deviation generally falls between $\sqrt{N}$ and $2\sqrt{N}$, which shows that high-resolution peak fitting can significantly increase the noise of a measurement. This is discussed in more detail in section 6. Calibration factors were determined using the 10-component calibration gas standard, other standard cylinders, and permeation sources (Veres et al., 2010).

Figure 3.8 compares the sensitivity of the H$_3$O$^+$ ToF-CIMS, during the SONGNEX campaign, to several other PTR-MS instruments reported in the literature. Sensitivities are reported as the ion signal per ppb integrated over 1 second (cps/ppb). The H$_3$O$^+$ ToF CIMS cps/ppb sensitivity is similar to the PTR-qMS (Figure 3.8 a) and is much higher than previous commercial ToF instruments (Figure 3.8 d). The sensitivity is similar to that of a PTR-ToF instrument using an ion funnel (Barber et al., 2012), but lower than that reported for a new prototype PTR-Qi-ToF instrument also using RF-only quadrupole ion guides (Sulzer et al., 2014). The cps/ppb sensitivity comparison to the PTR-qMS does not account for the duty cycle of the qMS: the ToF measures all masses simultaneously, while the qMS must step from one mass to another. The qMS duty cycle effectively reduces the sensitivity of the instrument: over a typical mass-scan cycle of 15 seconds, the qMS detects many fewer VOC ions than the ToF. A comparison of total counts over 15 seconds (Figure 3.8 b) shows that the H$_3$O$^+$ ToF-CIMS has a higher effective sensitivity. Finally, instrument detection limits can be compared (Figure 3.8 c). The detection limit accounts for the noise and background of a VOC ion measurement. The detection limits shown are for 1-second integration. (Detection limits are lower for longer averaging times.) Detection limits for the Sulzer et al. (2014) instrument were not reported.

Surprisingly, the removal of the SSQ did not significantly affect overall VOC sensitivity (Figure A3.5). This could mean that (1) the sensitivity gained by improved focusing of the SSQ was offset by ions
VOC sensitivities did increase significantly; most notably, methanol increased by a factor of 2. This is probably related to the low-mass cutoff in the SSQ.

![Graph showing sensitivity of the NOAA H$_2$O$^+$ ToF-CIMS during the SONGNEX 2015 mission compared to many other PTR-MS instruments reported in the literature. (a) Sensitivity in cps/ppb of methanol, acetone, and benzene for PTR-MS instruments. (b) Total ion counts in a period of 15s. (c) 1-s detection limits. Note the methanol detection limit is on the right axis. (d) Comparison of average VOC sensitivities (cps/ppbv) reported for PTR-ToF instruments. In (b) we assume a typical PTR-qMS operating cycle of 15s, with 1s dwell time for VOCs. This was typical of NOAA PTR-qMS deployment. References: (Blake et al., 2004; Tanimoto et al., 2007; Jordan et al., 2009b; Warneke et al., 2011; Barber et al., 2012; Sulzer et al., 2014; Warneke et al., 2015).]
4.2 Humidity dependence of VOC sensitivity

VOC sensitivity, in terms of normalized-counts-per-second per ppb (ncps/ppb), depends on ambient humidity. The humidity dependence is caused by two main factors.

First, the presence of neutral water molecules may affect the extent to which non-fragmentary proton-transfer occurs. For example, many VOCs react at different rates with $H_3O^+$ (m19) and with the water cluster $H_2O \cdot H_3O^+$ (m37). Benzene, for instance, has a proton affinity (proton affinity = 759 kJ mol$^{-1}$) between that of $H_2O$ (PA = 697 kJ mol$^{-1}$) and $H_2O \cdot H_2O$ (PA = 808 kJ mol$^{-1}$), and so it reacts only with $H_3O^+$ and not the cluster (ligand switching reactions with the cluster are also not favorable). As relative humidity increases, the reagent ion distribution in the drift tube shifts towards m/z 37 $H_2O \cdot H_3O^+$, fewer protonated benzene molecules are created per benzene, and the sensitivity decreases. (Proton affinities from Hunter and Lias (1998).)

Second, the measured intensity of the m/z 19 $H_3O^+$ reagent ion changes with humidity. VOC ion signals are normalized to m/z 19 $H_3O^+$. If the measured m/z 19 $H_3O^+$ is more abundant at high humidity, then normalized VOC sensitivity (ncps/ppb) will appear to be less at high humidity, although the native sensitivity (cps/ppb) does not change.

In conventional quadrupole instruments, humidity-dependent sensitivity is typically dealt with by normalizing the VOC ion signal to $I_{H_3O^+} + X_{VOC} \times I_{H_2O\cdotH_3O^+}$, where $I_{H_3O^+}$ is the ion signal of m/z 19 $H_3O^+$, $X_{VOC}$ is an experimentally-determined VOC humidity-dependence factor, and $I_{H_2O\cdotH_3O^+}$ is the ion signal of m/z 37 $H_2O \cdot H_3O^+$. This works well in situations where the measured $I_{H_3O^+}$ and $I_{H_2O\cdotH_3O^+}$ as a function of humidity reflect the actual ion abundances in the drift tube (even if they are not detected with the same efficiency), and the second effect (humidity dependence introduced by m/z 19 normalization) is small. This results in a situation where sensitivity changes linearly, and by a small amount, with humidity. Unfortunately, the transmission of m/z 19 $H_3O^+$ and m/z 37 $H_2O \cdot H_3O^+$ through the quadrupole ion guides greatly changes the distribution of reagent ions (see section 3), and we found that the conventional approach did not work.
To correct for humidity-dependent sensitivity, we first parameterized humidity using the ratio of m/z 37 H$_2$O H$_3$O$^+$ to m/z 19 H$_3$O$^+$ (R$_{37:19}$). R$_{37:19}$ increases as humidity increases. Then, we experimentally determined the sensitivity of a number of VOC molecules as a function of R$_{37:19}$. A double-exponential best-fit was found to best describe the sensitivity over the range of 0-100% relative humidity (Figure 3.9).

After removal of the SSQ, the humidity dependence due to m/z 19 H$_3$O$^+$ normalization became much smaller. The change in VOC sensitivity as a function of R$_{37:19}$ is now approximately linear for the majority of VOC species (Figure 3.9). VOC ncps can now be humidity corrected by:

$$ncps_{humidity\ corr.} = \frac{ncps}{1 + X_R \times R_{37/19}} = \frac{cps}{I_{H_3O^+} + X_R \times I_{H_5O_2^+}}$$

The humidity correction factor $X_R$ is determined experimentally. This is identical to the humidity correction applied to the NOAA PTR-qMS instrument (de Gouw and Warneke, 2007). We found that a limited number of compounds, most notably acetic acid, HCN, and HNCO, have non-linear sensitivity. These compounds are fit using a double-exponential function.

Figure 3.9. Dependence of normalized VOC sensitivities (ncps/ppb) as a function of humidity (a) with SSQ and (b) without SSQ. Traces are colored by functional group. The reciprocal of 1/m19 is shown as a reference for the influence of m19 H$_2$O$^+$ normalization on humidity dependence. Only VOCs that were measured with both instrument configurations are shown.
The modified (without SSQ) instrument is preferable, with respect to humidity-dependent VOC sensitivity. The humidity correction function is less complex. The magnitude of both humidity effects – m/z 19 normalization and chemical effects – is smaller for nearly all VOCs. The average humidity correction factor is approximately zero.

VOC sensitivity, in cps/ppb (removing the m19 normalization effect), can increase, decrease, or not change with humidity. Figure 3.10 shows several examples. In general, species that have a lower dipole moment and lower proton affinity experience a stronger negative humidity effect (Yuan et al., 2016a). The instrument configuration also has an effect: the extent to which cps/ppb sensitivity changes with humidity is smaller in the modified instrument (without SSQ), for all four species shown in Figure 3.10.

Toluene (Figure 3.10 a), like benzene, reacts more efficiently with m/z 19 H3O⁺ than with the water cluster, so its sensitivity decreases with increasing humidity. Other VOCs, such as acetone (Figure 3.10 b), have high proton affinity, react with both H3O⁺ and H2O∙H3O⁺, do not fragment, and therefore have very small humidity dependence.

A number of product ions of alcohols and aldehydes fragment by losing a water molecule (dehydration) (Španěl et al., 1997; Španěl and Smith, 1997). The example shown is isopropyl alcohol (Figure 3.10 c). The proton-transfer product of isopropyl alcohol is m/z 61 (C₃H₇OH⁺), but the a large part of the signal (35%) is detected at m/z 43 C₃H₇⁺, which is the parent ion minus H₂O. As the ambient humidity increases, the equilibrium shifts towards the parent ion and the sensitivity towards that VOC increases (Figure 3.10). Other ions can add a water molecule (hydrate) rather than fragmenting. These compounds, such as formic acid, have negative humidity dependence: the parent ion decreases, and the hydrated ion increases, as humidity increases.

Several compounds detectable by PTR-MS have a proton affinity only slightly higher than that of water (PA=691 kJ mol⁻¹). Important compounds in this category include H₂S (PA = 705 kJ mol⁻¹), formaldehyde (PA = 713 kJ mol⁻¹), and HCN (713 kJ mol⁻¹). For these compounds, the proton-transfer
back-reaction with H₂O (\textit{VOC} H^+ + H₂O → VOC + H₃O^+) is only slightly endothermic, and can be significant. The back reaction should increase with ambient humidity, and we found strong negative humidity dependence of sensitivity for H₂S and HCN. HCN was calibrated in both the original and modified instruments and had strong negative humidity dependence in both. Similarly, negative humidity dependence of formaldehyde sensitivity has been reported several times for other instruments (Warneke et al., 2011; Vlasenko et al., 2010).
Some non-oxygenated VOCs, such as isoprene (Figure 3.10 d), fragment extensively. The sensitivity of these VOCs decreased with increasing humidity in the instrument configuration with SSQ, and now increases with humidity in the modified instrument. SIFT-MS studies observed that fragmentation of monoterpenes decreased with increasing humidity (Wang et al., 2003). The authors suggested that proton transfer occurs through an energetic VOC-H$_3$O$^+$ intermediate. The intermediate can be stabilized by collision or temporary cluster with neutral water:

$$\text{VOC} + H_3O^+ \rightarrow [\text{VOC} \cdot H_3O^+]^*$$

$$[\text{VOC} \cdot H_3O^+]^* + H_2O \rightarrow [\text{VOC} \cdot H_3O^+ \cdot H_2O^+] + H_2O$$

$$[\text{VOC} \cdot H_3O^+] \rightarrow \text{VOC} \cdot H^+ + H_2O$$

The resulting VOC H$^+$ molecule is less energetic and less likely to fragment. This is a possible explanation for the behavior in the modified instrument. In the instrument with SSQ, it is possible that the quadupole settings did not favor the stabilizing VOC-H$_3$O-H$_3$O$^+$ cluster, although it still should have been present in the drift tube. It is possible that isoprene fragmentation did decrease with increasing humidity in the drift tube of the instrument with SSQ, but was masked by strongly fragmenting conditions in the SSQ.

5. High resolution peak fitting

5.1 Context

The resolution of the H$_3$O$^+$ ToF-CIMS ($m/\Delta m \approx 4500$) is high enough to distinguish isobaric compounds, but many peaks still overlap. Overlap with an adjacent peak can affect the accuracy and precision of fitted peak intensities (Cubison and Jimenez, 2015; Müller et al., 2011). To quantify this effect, we conducted controlled laboratory experiments using two sets of adjacent, overlapping peaks. We use the Tofware high-resolution peak-fitting software package to quantify the intensity of overlapping ions (Aerodyne Research Inc./ Tofwerk AG). Discussion in this section is also relevant to high-resolution data from AMS and other ToF-CIMS instruments.
The peak-fitting algorithm has been described by DeCarlo et al. (2006). A set of peaks is fit to each nominal mass. The peak set has several user-defined parameters: the number of peaks, their exact m/z locations, and the peak shape and width. We use a peak shape experimentally determined from the average shape of selected isolated ions (Timonen et al., 2016). The width of peaks at each mass (instrument resolution) is also experimentally determined (Figure A3.2). The fit is refined to minimize the error between the sum of the individual peaks and the measured intensity at the nominal mass. Users also control the mass calibration. The instrument records the time-of-flight of each ion, which must then be converted to m/z. To do this, we select a set of isolated ions that are constantly present in the mass spectrum, are readily identifiable, and whose exact m/z are known (Table 3.2). The calibration is performed by fitting a function $tof = a_1 (m/z)^{a_2} + a_2$ through the calibrant ions.

Table 3.2. Mass calibrant ions.

<table>
<thead>
<tr>
<th>Ion</th>
<th>m/z (Th)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_3$O$^+$</td>
<td>19.018</td>
</tr>
<tr>
<td>NO$^+$</td>
<td>29.997</td>
</tr>
<tr>
<td>O$_2^+$</td>
<td>31.989</td>
</tr>
<tr>
<td>H$_2$O$_2^+$</td>
<td>37.028</td>
</tr>
<tr>
<td>FeO$_2$H$_5^+$</td>
<td>90.948</td>
</tr>
<tr>
<td>FeO$_3$H$_7^+$</td>
<td>107.950</td>
</tr>
<tr>
<td>FeO$_4$H$_9^+$</td>
<td>125.961</td>
</tr>
<tr>
<td>C$_6$H$_3$Cl$_3$H$^+$</td>
<td>180.937</td>
</tr>
</tbody>
</table>
Inaccuracy could be very large (up to 100% for the range of peak overlap investigated), and the direction and magnitude of the error depended on the mass calibration error and uncertainty, the peak separation, and peak ratio.

### 5.2 Experiments

Several peak overlap experiments were conducted in the laboratory. In each experiment, two VOCs that have product ions at the same nominal mass were introduced into the instrument. The two VOCs were first measured independently to determine the instrument response without peak overlap effects. Then, both VOCs were introduced simultaneously and the abundance of one product ion was held constant, while the other was increased. A range of peak ratios from 0.01 to >10 were created. The peak ratio is defined here as the ratio of the variable-concentration VOC to the constant-concentration VOC. The peak ratio is derived from the isolated VOC baseline measurement and is not affected by peak overlap fitting errors. After high-resolution peak-fitting, the measurement precision (standard deviation/isolated peak intensity) and accuracy (fit intensity/isolated peak intensity) of the constant-concentration VOC were determined. Two sets of
overlapping peaks were explored, with different peak separations. Peak separation “χ” is defined as χ = dt/HWHM, where dt is the time-of-flight separation of the peaks and HWHM is the half-width-half-maximum of the peaks (Cubison and Jimenez, 2015).

The first experiment included benzaldehyde (m/z 107.049, C7H6OH+) as the constant VOC and o-xylene (m/z 107.086, C8H10H+) as the variable (neighboring) VOC (χ=3.66). Benzaldehyde was introduced at a constant concentration of about 1.2 ppb (175 cps) using a permeation cell, and o-xylene was increased from 0.7 to 7 ppb (250 to 2500 cps) using a calibration gas cylinder. Data from this experiment were used to assess the effects of mass calibration and peak shape settings in Tofware. The second experiment consisted of the water cluster with acetic acid (m/z 79.039, C2H6O3H+) as the constant VOC and benzene (79.0542, C6H6H+) as the variable (neighboring) VOC (χ=1.97). Acetic acid water cluster was introduced using an acetic acid permeation cell and humidified air to produce a peak intensity of 500 cps. Benzene was increased from 0.01 to 8 ppb (2 to 2000 cps) using the calibration gas cylinder. This experiment was repeated several times with different acetic acid water cluster intensities (achieved by changing the humidity), to assess the effect of overall peak intensity on peak overlap errors. For each acetic acid water cluster intensity, the isolated peak intensities were determined under the same controlled humidity conditions as the overlap experiment.

Two versions of Tofware were used in this work: v.2.5.1 (release date 12 June 2015) and v.2.5.6 (release date 7 March 2016). Unless otherwise noted, all data shown were analyzed with v.2.5.1. Version 2.5.6 included improvements to peak shape determination (differential smoothing in peak shape so as to better capture tip of peak; improved robustness of iterative peak width determination) and diagnostic tools. V2.5.6 was used to assess the effect of improved peak shape.

5.3 Results

Figure 3.12 shows the precision and accuracy of the benzaldehyde and acetic acid water cluster measurements as a function of relative peak ratio. When the benzaldehyde peak (held constant) is larger than, or the same size as, the xylene peak (neighbor), the measurement is accurate (returned peak intensity
m/z 107

A

benzaldehyde
C₇H₆OH⁺
(constant)
o-xylene
C₈H₁₀H⁺
(changing)

B

precision

C

accuracy

m/z 79

D

acetic acid
water cluster
C₂H₆O₃H⁺
(constant)

E

precision

F

accuracy

Figure 3.12. Results of peak overlap experiments.

Top panels (a,b,c): m/z 107 benzaldehyde and o-xylene. (a) Mass spectrum of nominal mass 107. (b) Precision of benzaldehyde measurement. The dashed line shows the noise expected from Poisson counting statistics of the isolated ion. (c) Accuracy of benzaldehyde measurement. Bottom panels (d, e, f): m/z 79 acetic acid water cluster and benzene. (d) Mass spectrum of nominal mass 79. (e) Precision of acetic acid water cluster measurement. Precision at four acetic acid water cluster intensities is shown: 500, 300, 130, and 100 cps. The cps refers to the signal intensity of the isolated ion. The dashed lines show the noise expected from Poisson counting statistics of the isolated ions. (f) Accuracy of acetic acid water cluster measurement. Accuracy at four signal intensities is shown.

= actual peak intensity), and the standard deviation agrees with the noise expected from Poissonian counting statistics (σ = √N/N). However, as the xylene peak (neighbor) becomes larger in comparison to the benzaldehyde peak (constant), the noise increases and the returned peak intensity of benzaldehyde decreases. For a ratio xylene:benzaldehyde = 10, the noise is 70% higher and the peak intensity 30% lower than expected. Similar behavior can be seen for the acetic acid water cluster (constant) with interference from benzene (neighbor). For a peak ratio of about 1, the acetic acid water cluster standard deviation is about 30-40% higher than that of the isolated peak. For a peak ratio of 10, the fitted intensity of the acetic acid water cluster is lowered by 40%. (Müller et al., 2011) found similar results for precision, but not
accuracy. For a peak ratio of ~1 and a separation $\chi=1.6$ (similar to benzene and acetic acid water cluster $\chi=1.97$), Müller et al. (2011) found an increase of about 14% of the standard deviation above the Poissonian counting error, which is somewhat lower than, but of the same magnitude as, the benzene and acetic acid water cluster experiment ($\chi=1.97$). However, for a peak 10 times smaller than its neighbor separated by $\chi=1.6$, Müller et al. (2011) found an increase of 2% in intensity: an inaccuracy much smaller, and in the opposite reaction, than the results from my benzene and acetic acid water cluster experiment. The disagreement and the decreased accuracy, may result from imperfect treatment of peak shape, which differs between software analysis packages. From the m/z 79 lab experiment, the signal intensity did not appear to have an effect on the accuracy.

The increase in noise due to large neighboring peaks is due to a combination of added noise from the larger peak, and imperfect peak fitting due to uncertainty in the m/z calibration (among other effects), and has been shown in several theoretical investigations of peak fitting (Cubison and Jimenez, 2015; Müller et al., 2011). Cubison and Jimenez (2015) suggest a power law for calculating the additional noise $\sigma_B$ on a peak overlapped by a large neighbor due to mass calibration error, given the peak ratio $R$ of large neighbor peak to small peak and the peak separation $\chi$:

$$\sigma_B = \frac{R}{0.6} \left[10^{0.6-0.41(\chi-0.4)-0.2(\chi-0.4)^2}\right]$$

This equation underpredicts the increased noise in the m79 experiment by a factor of 4, and in the m107 experiment by a factor of 250. It is important to note that the peak separation $\chi=3.66$ between benzaldehyde and xylene is outside of the “mass-calibration limited regime” described by the Cubison and Jimenez (2015) equation, and the parameterization may not be appropriate in this case. A factor of four underprediction is reasonable for the $\chi=1.97$ case, given possible additional uncertainty from mass calibration bias (M. Cubison, personal communication). The Cubison and Jimenez parameterization may be useful for identifying potential peak-overlap conflicts, but real-world precision may be much worse than predicted.
One additional contributor to imprecision and inaccuracy may be mass calibration bias (Corbin et al., 2015a). To assess the effect of mass calibration bias, the m107 overlap data were first fit using the standard set of mass calibrant ions used for field data (Table 3.2, Figure 3.12 a and b). The mass calibration accuracy at m/z 107 is approximately 9 ppm, which was determined by comparing the calibrated location of the measured peaks to the actual exact m/z. Then, the data were fit using a mass calibration with improved accuracy at m/z 107, by using C$_7$H$_6$OH$^+$ and C$_8$H$_{10}$H$^+$ and calibrant ions. The revised calibration accuracy is approximately 3 ppm. The accuracy improves at high peak ratios, and the noise due to peak fitting is reduced by about a factor of two. I conclude that overlapping peaks are sensitive to mass calibration bias, and that deliberately changing the mass calibration bias may be a useful diagnostic to identify peaks with severe overlap error.

An additional effect may be inaccurate peak shape or width. Tofware v2.5.6 included improved user controls over peak shape, especially in estimating intensity near the top of the peak and in the wings. Using Tofware v2.5.6 but the original mass calibration, the m107 experiment was re-fit. The noise is reduced by a factor of two, and the accuracy is dramatically improved. Peak shape and peak width clearly have a strong effect on peak fitting accuracy. However, there is limited exploration of the theoretical underpinnings of these effects in the literature. This should be a topic of further research.

6. Examples of improved measurement

Measurements from the H$_3$O$^+$ ToF-CIMS will be analyzed in detail in subsequent chapters. In this section, I provide a few examples from field data that demonstrate the improved measurement capability of the H$_3$O$^+$ ToF-CIMS relative to the PTR-qMS. Examples are taken from measurements during the SONGNEX 2015 aircraft campaign, which targeted oil and natural gas fields in the central and western US. The H$_3$O$^+$ ToF-CIMS is an improvement in terms of time resolution, mass resolution, and the number of species able to be measured.
Because the PTR-qMS must scan through a series of masses, the time resolution of any one VOC measurement decreases with the number of masses monitored. During previous aircraft campaigns, the PTR-qMS typically measured 10-15 masses, each with 1s dwell time. Figure 3.13 shows measurement of toluene and C8 aromatics over the Permian oil and natural gas field, Texas, using the H$_3$O$^+$ CIMS. Concentrated plumes of aromatics, each only a few seconds wide, were commonly detected on each flight. Superimposed over the ToF measurement is a simulated PTR-qMS measurement, using the typical m/z scan cycle. The plumes are not as well defined in the PTR-qMS measurement, the ion measurements are staggered in time, and it would be difficult to determine the relative enhancement ratios of various aromatics.

The mass resolution is greatly improved over the PTR-qMS, which has unit mass resolution (Figure 3.14).

The utility of the improved mass resolution is demonstrated by measurement of isobaric species C$_7$H$_6$OH$^+$ (benzaldehyde) and C$_8$H$_{10}$H$^+$ (C8 aromatics). Figure 3.15 shows the mass spectra and spatial distribution of these two compounds measured over the Permian oil and natural gas field in Texas during the SONGNEX mission (peaks fit with Tofware v. 2.5.6). The ion signals from the two VOCs are comparable in magnitude, but have very different spatial distributions. Xylenes are directly emitted, and benzaldehyde is an oxidation
product. A sum measurement of the two, as would be provided with a unit-mass-resolution PTR-qMS, would provide far less scientific information.

The ToF-CIMS also allows the measurement of many more ion masses. During the SENEX 2013 aircraft campaign, PTR-qMS measurements included 12 reported species. During the SONGNEX 2015 aircraft campaign, the H₃O⁺ ToF-CIMS measurements included 30 calibrated VOC species, and an additional 200 product ion masses that were enhanced above background. (These measurements are discussed in Chapter 4).

![Figure 3.15](image)

Figure 3.15. Measurement of m/z 107 over the Permian oil and natural gas field, Texas, during the SONGNEX mission. The flight track of the aircraft is shown in the bottom two panels. On the left, the track is colored and sized by the concentration of benzaldehyde (C₇H₆O); on the right, the track is colored and sized by the concentration of C₈ aromatics (C₈H₁₀). The top two panels show example high-resolution mass spectra measured within the boxed area of the flight track.
7. Conclusions

The development of the NOAA H$_2$O$^+$ ToF-CIMS is a major advance in our ability to measure VOCs. In this chapter I described the instrument configuration and characterization. The instrument was developed based on the Aerodyne ToF-CIMS and has 1-s detection limits of less than 100 ppt for many VOCs, which compares well to contemporary commercially available PTR-ToF instruments. An especially important set of results is the characterization of the effect of the RF-only segmented quadrupole ion guides on VOC and primary ion detection. These ion guides are used in the newest generation of commercial PTR-ToF and in other Aerodyne ToF-CIMS instruments, and can significantly change the measured distribution of primary ions, the sensitivity to VOCs, and the VOC humidity dependence. Although ion transmission overall was improved, compared to a lens system, the small segmented quadrupole (SSQ) limited the transmission of the m/z 19 H$_2$O$^+$ primary ion relative to larger masses. This caused the transmission of H$_2$O$^+$ to be humidity dependent, which complicated signal normalization and humidity-dependent sensitivity correction. Additionally, the removal of the SSQ changed the native humidity dependence of several VOCs, which further demonstrates that non-negligible VOC-ion reactions were continuing in the SSQ.

Explorations with high-resolution peak fitting showed that peak fitting could introduce data artifacts, including much higher noise and significant bias. Mass calibration accuracy and peak shape have a strong influence on noise and accuracy. These results qualitatively agree with investigations in the literature, but there does not exist a theoretical way to predict the bias resulting from peak fitting. In the final section of this chapter, I provided several examples of improved VOC measurement capability compared to the PTR-qMS. The separation of isobaric species, calculation of elemental formula from high mass resolution, and fast, simultaneous measurement of many species have provided many new scientific insights. Application of this improved measurement to VOC emissions and chemistry over oil- and natural gas-producing regions is discussed in the next chapter.
Chapter 4. Observations of VOC emissions and photochemical products over US oil- and gas-
producing regions using high-resolution H$_3$O$^+$ CIMS (PTR-ToF-MS)

Abstract

VOCs related to oil and gas extraction operations in the United States were measured by H$_3$O$^+$
chemical ionization time-of-flight mass spectrometry (H$_3$O$^+$ ToF-CIMS / PTR-ToF-MS) from aircraft
during the SONGNEX campaign in March-April 2015. This work presents an overview of major VOC
species measured in nine oil and gas producing regions, and a more detailed analysis of H$_3$O$^+$ ToF-CIMS
measurements in the Permian Basin within Texas and New Mexico. Mass spectra are dominated by small
photochemically produced oxygenates, and compounds typically found in crude oil: aromatics, cyclic
alkanes, and alkanes. Mixing ratios of aromatics were frequently as high as those measured downwind of
large urban areas. In the Permian, the H$_3$O$^+$ ToF-CIMS measured a number of underexplored or previously
unreported species, including aromatic and cycloalkane oxidation products, nitrogen heterocycles including
pyrrole (C$_4$H$_5$N) and pyrroline (C$_4$H$_7$N), H$_2$S, and a diamondoid (adamantane) or unusual monoterpene. I
additionally assess the specificity of a number of ion masses resulting from H$_3$O$^+$ ion chemistry previously
reported in the literature, including several new or alternate interpretations.

1. Introduction

Recent advances in fossil fuel extraction technology, especially horizontal drilling and hydraulic
fracturing, have enabled a surge in crude oil and natural gas production in several regions across the United
States over the past decade (US Energy Information Administration). A particular environmental concern
is the release of air pollutants. Emissions can affect global climate, by the release of greenhouse gases
(Miller et al., 2013; Brandt et al., 2014); regional air quality, by contributing ozone and particulate precursor
species (Kemball-Cook et al., 2010; Edwards et al., 2014; McDuffie et al., 2016); and local air quality, by
releasing air toxics harmful to human health (McKenzie et al., 2012; Adgate et al., 2014).

Detailed measurements of volatile organic compound (VOC) emissions, and their atmospheric
reaction products, are needed to understand and mitigate these air quality concerns. Several studies have
used gas chromatography (GC) techniques to characterize oil- and gas-related VOCs in relatively high chemical detail (Simpson et al., 2010; Gilman et al., 2013; Swarthout et al., 2013). These studies have demonstrated that comprehensive VOC characterization is invaluable for source identification and air quality modeling in these regions. To date, there are few such studies, and they have been limited in measurement of secondary species and in time resolution. The Permian Basin, located in west Texas and eastern New Mexico, is the physically largest and most productive oil field in the United States, but non-methane VOC measurements from this region have rarely been reported.

Proton-transfer-reaction mass spectrometry (PTR-MS) is a well-established chemical ionization technique used to measure VOCs, especially polar and aromatic species, in ambient air. This technique uses $\text{H}_3\text{O}^+$ reagent ions and can have time resolution of 1Hz or better. The recent development of PTR-MS instruments that use high-resolution time-of-flight mass analyzers (PTR-ToF-MS) has greatly expanded the number of measurable species, enhanced the technique’s suitability to mobile platforms, and improved our ability to speciate specific ion masses (Jordan et al., 2009b; Graus et al., 2010; Cappellin et al., 2011; Yuan et al., 2016a). For example, the resulting complex PTR-ToF-MS mass spectra in forested environments (Kim et al., 2010) and biomass burning (Brilli et al., 2014; Stockwell et al., 2015) have been reported. A recent study comparing PTR-ToF-MS and PTR-quadrupole MS instruments in an oil and gas producing region in Utah pointed to the scientific advances possible with the application of PTR-ToF-MS, especially the separate measurement of hydrocarbon masses from isobaric oxygenates, and the measurement of previously undetectable photo-oxidation products (Warneke et al., 2015). In this work PTR-MS refers to the proton-transfer technique, and PTR-ToF-MS refers to PTR-MS instruments with a high-resolution time-of-flight mass analyzer. The instrument discussed in this work is called “$\text{H}_3\text{O}^+$ ToF-CIMS”, an instrument similar to the PTR-ToF-MS but developed at NOAA.

This work comprises a detailed analysis of PTR-ToF-MS mass spectra obtained from measurements in oil- and gas-producing regions, supported by a comprehensive suite of other chemical instrumentation. I outline an interpretation of PTR-ToF-MS measurements in these regions, and report
observed mixing ratios of commonly measured PTR-MS species in nine oil and gas producing regions. I present detailed VOC observations for the Permian Basin. This work provides detailed information about the VOC chemistry of these regions, will aid in the interpretation of PTR-MS (especially PTR-ToF-MS) measurements in oil and gas producing regions, and will support future analysis of ambient measurements in these regions.

2. Methods

2.1 Measurement location and context

Measurements were made from the NOAA WP-3D Orion research aircraft during the Shale Oil and Natural Gas Nexus (SONGNEX) campaign in March and April 2015. The SONGNEX campaign surveyed nine large oil and natural gas production regions in the central United States, several smaller producing regions, and locations with associated infrastructure. All research flights took place during daytime (late morning to mid-afternoon). The aircraft was equipped with a suite of chemical and meteorological instrumentation, which is described in section 2.2. This work reports measurements in nine regions: Bakken (ND), Upper Green River (WY), Uintah (UT), Denver-Julesburg (CO), San Juan (CO, NM), Permian (NM, TX), Barnett (TX), Eagle Ford (TX), and Haynesville (TX, LA) (Figure 4.1a).

SONGNEX measurements coincided with a peak in fossil fuel production in many of these regions, but were just after a downturn in the drilling of new wells due to a drop in the price of crude oil (Figure 4.1b, 4.1c). Analysis is restricted to data collected in the fossil fuel producing areas of the basins, and within the PBL (typically \( \leq 600\text{m AGL} \)). Selection of data is shown in Figure A4.2.

The Permian oil and gas field, located in western Texas and eastern New Mexico, was surveyed on three flights, on April 6, April 9, and April 23, 2015. Detailed interpretation of the \( \text{H}_2\text{O}^+ \) ToF-CIMS data focuses on measurements taken during the Permian flight on April 23. This flight featured high signal on many VOC masses, providing the best overall signal-to-noise ratio of any SONGNEX flight and allowing the observation of many VOCs that may have been below detection limit on other flights. Additionally, there are few non-oil and gas emission sources in this region, which simplifies the interpretation of VOC
measurements. During the April 23 flight, the average boundary layer temperature was 19 °C, the relative humidity ranged from 20-80% (average 34%), and wind speeds were typically between 2 and 10 m s$^{-1}$, averaging 5.4 m s$^{-1}$. The maximum concentration of ozone measured was 62 ppbv, and the average 49 ppbv.

The Permian Basin is an approximately 200 000 km$^2$ area encompassing a number of geologically distinct fossil fuel producing reservoirs, including several shale oil formations. The region is characterized by significant and intense oil production activity (accounting for nearly 20% of 2013 US domestic oil production), currently largely driven by recent development of shale oil formations (Budzik and Perrin,
As of September 2015, there were approximately 124,000 actively producing oil wells and 10,000 gas wells in this region, and approximately 1300 new wells were drilled in April 2015 (Railroad Commission of Texas, 2017; State of New Mexico Oil Conservation Division, 2017). Point sources reported in the NEI 2011 inventory are largely associated with oil and gas production, including, for example, refineries, processing facilities, compressor stations, and tank batteries. The region has a population of 1 million, of whom about one-fifth live in the largest urban area, Midland-Odessa (U.S. Census). The climate is arid and the land cover consists mainly of desert and grassland. The April 23 SONGNEX flight track; locations of oil and gas wells, urban areas, and NEI 2011 point sources, and the spatial distributions of a few VOCs of interest are shown in Figure 4.2.

Figure 4.2. NOAA P3 flight track during the April 23 Permian flight. (a) April 23 flight track; wind direction; locations of oil and gas wells, NEI 2011 point sources, and the Midland-Odessa urban area. NEI point sources are sized by total reported VOC emission, ranging in the area shown from 0-400 ton/year. (b) Flight track colored and sized by toluene (0-1.7 ppbv). (c) Flight track colored and sized by acetaldehyde (0-3.6 ppbv). (d) Flight track colored and sized by H$_2$S (0-8 ppbv). (e) Flight track colored and sized by m/z 71.049 C$_4$H$_6$OH$^+$ (0-86 normalized counts per second).
To support the interpretation of SONGNEX H$_3$O$^+$ ToF-CIMS measurements, this work also refers to measurements taken by an Ionicon PTR-ToF-MS instrument in the Uintah Basin, Utah, oil and gas field during winter of 2013. The Ionicon PTR-ToF-MS instrument relies on the same measurement principle as the SONGNEX H$_3$O$^+$ ToF-CIMS and has similar mass resolution. The PTR-ToF-MS Uintah Basin measurements have been previously described by Warneke et al. (2015), and a comparison between the H$_3$O$^+$ ToF-CIMS and PTR-ToF-MS instruments is given by Yuan et al. (2016a). Finally, I include H$_3$O$^+$ ToF-CIMS headspace measurements (at 25 °C) of a crude oil sample. The sample was purchased from ONTA (Geology) Goal and Petroleum Inc. and is a blend of oil from several reservoirs in West Texas. The sample was bottled at a central collection facility after transport in tanker trucks and before being sent to a refinery. It is possible that some VOCs were removed prior to transport: sulfur and nitrogen-containing organics are often removed at processing facilities, although I do not know how this sample was treated at the collection facility. Some of the most highly-volatile VOCs may have been depleted during transport.

2.2 Instrumentation

2.2.1 Description of H$_3$O$^+$ ToF-CIMS instrument

The H$_3$O$^+$ ToF-CIMS and its operation during the SONGNEX campaign have been previously reported (Yuan et al., 2016a). The basic operational principle is the same as other PTR-MS instruments. H$_3$O$^+$ ions are generated from water vapor in a hollow cathode discharge ion source. The H$_3$O$^+$ reagent ions are then mixed with ambient air, containing VOCs, in a drift tube section. The proton from H$_3$O$^+$ is transferred to VOCs with sufficiently high proton affinity, and the resulting ionized VOCs are transferred to a mass analyzer (in the H$_3$O$^+$ ToF-CIMS, VOC ions are guided through a set of RF-only segmented quadrupoles to a time-of-flight unit). The hollow cathode, drift tube, pressure controlled inlet, background, and calibration components are custom built; the ion transmission and time-of-flight analyzer were produced by Aerodyne Research Inc./ToFwerk. The H$_3$O$^+$ ToF-CIMS has a drift tube E/N (electric field strength divided by number density) of about $120 \times 10^{17}$ Td (V cm$^2$). Data are presented in this work at 1s time resolution unless otherwise noted.
During field operation, the instrument background was determined for 90 seconds every 20-40 minutes by flowing ambient air through a catalyst, and a 10-component gas standard was added for 90 seconds every 1-2 hours (single-point calibration) to record instrument stability and sensitivity. In addition to the in-flight single-point calibrations, multi-point calibrations were performed at the beginning and end of each flight. A small amount of trichlorobenzene (C₆H₃Cl₃) was continuously introduced into the instrument as a mass calibrant. Data were analyzed using Tofware high resolution peak-fitting software (Aerodyne Research Inc./Tofwerk). Data were then corrected for humidity-dependent sensitivities and background-subtracted. In addition to the in-flight calibrations, laboratory calibrations of a larger number of species were performed using standard cylinders and permeation tubes. More details on the data quality assurance procedures related to instrument operation, background subtraction, humidity dependence, and calibration are included in Yuan et al. (2016a) and in Chapter 3.

The H₃O⁺ ToF-CIMS instrument has a mass resolution of approximately 3900-5900 m/ m over the mass range discussed in this work (m/z 12-200), which is sufficient to determine the elemental formulas of most detected ion masses. Evaluation of data quality related to high-resolution peak-fitting are discussed in Supplementary Information (Section A4.1).

In this work I report signal intensity using normalized counts-per-second (ncps), and VOC mixing ratio (ppbv) for calibrated species. Normalized counts-per-second (ncps) is the instrument signal relative to 10⁶ H₃O⁺ ion counts, corrected for humidity effects, and background subtracted.

VOC sensitivities were determined by (1) direct calibration, where available; (2) calculated using proton-transfer rate constants, either known or calculated based on polarizability and dipole moment (Sekimoto et al., 2017); or (3) an average sensitivity determined from the calibrated and calculated sensitivities. Accuracy is within 15% for directly calibrated compounds and generally within a factor of two for calculated sensitivities. Some ion masses, such as m/z 45.992 NO₂⁺ (Section 3.4.4) and m/z 81.070 C₆H₅⁺ (Section 3.4.3) have an ambiguous interpretation and these are discussed in terms of instrument signal (ncps) and not mixing ratio.
Measured 1-s detection limits (for a signal-to-noise ratio of 3) range from approximately 40 pptv (aromatics) to 400 pptv (methanol). Some mixing ratios reported in this work are smaller than 40 pptv. In a few cases, the signal-to-noise ratio is less than three, but variability is still discernable, and these species are discussed mostly for the absence of significant enhancement (e.g. styrene, cresol). Other species are presented as an average over a longer period of time: for example, average boundary layer enhancements presented in Figure 4.5, and time series in Figure 4.13. As averaging time increases, the limit of detection decreases: a typical aromatic compound with 1s detection limit of 40 pptv (sensitivity of 500 count ppbv\(^{-1}\) s\(^{-1}\), background of 5 counts per second) has a 10s detection limit of about 9 pptv (a calculation is included in the supplementary information, Section A4.2).

2.2.2 PTR-MS application to oil and gas emissions: strengths and limitations

In the WP-3D SONGNEX payload, the primary strengths of the H\(_3\)O\(^+\) ToF-CIMS include measurement of small acids and carbonyls not detected by other instruments, and a much higher measurement rate of aromatics and cyclic alkanes, which were also measured by the whole air sampler, which typically collected sample for five seconds once every three minutes (Lerner et al., 2017). Aromatics and compounds with heteroatoms are generally detected sensitively (aromatics: measured average 180 ncps/ppbv, polar compounds: 200 ncps/ppbv) with a few exceptions of compounds that can dissociate by dehydration, such as small alcohols and aldehydes (de Gouw and Warneke, 2007). Cyclopentane and cyclohexane cannot be detected, but alkyl-substituted cyclic alkanes are detected, at approximately 5% of the sensitivity of aromatics. Alkenes containing four or more carbon atoms are detected sensitively (estimated average 300 ncps/ppbv), although larger alkenes can fragment at the high E/N conditions used in our instrument (Gueneron et al., 2015).

PTR-MS is notably limited in its measurement of alkanes: saturated alkanes smaller than hexane have too low proton affinity to be detected, and C6 and larger branched-and straight-chain alkanes are detected with very low sensitivity, reacting with H\(_3\)O\(^+\) at a rate one or two orders of magnitude slower than aromatics (Arnold et al., 1998). Additionally, the larger alkanes fragment extensively (Gueneron et al.,
This behavior makes alkanes difficult to measure sensitively and selectively. This is particularly limiting in measurements of emissions from oil and gas operations, where alkanes are typically dominant in terms of mixing ratio. NO$_2^+$ cannot be converted to a mixing ratio in a meaningful way and was excluded from the concentration comparison. For hydrocarbons, an average sensitivity was applied (Section 2.2.1).

During SONGNEX, fast measurement of methane and ethane were provided by cavity ring-down and direct-absorption spectroscopy (respectively), and speciated C2-C8 alkanes were measured by whole-air-sampling/GC-MS. Data from a number of other chemical instruments that were deployed during the SONGNEX mission are used in this analysis. Descriptions of these instruments are given in Table 4.1. Further information can be found at https://esrl.noaa.gov/csd/groups/csd7/measurements/2015songnex/P3/datainfo.html.
<table>
<thead>
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<th>Name of instrument</th>
<th>Species measured</th>
<th>Measurement technique</th>
<th>Citation or details</th>
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<tr>
<td>iWAS/GC-MS (improved Whole Air Sampler)</td>
<td>C2-C6 alkanes, Select cycloalkanes, C6-C8 aromatics, Small alkyl nitrates, Isoprene, Monoterpenes, Ethene, Ethyne, Methanol</td>
<td>Whole-air canister sampling followed by offline GC-MS analysis</td>
<td>(Lerner et al., 2017)</td>
</tr>
<tr>
<td>Aerodyne C2H6 instrument</td>
<td>Ethane, Methane CO2</td>
<td>Tunable infrared laser direct absorption spectroscopy</td>
<td>(Yacovitch et al., 2014)</td>
</tr>
<tr>
<td>Picarro CO2/CH4 instrument</td>
<td>Peroxyacetyl nitrates: PAN, PPN, MPAN, APAN</td>
<td>Cavity ring-down spectroscopy</td>
<td>(Peischl et al., 2012)</td>
</tr>
<tr>
<td>PAN CIMS</td>
<td>Nitric acid, Formic acid</td>
<td>Thermal dissociation/ I-chemical ionization mass spectrometry</td>
<td>(Slusher et al., 2004)</td>
</tr>
<tr>
<td>In-Situ Airborne Formaldehyde (ISAF)</td>
<td>Formaldehyde</td>
<td>Laser-induced fluorescence</td>
<td>(Cazorla et al., 2015)</td>
</tr>
<tr>
<td>Picarro G1204 H2S instrument</td>
<td>H2S</td>
<td>Cavity ring-down spectroscopy</td>
<td>Manufacturer specifications: 10 ppb 5-s LoD (1σ) ~5 second measurement interval May experience interference from organics</td>
</tr>
<tr>
<td>NO/NO2/NOy Chemiluminescence</td>
<td>NO, NO2, NOy</td>
<td>NO by NO/O3 chemiluminescence, NO2 by photolysis and NO/O3 chemiluminescence, NOy by Au converter and NO/O3 chemiluminescence</td>
<td>(Ryerson et al., 2000; Pollack et al., 2010)</td>
</tr>
<tr>
<td>HNO3/HCOOH CIMS</td>
<td>Nitric acid, Formic acid</td>
<td>I-chemical ionization mass spectrometry</td>
<td>(Neuman et al., 2016)</td>
</tr>
<tr>
<td>NOx CaRDS</td>
<td>NO, NO2, NOy</td>
<td>Cavity ring-down spectroscopy</td>
<td>(Wagner et al., 2011)</td>
</tr>
</tbody>
</table>

Table 4.1. SONGNEX chemical instrumentation.
3. Results and Discussion

3.1 Overview of H$_3$O$^+$ ToF-CIMS measurements

In this section, I provide a comparison of the mixing ratios of several volatile species between all flights made in the San Juan, Uintah, Upper Green River, Denver-Julesburg, Barnett, Permian, Haynesville, Bakken, and Eagle Ford regions. Species measured by H$_3$O$^+$ ToF-CIMS that are included in this comparison are the sum of C6-C10 aromatics, methanol, H$_2$S, and acetone. Figure 4.3 (next page) shows an overview of the mixing ratios of these compounds in the boundary layer during each flight. Additionally, monoterpenes (measured by iWAS/GC-MS), NO$_x$ (measured by the chemiluminescence instrument), CH$_4$ (measured by cavity ring-down spectroscopy), and average wind speed within the boundary layer are shown in Figure 4.3 for chemical and meteorological context.

BTEX species (benzene, toluene, and C8 aromatics), and higher weight aromatics, are important air toxics and ozone and aerosol precursors that are commonly reported in VOC measurements of oil and gas-producing regions. PTR-MS measures these compounds with high specificity and sensitivity (de Gouw and Warneke, 2007). Figure 4.3a shows that aromatics concentrations in oil and gas basins were typically high – comparable to concentrations downwind of large urban areas.

The H$_3$O$^+$ ToF-CIMS measurement of benzene, toluene, and C8 aromatics agrees well with measurements made by whole-air-sampling followed by GCMS analysis (iWAS/GC-MS) (Yuan et al., 2016a; Lerner et al., 2017). There were large differences in observed mixing ratios between basins. On all flights, sharp, concentrated plumes of aromatics were encountered (resulting in maximum and average mixing ratio much higher than median). Large differences in mixing ratio between different flights in the same basin (e.g. Uintah, Denver-Julesburg) are partially the result of differences in meteorological conditions while in other basins (Permian, Haynesville, Upper Green River, Eagle Ford, Bakken), average mixing ratios were more consistent between flights. Benzene was not measured by the H$_3$O$^+$ ToF-CIMS during the March 24 San Juan flight due to an instrument issue.
Figure 4.3. Mixing ratios observed within the boundary layer during SONGNEX flights. Description of each panel continued on next page.
For comparison, Figure 4.3 also shows boundary layer statistics from two flights during other recent P3 aircraft campaigns: SENEX (June 16 2013 flight, Atlanta GA metropolitan area) and CALNEX (May 05 2010 flight, Los Angeles CA metropolitan area). SENEX and CALNEX data are from a PTR-quadrupole MS instrument. The maximum mixing ratios of aromatics during every SONGNEX flight were considerably higher than those measured during SENEX and CALNEX (note the log scale); averages within several basins (especially Uintah, Denver-Julesburg, and Permian) were comparable to or higher than aromatics measured over the Los Angeles metropolitan area (population of 18 million).

H$_2$S is an air toxic that can be emitted from oil and gas sources, and can seriously harm human health (Tarver and Dasgupta, 1997; Li et al., 2014). Significant enhancements of H$_2$S were seen only in the Permian and Haynesville regions (Figure 4.3c). All three Permian flights saw broad enhancements in H$_2$S likely associated with oil and gas production. Emissions from a paper mill were captured during the Haynesville flights and a mixing ratio of 27.7 ppbv was measured 20.5 km downwind of the point source, which was the highest H$_2$S mixing ratio measured during SONGNEX. The Eagle Ford flights had a higher limit-of-detection due to an unknown instrument issue and the maximum mixing ratio is not statistically significant.

Oxygenated compounds provide insight into photochemical aging, and comprised the majority of H$_3$O$^+$ ToF-CIMS product ion signal. The most abundant oxygenated compounds were methanol and small (C1- C4) carbonyls and acids. These compounds include m/z 45.034 C$_2$H$_4$OH$^+$ (acetaldehyde), m/z 59.049 C$_3$H$_6$OH$^+$ (acetone), m/z 73.065 C$_4$H$_8$OH$^+$ (2-butanone), m/z 61.028 C$_2$H$_4$O$_2$H$^+$ (acetic acid), and m/z 75.044 C$_3$H$_6$O$_2$H$^+$ (propionic acid). Support for interpretation of these ion masses is given in Section 3.4.1.
Mixing ratios of acetone were similar in each basin, with average mixing ratios within a range of about 1.5 ppb (Figure 4.3b). Mixing ratios of acetaldehyde, MEK, and acetic acid for each flight are in Figure A4.3. The relative abundances of oxygenates were generally similar between basins (Figure 4.4), although there was higher variability in organic acids and formaldehyde. The highest relative abundances of organic acids were observed in the Denver-Julesburg Basin and are likely due to primary emissions from concentrated animal feeding operations and not photochemistry (Eilerman et al., 2016; Yuan et al., 2017).

Figure 4.4 compares the distribution of oxygenates to that measured during the UBWOS 2013 campaign (Utah Division of Air Quality, 2014), the SENEX and CALNEX flights, and the CALNEX ground site in Los Angeles (Veres et al., 2011; Warneke et al., 2013). The mix of VOC precursors from oil and gas fields (dominated by small alkanes) is very different from urban and biogenically influenced air. However, the mix of products was similar to that measured during CALNEX. The similarity between the SONGNEX and CALNEX profiles is somewhat surprising since it has been shown that the oxidation mechanisms in urban and oil and gas producing regions are quite different (Yuan et al., 2015). The distribution of carbonyls was similar to that measured during the SENEX flight, but had significantly lower formaldehyde and formic acid, likely due to the much lower concentration of their precursor, isoprene.
Methanol (detected at m/z 33.034 CH₃OH⁺) was the single most abundant VOC detected by the H₃O⁺ ToF-CIMS. There is agreement to within the stated uncertainties between the H₃O⁺ ToF-CIMS measurement and the iWAS/GC-MS measurement (R²= 0.9, slope = 1.23), despite the difficulty in retrieving methanol from the whole-air-sampling system (Lerner et al., 2017). There was high variability in methanol mixing ratios between basins, between flights within the same basin, and within individual flights (Figure 4.3d). Also shown, in Figure 4.3f, is the iWAS/GC-MS measurement of monoterpenes, as a proxy for biogenic emissions.

The two flights with the highest methanol concentrations were the April 25 Haynesville flight, and the April 23 Permian flight, both of which had mixing ratios comparable to those observed during SENEX, a summertime campaign over a biogenically productive region. All three Permian flights had high methanol mixing ratios.

To summarize, oil and gas-producing regions, even those in rural areas such as the Permian and Uintah basins, can have VOC mixing ratios comparable to those measured in urban areas. The concentrations and relative distribution of photochemically produced species were relatively similar between basins. There are significant differences between the basins in the mixing ratios and composition of primary compounds such as aromatics and H₂S. Forthcoming work, including measurements from iWAS/GC-MS, will investigate these differences and their origins in greater detail.

3.2 Overview of measurements in the Permian Basin

The highest overall mixing ratios of VOCs were detected during the April 23 flight over the Permian Basin. In the following sections I provide a detailed interpretation of PTR-ToF-MS mass spectra in oil and gas producing regions, based on observations in the Permian Basin.

An averaged mass spectrum from the boundary layer in the Permian Basin flight on April 23 is shown in Figure 4.5a, where all peaks shown are well above the detection limit. Enhancements are relative to the average mixing ratio in a ten-minute free-troposphere measurement immediately prior to descent into the basin. (The time period and altitude of this measurement are shown in Figure A4.2).
Compounds containing one or two oxygen atoms dominate the product ions measured by the $\text{H}_3\text{O}^+$ ToF-CIMS. These oxygenates are comprised mainly of methanol (m/z 33.034 CH$_3$OH$^+$) and small photochemical products. Other important ions include masses typically attributed to aromatics and cyclic.

Figure 4.5. Overview of $\text{H}_3\text{O}^+$ ToF-CIMS mass spectra measured during the April 23 Permian flight. The categories “HC”, “HCO$_1$”, “HCO$_2$”, etc. mean hydrocarbon species (without S or N) with no oxygen, with one oxygen atom, with two oxygen atoms, etc. Top: average mass spectrum, colored by elemental composition. Large pie chart: overall VOC composition. Color code is the same as mass spectrum. Small pie charts: composition of oxygenated (top), HC-only (middle), and N- and S-containing species (bottom). For all pie charts, the composition in terms of both relative instrument signal (ncps, left column) and mixing ratio (ppb, right column) is shown. See text for a description of which species were included in the mixing ratio charts, and how concentrations were calculated.
alkanes; m/z 34.995 H₂S H⁺ (hydrogen sulfide); and m/z 45.992 NO₂⁺. Figure 4.5b compares the average boundary layer concentrations of species detected by H₃O⁺ ToF-CIMS. NO₂⁺ cannot be converted to mixing ratio in a meaningful way and was excluded from the concentration comparison. For fragmentary hydrocarbons, an average sensitivity was applied (Section 2.2.1). It can be seen that methanol and H₂S, while comprising a relatively small portion of the overall signal, are actually quite important in terms of actual abundance.

The relationship between major H₃O⁺ ToF-CIMS product ion signals measured over the Permian and the West Texas crude oil headspace sample is shown in Figure 4.6. Photochemical products like the small oxygenates, and methanol, are greatly enhanced compared to hydrocarbon masses, which are generally similar to the composition of crude oil. Alkane and alkene masses are somewhat more abundant relative to aromatics in the SONGNEX measurements, compared to the crude oil. This could be due to compositional differences between crude oil and VOC emission sources in the Permian, additional signal on alkane masses from photochemical products (Section 3.2.4), or photochemical removal of aromatics.

![Figure 4.6](image_url)

Figure 4.6. Comparison of H₃O⁺ ToF-CIMS measurement of VOCs over the Permian Basin to VOCs evaporated from West Texas Crude oil.

The values reported are the average boundary-layer enhancement in signal (ncps) during the SONGNEX April 23 flight, and the signal (ncps) relative to the most abundant mass (m/z 57.070 C₄H₉⁺) in the West Texas Crude oil headspace.
A few species, particularly $\text{H}_2\text{S}$, were enhanced in the Permian but not detected in the crude oil. There are large differences in the $\text{H}_2\text{S}$ content of various Permian basin reservoirs (Railroad Commission of Texas) and it is possible that our crude oil sample was derived from low-sulfur-content reservoirs, or that sulfur species were removed prior to bottling.

During the April 23 flight, several compositionally distinct air masses were sampled (Figure 4.2). One air mass, in the southwestern part of the flight path, was enriched in aromatics, methane, ethane, and other primary compounds (less aged); another, to the east, was relatively more enriched in oxygenates that are typically photochemically produced, such as acetone, acetaldehyde, and PAN species (more aged). HYSPLIT back-trajectory modeling indicates that over the 24 hours prior to sampling, the more aged air mass circulated over the southwestern part of the oil field. The highest concentrations of acetone and acetaldehyde occur over the topographically lower areas of the flight. A reasonable explanation for the more aged air mass is that it consists of emissions and chemical products from the previous day pooled in low-lying areas. Most VOCs are enhanced in the less-aged spatial distribution (e.g. toluene), the more-aged spatial distribution (e.g. acetaldehyde), or a combination of the two (e.g. $\text{m/z 83.086 C}_6\text{H}_{10}\text{H}^+$). Figure 4.7 compares the correlation of the measured VOCs with toluene, a primary emission, and acetaldehyde, a secondary product. Alkanes, aromatics and cycloalkanes have a higher correlation with toluene, while oxygenates have a higher correlation with acetaldehyde. A small number of species, such as $\text{H}_2\text{S}$ and $\text{m/z 71.049 C}_4\text{H}_8\text{OH}^+$, have different distributions. The physical separation between less and more aged emissions during this flight was used to help identify VOC ions and to interpret their source.
The three transects in the western part of the flight path contain similar VOC composition, but the concentrations of toluene, C8 aromatics, and larger aromatics decrease relative to benzene from south to north. The relative decreases of the more reactive aromatics is likely the result of longer photochemical processing, which is consistent with the southerly wind direction during the flight, generally lower concentrations from south to north, and the time of each transect (northernmost transect latest in the day). I used the ratios of toluene, C8 aromatics, and C9 aromatics to benzene to calculate a relative OH exposure for each transect, in order to explore photochemical aging of other VOCs. This method has been used extensively in atmospheric chemistry (de Gouw et al., 2005; Warneke et al., 2013) and details are shown in the supplementary information (SI Section 3). Not all species had significant enhancement in this area of

Figure 4.7. Correlation of H$_2$O$^+$ ToF-CIMS VOC ion masses with toluene, representative of less aged emissions, and with acetaldehyde, representative of more aged emissions. Toluene and acetaldehyde were selected for this analysis because they have high signal-to-noise ratio and unambiguous VOC ion interpretation.
the flight (e.g. H_2S had a different spatial distribution), so I was not able to use this method to investigate photochemical aging these species.

In the following discussion, I examine several groups of compounds measured during the April 23 Permian flight in greater detail: hydrocarbons (aromatic, cyclic alkane, alkene, and alkane masses), secondary compounds, and compounds with heteroatoms. Table 4.2 lists ion masses discussed in this work and our interpretation of that measurement. Table 4.2 also highlights (in bold text) measurements that provide new understanding of atmospheric composition and chemistry: VOCs that have been previously unreported or underexplored, and VOC ion masses where our assessment is a new interpretation of a mass previously reported in the literature.
<table>
<thead>
<tr>
<th>Ion Exact Mass (Th)</th>
<th>Ion formula</th>
<th>Previously reported interpretations</th>
<th>Interpretation in oil and gas producing regions</th>
<th>Max boundary layer enhancement (ppbv) during April 23 flight</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.0335</td>
<td>CH$_3$OH$^+$</td>
<td>Methanol (de Gouw and Warneke, 2007; Blake et al., 2009)</td>
<td>Methanol</td>
<td>19.09</td>
</tr>
<tr>
<td>34.995</td>
<td>H$_2$S$^+$</td>
<td>Hydrogen sulfide (Li et al., 2014)</td>
<td>Hydrogen sulfide</td>
<td>12.6</td>
</tr>
</tbody>
</table>
| 41.0386            | C$_3$H$_5^+$ | General alkane/VOC fragment (Gueneron et al., 2015)  
MBO fragment (Kim et al., 2010); propyne (Stockwell et al., 2015) | General alkane/VOC fragment | |
| 43.0178            | C$_2$H$_5$OH$^+$ | Biogenic aldehyde fragment (Kim et al., 2010; Ruuskanen et al., 2011)  
Acetic acid fragment (de Gouw et al., 2003; Müller et al., 2012) | Fragment of acetic acid | |
| 43.0542            | C$_3$H$_5^+$ | General alkane/VOC fragment (Gueneron et al., 2015)  
Propene (Kuster et al., 2004; Knighton et al., 2012; Stockwell et al., 2015) | General alkane/VOC fragment | |
| 45.0335            | C$_2$H$_4$OH$^+$ | Acetaldehyde (de Gouw and Warneke, 2007; Blake et al., 2009) | Acetaldehyde | 3.6 |
| **45.9924** | NO$_2^+$ | PAN (de Gouw et al., 2003; Müller et al., 2012; Kaser et al., 2013) | Unresolvable NO$_2$ species | |
| 57.0699            | C$_3$H$_5^+$ | General alkane/VOC fragment (Gueneron et al., 2015)  
Butenes (Karl et al., 2003) | General alkane/VOC fragment | |
| 59.0491            | C$_3$H$_6$OH$^+$ | Acetone (de Gouw and Warneke, 2007; Blake et al., 2009) | Acetone (negligible contribution from propanal) | 6.17 |
| 61.0284            | C$_2$H$_5$O$_2$H$^+$ | Acetic acid (de Gouw et al., 2003) | Acetic acid | 1.57 |
| **68.0495** | C$_3$H$_5$NH$^+$ | Pyrrole (Brilli et al., 2014; Stockwell et al., 2015) | Pyrrole | 0.04 |
| **69.0699** | C$_3$H$_5^+$ | Isoprene (Blake et al., 2009)  
Cycloalkane fragment (Gueneron et al., 2015)  
MBO fragment (Kim et al., 2010) | Cycloalkane fragment + secondary species fragment | |
| 70.0651            | C$_4$H$_7$NH$^+$ | Butane nitrile (Brilli et al., 2014) | Pyrroline (dihydropyrrole) | 0.21 |
| 71.0491            | C$_5$H$_7$OH$^+$ | Biogenic MVK/methacrolein (Blake et al., 2009) | MVK/methacrolein /dihydrofuran | 0.54 |

Table 4.2. Significant ion masses and interpretation.  
Mixing ratio (ppbv) enhancements are listed only for non-fragmentary ions of relatively certain identification. Ion masses with VOC interpretation of particular interest are highlighted using bold text.
<table>
<thead>
<tr>
<th>Ion Exact Mass (Th)</th>
<th>Ion formula</th>
<th>Previously reported interpretations</th>
<th>Interpretation in oil and gas producing regions</th>
<th>Max boundary layer enhancement (ppbv) during April 23 flight</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.0855</td>
<td>C₅H₁₁⁺</td>
<td>General alkane/VOC fragment</td>
<td>General alkane/VOC</td>
<td></td>
</tr>
<tr>
<td>73.0648</td>
<td>C₄H₈OH⁺</td>
<td>2-butanone (MEK)</td>
<td>2-butanone (MEK)</td>
<td>1.96</td>
</tr>
<tr>
<td>75.0441</td>
<td>C₅H₁₀O₂H⁺</td>
<td>Propionic acid</td>
<td>Propionic acid</td>
<td>0.48</td>
</tr>
<tr>
<td>77.0233</td>
<td>C₆H₁₄O₃H⁺</td>
<td>PAN (Hansel and Wishaler, 2000)</td>
<td>Unknown species + PAN</td>
<td></td>
</tr>
<tr>
<td>79.0542</td>
<td>C₆H₁₀⁺</td>
<td>Benzene</td>
<td>Benzene</td>
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<tr>
<td>81.0699</td>
<td>C₄H₈⁺</td>
<td>Monoterpene fragment</td>
<td>Cyclopentyl aldehyde fragment (tentative)</td>
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<tr>
<td>83.0855</td>
<td>C₆H₁₄⁺</td>
<td>Methylcyclopentane (Yuan et al., 2014; Gueneron et al., 2015)</td>
<td>Methylcyclopentane +</td>
<td></td>
</tr>
<tr>
<td>85.0648</td>
<td>C₆H₁₂OH⁺</td>
<td></td>
<td>Cyclopentanone</td>
<td>0.11</td>
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<tr>
<td>87.0441</td>
<td>C₅H₁₆O₂⁺</td>
<td>Aromatic oxidation product</td>
<td>Aromatic oxidation product</td>
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<td>C₆H₁₀OH⁺</td>
<td>C₅ carbonyls (Fall et al., 2001)</td>
<td>C₅ carbonyls</td>
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<td></td>
<td>MBO (Kim et al., 2010;Fall et al., 2001)</td>
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<td></td>
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<td>93.0699</td>
<td>C₇H₁₆⁺</td>
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<td>Toluene</td>
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<td>95.0855</td>
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<td>Terpene fragment</td>
<td>C₇ cycloaldehyde fragment (tentative)</td>
<td>0.12</td>
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<tr>
<td>97.1012</td>
<td>C₇H₁₃⁺</td>
<td>C₇ cycloalkanes</td>
<td>Methylcyclohexane + secondary species fragment</td>
<td></td>
</tr>
<tr>
<td>99.0804</td>
<td>C₇H₁₀OH⁺</td>
<td>Hexenal</td>
<td>C₆ cycloalkane oxidation products (tentative)</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(Fall et al., 2001;Ruuskanen et al., 2011;Park et al., 2013)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>101.0597</td>
<td>C₈H₁₂O₂⁺</td>
<td>Aromatic oxidation product</td>
<td>Aromatic oxidation product</td>
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</tr>
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</table>

Table 4.2 (continued)
<table>
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<tr>
<th>Ion Exact Mass (Th)</th>
<th>Ion formula</th>
<th>Previously reported interpretations</th>
<th>Interpretation in oil and gas producing regions</th>
<th>Max boundary layer enhancement (ppbv) during April 23 flight</th>
</tr>
</thead>
<tbody>
<tr>
<td>101.0961</td>
<td>C₆H₁₂OH⁺</td>
<td>Hexanal (Rinne et al., 2005;Brilli et al., 2014)</td>
<td>C6 carbonyls</td>
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<td>105.0699</td>
<td>C₅H₁₀H⁺</td>
<td>Styrene (Kuster et al., 2004)</td>
<td>Styrene</td>
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</tr>
<tr>
<td>107.0491</td>
<td>C₇H₁₀OH⁺</td>
<td>Benzaldehyde (de Gouw et al., 2003)</td>
<td>Benzaldehyde</td>
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<tr>
<td>107.0855</td>
<td>C₈H₁₀H⁺</td>
<td>C8 aromatics (de Gouw and Warneke, 2007;Blake et al., 2009)</td>
<td>C8 aromatics</td>
<td>0.65</td>
</tr>
<tr>
<td>111.1168</td>
<td>C₂H₁₅⁺</td>
<td>C8 cycloalkanes (Yuan et al., 2014;Warneke et al., 2015;Gueneron et al., 2015)</td>
<td>C8 cycloalkanes +</td>
<td></td>
</tr>
<tr>
<td>113.0961</td>
<td>C₇H₁₂OH⁺</td>
<td>Heptenal (Brilli et al., 2014)</td>
<td>Cycloalkane oxidation product (tentative)</td>
<td>0.06</td>
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<tr>
<td>115.1117</td>
<td>C₇H₁₄OH⁺</td>
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<td>C7 carbonyls</td>
<td>0.03</td>
</tr>
<tr>
<td>121.1012</td>
<td>C₉H₁₃H⁺</td>
<td>C9 aromatics (de Gouw and Warneke, 2007;Blake et al., 2009)</td>
<td>C9 aromatics</td>
<td>0.25</td>
</tr>
<tr>
<td>125.1325</td>
<td>C₉H₁₇⁺</td>
<td>C9 cycloalkanes (Yuan et al., 2014;Warneke et al., 2015;Gueneron et al., 2015)</td>
<td>C9 cycloalkanes + secondary species</td>
<td></td>
</tr>
<tr>
<td>135.1168</td>
<td>C₁₀H₁₄H⁺</td>
<td>C10 aromatics (de Gouw and Warneke, 2007;Blake et al., 2009)</td>
<td>C10 aromatics</td>
<td>0.08</td>
</tr>
<tr>
<td>137.1325</td>
<td>C₁₀H₁₅H⁺</td>
<td>Monoterpenes (de Gouw and Warneke, 2007;Blake et al., 2009)</td>
<td>Adamantane or mystery monoterpane</td>
<td>0.09</td>
</tr>
<tr>
<td>151.1481</td>
<td>C₁₁H₁₈H⁺</td>
<td></td>
<td>Methyl adamantane (tentative)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2 (continued)
3.3 Hydrocarbon masses

3.3.1 Aromatics

Alkyl-substituted aromatic species are commonly measured by PTR-MS and the interpretation of these ion masses is well established (de Gouw and Warneke, 2007; Blake et al., 2009). Aromatics can be important to the photochemical production of ozone in oil and gas producing regions, and can have high yields of secondary organic aerosol (Henze et al., 2008; Edwards et al., 2014). Quantifying the distribution of these species emitted from oil and gas sources is important to modeling work and to distinguishing between oil and gas and urban sources.

Figure 4.8 summarizes the distribution of C7 C10 alkyl-substituted aromatics relative to benzene measured during SONGNEX and compares the findings with other sources. This figure compares (1) measurements from all flights, (2) the average aromatics enhancement over the Permian during the April 23 flight, (3) fresh emissions sampled in a plume from a point source (a natural gas processing plant, 32.49N 101.35W) on the April 6 and April 9 Permian flights, (4) aromatics in the headspace of West Texas crude oil, (5) a literature survey of oil and gas sources, and (6) a literature survey of urban sources. The profiles of the average for all SONGNEX flights, and of aromatics measured in the Permian, are similar to the profile typically measured in oil and gas producing regions. The Permian profile is very similar to the composition of West Texas crude oil, and there is significant diversity in aromatics profiles between different oil and gas regions and sources. The average oil and gas profile is clearly differentiated from urban emissions (vehicular sources) by roughly equal enhancements of toluene and benzene, followed by a steady decrease in enhancement with increasing carbon number. The average oil and gas, and urban composition shown in Figure 4.8d were calculated by averaging all oil and gas sources (panels a and b) and all literature profiles shown in panel 4.8c for the urban profile.
The H$_3$O$^+$ ToF-CIMS also allowed for the investigation of more highly alkyl-substituted aromatics with 4 double bond equivalents; and less saturated aromatics, including PAHs and styrenes. During the April 23 Permian flight, I found that benzene and C7-C9 alkyl substituted aromatics were by far the most abundant aromatic species, accounting for 95% of total aromatic signal. These species were observed in both broad enhancements and in localized plumes from point sources. No PAHs with significant enhancement (above estimated 1s detection limit of 30-40 pptv) were observed. Over all flights, styrene (m/z 105.070 C$_8$H$_8$H$^+$) was consistently enhanced by up to 1.1 ppbv in plumes from point sources, and up to 60 pptv during one leg of the April 6 flight, where it was not correlated with other aromatics.

Figure 4.8. Comparison of C6-C10 aromatics distribution. Y-axis (molar ratio to benzene) is the same in each panel. (a) Measurements by H$_3$O$^+$ ToF-CIMS: SONGNEX flights and West Texas crude oil headspace. (b) Aromatic profiles from published studies of oil and gas fields, condensate tanks, oil tanks, and water storage tanks. (c) Aromatics profiles from published studies of urban areas and vehicle exhaust. (d) Average profiles of all oil and gas sources (panels a and b) and urban sources (panel c).
3.3.2 Cycloalkanes

Cycloalkanes are an important component of crude oil (Smith, 1968; National Research Council, 1985; Drozd et al., 2015), and have been detected by GC in significant concentrations in the atmosphere over oil and gas producing regions (Simpson et al., 2010; Gilman et al., 2013; Edwards et al., 2014). Although cycloalkanes are measured by PTR-MS with lower sensitivity than aromatics, the resulting product ions are still detectable. I find that cycloalkane product ions are not specific for cycloalkanes, but may still be useful for characterizing the VOC composition of air masses, and may be specific for cycloalkanes in relatively unaged air masses.

Several previous laboratory and field experiments have explored the PTR-MS response to cycloalkanes. PTR-MS is somewhat less sensitive to cyclic alkanes than to aromatics and oxygenates (Midey et al., 2003; Gueneron et al., 2015). At the E/N conditions in our instrument, cycloalkanes experience significant fragmentation, creating important product ions at m/z 69.070 C₆H₉⁺, 83.086 C₈H₁₁⁺, 85.101 C₈H₁₃⁺, 97.101 C₆H₁₃⁺, 111.117 C₈H₁₅⁺, and 125.132 C₁₀H₁₇⁺ (Midey et al., 2003; Warneke et al., 2003; Yuan et al., 2014; Gueneron et al., 2015). Cyclic alkanes have been measured with PTR-MS in crude oil using a GC interface (Yuan et al., 2014), and in ambient air in the Uintah basin (Warneke et al., 2014); based on these measurements I expect that m/z 69.070 is produced generally by C₆-C₉ cycloalkanes; m/z 83.086 mainly from methylcyclopentane, cyclohexane, and methylcyclohexane; m/z 85.101 mainly by methylcyclopentane; m/z 97.101 mainly by methylcyclohexane; and m/z 111.117 and 125.132 by C₉ and C₁₀ cycloalkanes, respectively. These masses were clearly enhanced in H₃O⁺ ToF-CIMS measurements over the Permian and other basins. Cumulatively, they account for 50% of the hydrocarbon concentration (ppbv) measured by H₃O⁺ ToF-CIMS.

Chemically specific measurements of methylcyclohexane and cyclohexane were made by iWAS/GC-MS. The comparison between the H₃O⁺ ToF-CIMS and iWAS/GC-MS methylcyclohexane measurements shows that the H₃O⁺ ToF-CIMS measurement is on average three times higher and the correlation coefficient R² is 0.71. The ratio of m/z 97.101 to iWAS methylcyclohexane is higher in the more
aged air mass (Figure 4.9a). This suggests that m/z 97.101 includes a significant contribution from a secondary VOC that fragments to produce C$_7$H$_{13}^+$. Some possibilities include an aldehyde or alcohol with formula m/z 115.112 C$_7$H$_{14}$OH$^+$ (e.g. heptanal or methylcyclohexanol) or a larger molecule (e.g. m/z 129.127 C$_8$H$_{16}$OH$^+$ losing –CH$_3$OH).

Comparisons of methylcyclohexane between other GC and PTR-MS instruments previously deployed in the Uintah Basin, Utah, indicate that this behavior is not an H$_3$O$^+$ ToF-CIMS specific issue and is not unique to the Permian Basin. In the winter of 2012, when photochemistry was low, quadrupole PTR-MS m/z 97 measurements agreed with the methylcyclohexane measurement from a GC-MS instrument within 23% (Warneke et al., 2014). However, in the winter of 2013, when photochemistry was much higher (Edwards et al., 2014), the relationship between PTR-ToF-MS m/z 97.101 C$_7$H$_{13}^+$ and GC-FID methylcyclohexane was dependent on photochemical exposure (Figure 4.9b).

The relatively high correlations of other cycloalkane indicator masses (m/z 83.086, m/z 69.070, m/z 111.117, etc.) with acetaldehyde suggest that they too experience interference from similar secondary products (Figure 4.7). The secondary compounds could be cycloalkane oxidation products, or other alcohols.
or aldehydes, which fragment by losing a water molecule -- a common PTR-MS fragmentation mechanism (Yuan et al., 2016a).

### 3.3.3 Interpretation of hydrocarbon ion masses in oil and gas regions

The H$_3$O$^+$ ToF-CIMS measurements during SONGNEX offer new insights into some VOC ion masses commonly measured by PTR-MS.

It is clear from the comparison to iWAS/GC-MS measurement of isoprene (Figure 4.10, next page) that m/z 69.070 C$_5$H$_9$+ is not isoprene, which is the dominant contributor in many air masses (de Gouw and Warneke, 2007; Blake et al., 2009). I interpret it as the sum of a cycloalkane fragment and a secondary compound from the oxidation of oil and gas precursor emissions; several other studies have also suggested non-biogenic interpretations of this mass (Yuan et al., 2014; Gueneron et al., 2015). Similarly, m/z 137.132 C$_{10}$H$_{16}$H$^+$, usually interpreted as monoterpenes, was enhanced far above the monoterpene species (α- and β-pinene) detected by iWAS/GC-MS. M/z 137.132 C$_{10}$H$_{16}$H$^+$ was also observed using a PTR-ToF-MS instrument in the Uintah Basin, UT in winter of 2013 (Figure A4.4). The Uintah observations indicate that this unknown species is emitted in several oilfields and is likely not an instrument artifact. Possible alternative sources of this VOC ion mass are (1) another isomer of C$_{10}$H$_{16}$, but not a monoterpene; (2) a monoterpene species not detected by iWAS/GC-MS; or (3) another species, such as an alcohol or aldehyde, which fragments to m/z 137.132. Each possibility is discussed in more detail below.

1. **Other C$_{10}$H$_{16}$ isomer.** Other, non-terpene isomers of C$_{10}$H$_{16}$ are found in fossil fuels. In particular, the presence of “diamondoids”, characterized by cage-like structures, is well known (Dahl et al., 1999; Araujo et al., 2012). The smallest diamondoid molecule, adamantane (tricyclo[3,3,1,1(3,7)]decane, C$_{10}$H$_{16}$), has a tetrahedral structure formed by three cyclohexane rings (Figure 4.10). Adamantane can have concentrations from <1% to 100% of typical benzene concentrations in crude oil (Verma and Tombe, 2002; Araujo et al., 2012). In the Permian atmospheric measurement, m/z 137.132 C$_{10}$H$_{16}$H$^+$ was up to 20% the concentration of benzene (assuming similar sensitivity as monoterpenes). Alkyl-substituted adamantanes are relatively abundant (Stout and Douglas, 2004; Wang et al., 2006). Enhancement of m/z
was detected, but larger molecules were below the detection limit of the H$_3$O$^+$ ToF-CIMS during this flight. The measured headspace of West Texas Crude showed relative enhancements of n(CH$_2$)-substituted C$_{10}$H$_{16}$ that are more consistent with the adamantane series than with terpenes, where enhancements at every n(C$_5$H$_8$) would be expected, but the evidence is not conclusive (Figure A4.5). Adamantane has a longer retention time than the GC elution time used for the iWAS samples, so iWAS/GC-MS was not able to confirm or exclude the presence of this molecule.
(2) *Other monoterpenes.* Terpene-derived (“isoprenoid”) saturated compounds are known to be in crude oil, and some larger molecules such as phytane and pristane are used as geochemical biomarkers (Tissot and Welte, 1984). There is less information available about the presence of unmodified monoterpenes, but the presence of an unusual monoterpenes (such as limonene) derived from crude oil or industry solvents is certainly possible. Data from the iWAS/GC-MS was again inconclusive, but suggested that it was not limonene.

(3) *Fragment of another species.* M/z 137.132 C_{10}H_{16}H^+ is not likely to be a fragment of another species. No oxygenated species were detected that could easily fragment to produce m/z 137. A larger hydrocarbon could fragment to this mass. However, in crude fuels, hydrocarbon concentrations in a particular homologous series generally decrease with carbon number. An anomalously intense larger mass would require its own explanation.

I do not currently have enough information to state conclusively if the observed m/z 137.132 C_{10}H_{16}H^+ ion is from adamantane, a monoterpenes, or another isomer. Collection of more evidence is outside the scope of this chapter and is currently under separate investigation. If the observed C_{10}H_{16} molecule is indeed adamantane, it represents a previously undetected class of atmospheric VOCs. Regardless of identity, this observation highlights that there may be significant emissions of higher-mass hydrocarbons from fossil fuels that are rarely measured. These compounds could be used to identify emission sources, and could potentially be SOA precursors (de Gouw et al., 2011).

3.3.4 *Other hydrocarbon masses*

The H_3O^+ ToF-CIMS also measured other hydrocarbon signals that could not be tied to a single VOC, and these hydrocarbon masses comprise a significant fraction of the total hydrocarbon signal (Figure 4.5). These other important hydrocarbon ion masses include m/z 41.039 C_3H_4H^+, m/z 43.054 C_3H_6H^+, m/z 57.070 C_4H_8H^+, and m/z 71.086 C_5H_{10}H^+. Unit-mass-resolution PTR-MS has not been able to investigate these ions because of strong interference from isobaric masses, such as C_2H_5OH^+ at m/z 43.018. Several studies have reported that these masses are non-specific and are produced by alkenes, and fragmentation of
alkanes, alkenes, aldehydes, and alcohols (Buhr et al., 2002; Jobson et al., 2005; Gueneron et al., 2015). Laboratory tests with the H$_3$O$^+$ ToF-CIMS confirmed that multiple alkane and alkene VOCs present during the April 23 flight (as measured by iWAS/GC-MS) fragment to these masses. These ion masses had significant intensity in both the southwestern (less aged) and eastern (photochemically enhanced) areas of the flight, suggesting contributions from fragments of both primary and secondary species.

3.4 Hydrocarbon oxidation chemistry

3.4.1 Major secondary compounds

My interpretation of the most abundant photochemically produced ion masses is consistent with interpretations often presented in the literature: m/z 45.034 C$_2$H$_4$OH$^+$ is specific for acetaldehyde, m/z 59.049 C$_3$H$_6$OH$^+$ for acetone, m/z 73.065 for MEK, m/z 61.028 C$_2$H$_4$O$_2$H$^+$ for acetic acid, and m/z 75.044 C$_3$H$_6$O$_2$H$^+$ for propionic acid.

The carbonyl species with more than three carbon atoms have both ketone and aldehyde isomers, and both isomers could be products of alkane oxidation. For example, oxidation of propane in the presence of NO$_x$ is expected to yield approximately 26% propanal and 74% acetone (Calvert et al., 2008). The ratio of propanal to acetone has been measured to be 0.17 (Uintah Basin, 2012, Edwards et al. (2013)), 0.19 (Uintah Basin, 2014), and 0.22 (Denver-Julesburg basin, Gilman et al. (2013)) in oil and gas producing regions, compared to 0.06 in an urban area (Los Angeles, Borbon et al. (2013)). However, almost all of the signal at H$_3$O$^+$ ToF-CIMS m/z 59.049 C$_3$H$_6$OH$^+$ can be attributed to acetone. The PTR-MS reaction of H$_3$O$^+$ with propanal is dissociative, and the sensitivity of the H$_3$O$^+$ ToF-CIMS to propanal at m/z 59.049 is only 3% that of acetone. Acetone therefore dominates the signal at this mass, and I assume similar behavior for higher-mass carbonyls.

Abundances of larger masses in the 1-double bond equivalent, 1-oxygen homologous series decrease rapidly with carbon number; these are most likely also carbonyls derived from alkanes. m/z 43.018 C$_2$H$_4$OH$^+$ was identified as a fragment of acetic acid from laboratory tests.
Glycolaldehyde (m/z 61.028 C₂H₄O₂H⁺) and hydroxyacetone (m/z 75.044 C₃H₆O₂H⁺) could be interferences to acetic acid and propionic acid, respectively. However, these compounds have been mainly reported in environments affected by biogenic emissions and biomass burning, and acetic acid has been shown to be the dominant contributor to m/z 61.028 C₂H₄O₂H⁺ in several environments (Karl et al., 2007; Fu et al., 2008; Haase et al., 2012).

3.4.2 Aromatic oxidation products

Aromatic oxidation products are of particular interest, as they have been shown to be an important source of radicals that drive ozone formation in oil and gas producing regions (Edwards et al., 2014). From laboratory and chamber studies, expected aromatic oxidation products include various diketones, phenols and nitrophenols, benzaldehyde-type compounds (from toluene and larger aromatics), and furanones (Wagner et al., 2003; Bloss et al., 2005; Wyche et al., 2009; Yuan et al., 2016b). PTR-MS can detect phenols, benzaldehydes, and furanones (Müller et al., 2012); detection of some dicarbonyls, such as glyoxal and methylglyoxal, may be difficult due to fragmentation, strong humidity dependence, and interference from other species (Pang et al., 2014; Stönner et al., 2017).

By far the most abundant aromatic oxidation product detected was m/z 107.049 C₇H₆OH⁺, benzaldehyde (max. 360 pptv). Phenol (C₆H₅O), cresol (C₇H₈O), and methylfuranone (C₅H₆O₂) were detected at only an estimated 30-40 pptv maximum enhancement. Cresols, diketones, and furanones are expected to have a much higher yield at the observed NOₓ concentrations (average 1.1 ppb) (Smith et al., 1998; Müller et al., 2012), but are also much more reactive (Bierbach et al., 1994; Atkinson and Arey, 2003).

Müller et al. (2012) reported several unidentified masses resulting from chamber oxidation of trimethylbenzenes: m/z 87.044 C₄H₆O₂H⁺ and m/z 101.060 C₅H₈O₂H⁺. These masses were also detected during the April 23 SONGNEX flight, and they were quite significant relative to other oxygenates- m/z 87.044 at approximately 10% of the signal intensity of acetic acid. I classify these as aromatic oxidation products but do not have enough information to suggest a structure.
3.4.3 Cycloalkane oxidation products

The H$_3$O$^+$ ToF-CIMS detected several potential cycloalkane oxidation products as shown in Figure 4.11. The 2-double bond equivalent, 1-oxygen homologous series (C$_n$H$_{2n-2}$OH$^+$) does not decrease monotonically with carbon number: the species with four carbons (m/z 71.049 C$_4$H$_6$OH$^+$) and 6 carbons (m/z 99.080 C$_6$H$_{10}$OH$^+$) are the most abundant (Figure 4.11a). In addition, m/z 71.049 C$_4$H$_6$OH$^+$ has a somewhat different spatial distribution than other oxygenates, including much higher intensity in the central part and sections of the northern part of the field, and may have a primary source (Section 3.4.4). The enhancement of the C6 oxygenate points to cycloalkane precursors. Similar ion masses were measured by the PTR-ToF-MS instrument deployed in the Uintah Basin, UT, in 2013 (Figure 4.11b).

![Figure 4.11.](image)

Figure 4.11. Ion masses related to cycloalkane oxidation products. The x-axis is the number of carbon in the molecule. (a) C$_x$H$_{2x-2}$O oxygenates measured in the Permian basin during SONGNEX. (b) Cycloalkane precursors (measured by GC) and C$_x$H$_{2x-2}$O oxygenates measured in the Uintah basin during UBWOS. Panels a and b show the same ion masses. (c) Possible dehydration masses (C$_x$H$_{2x-4}$O) of the oxygenates shown in (a), measured in the Permian basin. (d) Possible dehydration masses of the oxygenates shown in (b), measured in the Uintah basin.
The smallest cycloalkane that exists in significant amounts in fossil fuels is cyclopentane (C5), but we might expect the C6 products to be more abundant because C6 precursors can be more abundant than C5 in oilfields (Simpson et al., 2010; Gilman et al., 2013). Additionally, OH reacts faster with substituted cycloalkanes (starting at C-6, methylcyclopentane) than unsubstituted cycloalkanes, although this probably has a smaller effect on ambient composition than the emissions composition (Calvert et al., 2008). Figure 4.11 also shows the cycloalkane precursors in the Uintah Basin, measured by GC techniques (Edwards et al., 2013; Edwards et al., 2014). The suggested oxygenated products have a similar distribution by carbon number. Data are not available from iWAS/GC-MS to show a similar precursor distribution for the Permian flight.

The C6 cycloalkane oxidation product (C6H10OH+) could be a ketone (methylcyclopentanone or cyclohexanone), or cyclopentyl aldehyde. Aldehyde ions often fragment in PTR-MS by loss of H2O (Buhr et al., 2002). The fragmentary product of C6H10OH+ dehydration, m/z 81.070 C6H8H+, was significantly enhanced and correlated with photochemical species. Similar ions (m/z 95.086 C7H10H+, m/z 109.101 C6H12H+, etc.) also correlated with photochemical species and may also be fragments of cycloalkyl aldehydes. These ion masses were also seen by the PTR-ToF-MS in Utah in 2013, and showed behavior consistent with photochemical species (Figure A4.4).

3.4.4 PAN and reactive nitrogen tracers

It has been previously reported that PTR-MS detects peroxy acetyl nitrate (PAN) at the protonated parent mass m/z 122.008 C2H3NO3H+, at m/z 77.023 C3H5O3H+, and at m/z 45.992 NO2+. Similarly, peroxy propionyl nitrate (PPN) is detected at m/z 91.039 C3H6O3H+ (Hansel and Wisthaler, 2000; de Gouw and Warneke, 2007; Kaser et al., 2013). However, m/z 77.023 may include contributions from another species such as acetone water cluster or peroxyacetic acid, and m/z 45.992 is not expected to be universally specific to PAN (de Gouw and Warneke, 2007; Kaser et al., 2013).

During the April 23 SONGNEX flight over the Permian, there was no peak detected at m/z 122.008 C2H3NO3H+. m/z 77.023 C3H5O3H+ and 91.039 C3H6O3H+ were detected at moderate and low intensities (4
ncps and 2 ncps average enhancement, respectively) and m/z 45.992 NO$_2^+$ was one of the most abundant ions detected (28 ncps average enhancement, similar to the average enhancement of benzene). M/z 77.023, m/z 91.039, and m/z 45.992 are compared to several independent measurements of reactive nitrogen: PAN, PPN, NO$_y$, NO$_y$-NO, and ethyl and propyl alkyl nitrates in Figure A4.6. When looking at all the SONGNEX flights, the slope of m/z 45.992 NO$_2^+$ versus NO$_y$-NO (which represents all NO$_x$ oxidation products, including PAN), and the slope of m/z 77.023 versus PAN, vary significantly between different environments. Figure 4.12 shows the relationship between m/z 77.023 and PAN. Comparison of m/z 45.992 NO$_2^+$ with PAN is included in the supplemental information (Figure A4.7). The slope of m/z 45.992 vs NO$_y$ depends on the composition of NO$_x$ (Figure A4.8a). The range of slopes probably depends on the atmospheric variability of NO$_x$, and not instrument conditions: the slope of m/z 77.023 vs PAN is not dependent on instrument conditions such as drift tube humidity (Figure A4.8b), which is consistent with behavior reported by Hansel and Wisthaler (2000).

These measurements suggest that these product ions cannot be attributed to PAN-type compounds only. Product ions at m/z 45.992 NO$_2^+$ almost certainly derive from a number of NO$_x$ species, with a range

Figure 4.12. Relationship between m/z 77.023 C$_2$H$_4$O$_3$H$^+$ measured by H$_3$O$^+$ ToF-CIMS and PAN.
of response factors; and there are probably at least two species that contribute to m/z 77.023 C₂H₄O₃H⁺.

3.5 Other compounds with heteroatoms

VOC emissions from oil and gas operations are distinctly different from other commonly studied sources (urban areas, forests) with respect to the presence of non-photochemical species containing nitrogen, sulfur, and oxygen heteroatoms. In this section I discuss cyclic nitrogen-containing species, H₂S, and two oxygenated species: methanol and m/z 71.049 C₄H₆OH⁺.

3.5.1 Cyclic organic nitrogen species

An especially interesting observation is the broad enhancement of several nitrogen-containing organic species during the Permian flights. The most clearly enhanced ion, m/z 70.065 C₄H₇NH⁺, has signal intensity approximately 15% that of m/z 93.070 C₇H₈H⁺, toluene (Figure 4.13).

C₄H₇N has several possible isomers, each with two degrees of unsaturation: a cyclic alkene structure (pyrroline) and several non-cyclic structures (C₄ nitriles). Using mass spectral context, I suggest a cyclic structure for this compound. Time series of the homologous series (CₙH₂ₙ₋₁NH⁺) including C₄H₇NH⁺ are shown in Figure 4.13. The species having one, two, and three carbon atoms are not enhanced above background, whereas species containing four or more carbon atoms are enhanced and correlated with aromatic compounds (Figure 4.13, Figure A4.9). A cyclic structure is the most likely explanation for this pattern. A similar argument can be made for the homologous series (CₙH₂ₙ₊₃NH⁺) having three degrees of unsaturation (pyrroles). The series with two (CₙH₂ₙ₊₁NH⁺, pyrrolidines) and four (CₙH₂ₙ₋₅NH⁺, pyridines) degrees of unsaturation were not significantly enhanced. Notably, m/z 84.081 C₅H₉NH⁺ had a different distribution than other cyclic nitrogen compounds during the April 23 flight, with high mixing ratios in the eastern and western parts of the field, and overall correlated better with the photochemically produced species. I speculate that this mass may include a fragment of a photochemical product, analogous to the interference with cycloalkanes discussed in section 3.2.2. Pyrroline (m/z 70.065) was enhanced by up to 200 pptv, and its concentration was typically comparable to C8 and C9 aromatics. Pyrrole (m/z 68.050) had a maximum enhancement of 40 pptv.
Figure 4.13. Time series of the homologous series of nitrogen-containing masses C<sub>n</sub>H<sub>2n-1</sub>NH<sup>+</sup> from n=2 to n=6 during the Permian basin flights on April 23, April 6, and April 9. Toluene and pyrrole are also shown. The y-axis is in units of normalized counts per second (instrument signal) for all ion masses (including toluene, C<sub>7</sub>H<sub>8</sub>H<sup>+</sup>). Ten-second box averages of all species are shown for clarity. Data collected during vertical profiles are included in these time series, to show low concentrations outside of the boundary layer. Right: some possible isomers for each mass. An example of a cyclic structure is given in the left column, and an example of a non-cyclic structure in the right column.
Organic nitrogen species detected over the Permian may have originated from the crude oil. American shale oils can contain upwards of 2% nitrogen by weight, and a number of aromatic organic nitrogen species have been quantified in crude oil (Morandi and Jensen, 1966; Holmes and Thompson, 1983; Mushrush et al., 1999; Williams and Chishti, 2001). Porphyrins, nitrogen-containing geochemical fossils derived from chlorophyll, are known to exist in crude oil and contain both pyrrole and pyrroline as subunits (Figure 4.14); aromatic nitrogen species may also form through chemical processes in the oil reservoir. There are large differences in nitrogen content and speciation between reservoirs, which could explain why these species were detected in some regions and not in others (Baxby et al., 1994; Li et al., 1995; Oldenburg et al., 2007).

The reactivity of pyrroline is not known. I analyzed the relative decrease in C₄H₇N in the western half of the field as a function of OH exposure (see section 3.1), and estimated the rate constant with OH to be in the range of (1.3-2.0)×10⁻¹¹ cm³ molecule s⁻¹ with a best estimate of 1.7×10⁻¹¹ cm³ molecule s⁻¹ (details in SI). Saturated nitriles have much slower reactivity with OH – reported values are around 2×10⁻¹⁴ cm³ molecule s⁻¹ (Harris et al., 1981; Atkinson et al., 2006) – so this high OH reactivity is further evidence that C₄H₇N is not a nitrile. A similar analysis of C₄H₅N gave a rate constant of 2.5×10⁻¹¹ cm³ molecule s⁻¹, which is much slower than the reported value for pyrrole (1×10⁻¹⁰ (Wallington, 1986)) but faster than butenenitrile (1.4×10⁻¹¹ (Grosjean and Williams, 1992)). The pyrrole analysis is much less certain than that of pyrroline, due to the overall lower signal and higher noise. The rate constants for pyrroline and especially pyrrole could be significantly underestimated. In previous work, it has been shown that for fast-reacting species, the derived rate constant was approximately constant and similar to the rate of the fastest-reacting aromatic used to calculate OH exposure (de Gouw et al., 2005). In my analysis, the fastest-reacting aromatic
considered was C10 aromatics, with a rate constant of \(2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule s}^{-1}\). This may explain why the derived rate constant for pyrrole was lower than expected.

Heterocycles are highly reactive with nitrate radicals, especially pyrrole (\(k=4.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)) (Atkinson et al., 1985; Cabañas et al., 2004). If pyrroline is similarly reactive, then nitrogen heterocycles could potentially dominate VOC nitrate reactivity in oil and gas fields, because most other VOCs measured during SONGNEX (aromatics and aliphatics) have low reaction rates with nitrate radicals (\(k \approx 10^{-18}-10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\)). A comparison of nitrate reactivity for species measured during SONGNEX, and a comparison to nitrate loss rates reported in the literature, are given in the supplementary information (Figure A4.10, Section A4.4). I looked for species with two nitrogen atoms, but at our instrument resolution, they are extremely difficult to separate from isobaric hydrocarbon species unless they have very high signal intensity.

### 3.5.2 Hydrogen sulfide

Measurement of \(\text{H}_2\text{S}\) with PTR-MS has been described by Li et al. (2014). The \(\text{H}_3\text{O}^+ \text{ToF-CIMS}\) improves on the instrument described by Li et al. (2014) as the high mass resolution avoids the isobaric background interference from isotopes of methanol and \(\text{HO}_2^+\). \(\text{H}_2\text{S}\) is detected at \(m/z\) 34.995 \(\text{H}_2\text{S}^+\) and was calibrated directly using a standard cylinder.

A comparison with the Picarro \(\text{H}_2\text{S}\) instrument is shown in Figure 4.15. There is good quantitative agreement between the two measurements. Compared to the Picarro instrument, the \(\text{H}_3\text{O}^+ \text{ToF-CIMS}\) \(\text{H}_2\text{S}\) measurement is more precise, and the 1s data are simultaneous with other \(\text{H}_3\text{O}^+ \text{ToF-CIMS}\) measurements, allowing easy comparison. The \(\text{H}_3\text{O}^+ \text{ToF-CIMS}\) \(\text{H}_2\text{S}\) measurement had a 3σ detection limit of 2.3 ppbv for a 1-s measurement (or 0.8 ppbv over the 6s measurement period of the Picarro instrument).

\(\text{H}_2\text{S}\) had a maximum concentration of 12.6 ppb during the April 23 Permian flight, comparable to butanes. No other sulfur-containing species measurable with the \(\text{H}_3\text{O}^+ \text{ToF-CIMS}\) were enhanced above an estimated 1s 3σ detection limit of 30 pptv. (A few sulfur-containing species, such as \(m/z\) 121.032 \(\text{C}_4\text{H}_8\text{SO}_2\text{H}^+\), have non-zero intensity but are instrument contaminants).
Figure 4.15. Scatterplot and time-series H₂S comparison between H₃O⁺ ToF-CIMS and Picarro CaRDS instruments.
(a) Scatterplot of H₃O⁺ ToF-CIMS vs Picarro H₂S for April 23 flight (Permian). Data points when the aircraft was ascending (red) and descending (blue) are highlighted. (b) Scatterplot of H₃O⁺ ToF-CIMS vs Picarro H₂S for April 4 flight (Haynesville). (c) Time series during the April 23 flight. The H₃O⁺ ToF-CIMS measurement has been averaged to a 6 second time basis. The Picarro H₂S is offset by 2 ppb (the intercept in panel a). The 1-s and 6-s detection limits for the H₃O⁺ ToF-CIMS are shown by dashed red lines.
3.5.3 Methanol

Methanol was the most abundant VOC detected by $\text{H}_2\text{O}^+$ ToF-CIMS during the April 23 Permian flight. In this section I discuss some possible sources.

Methanol is used by the oil and gas industry. Significant primary emissions, especially from produced water storage infrastructure and storage containers on wellpads, have been measured in the Uintah Basin (Warneke et al., 2014; Mansfield et al., 2016). Industry uses of methanol include addition at wellheads or further downstream in pipelines to prevent methane hydrate formation (Anderson and Prausnitz, 1986), to inhibit corrosion and scaling, as a lubricant, and as a solvent in other applications (Mansfield et al., 2016). A more detailed investigation of methanol sources is outside the scope of this chapter.

Globally, the dominant net source of methanol is direct biogenic emission, although there is a substantial and poorly constrained source from secondary production and oceans (Jacob et al., 2005; Millet et al., 2008). Primary biogenic emissions can explain the high mixing ratios over the Haynesville region, but not over the Permian, given the absence of other biogenic VOCs.

Lewis et al. (2005) calculated rates of photochemical production of methanol from a set of VOC precursors, the most important of which were methane, iso-butane, iso-pentane, and acetaldehyde. The magnitude of photochemical methanol production in the Permian was estimated by scaling the Lewis et al. precursor concentrations to the highest observed Permian VOC concentrations during the April 23 flight. Only 1-2 ppb of methanol would have formed after 2-3 days of aging – a small amount compared to the measured average 6 ppb and maximum 19 ppb. It should be noted that the Lewis et al. (2005) calculations were in the remote marine boundary layer and the photochemical production rate in the Permian could be different. Methanol does have a much stronger correlation with photochemical species than with primary aromatic species (Figure 4.7), but it also has a relatively long atmospheric lifetime.
3.5.4 M/z 71.049 C₄H₆OH⁺

M/z 71.049 C₄H₆OH⁺ is typically interpreted as the sum of methyl vinyl ketone (MVK) and methacrolein, two carbonyl products of isoprene oxidation (de Gouw and Warneke, 2007), but isoprene was too low to produce the measured amount of C₄H₆OH⁺ in the Permian Basin. C₄H₆OH⁺ had a spatial distribution that differed from photochemically produced species, including a much larger enhancement in the central part of the flight and several north-south oriented plumes running the length of the surveyed area (Figure 4.2). Additionally, C₄H₆OH⁺ was enhanced above what might be expected from the distribution of precursor species and the enhancements of similar oxygenates (Figure 4.11). The enhancement in the more aged area of the field suggests that a large part of this ion signal is generated by a photochemical species, but there may be other contributions. Using the H₃O⁺ ToF-CIMS average sensitivity factor for methyl vinyl ketone (MVK) and methacrolein, the maximum boundary-layer enhancement of this species was 540 pptv.

The other carbonyl isomer, crotonaldehyde, has been reported in biomass burning emissions (Karl et al., 2007), which were not evident during this flight. It is possible that MVK, methacrolein, or crotonaldehyde could be directly emitted by anthropogenic sources, or photochemically derived from a non-biogenic species. The cyclic isomer, dihydrofuran, is the oxygenated analogue of the nitrogen heterocycle (pyrrole) discussed in section 3.4.1. Dihydrofurans are known to be products of OH oxidation of alkanes (Lim and Ziemann, 2005).

Preliminary iWAS/GC-MS measurements show strong correlation between MVK, methacrolein, and m/z 71.049 C₄H₆OH⁺. The appropriate mass for dihydrofuran was not included in the selected-ion-scan window of the iWAS GC quadrupole MS. Other evidence is needed to identify the predominant isomer(s), and determine if there is a significant interference to PTR-MS measurements of biogenic MVK and methacrolein in oil and gas producing regions.
4. Conclusions

I have analyzed PTR-ToF-MS mass spectra from aircraft measurements over several US oil and gas producing regions. My analysis is supported by comparison to independent co-deployed instrumentation. I present a comparison between nine oil and gas basins of mixing ratios of aromatics, major secondary species, methanol, and hydrogen sulfide. In every basin, measurements from \( \text{H}_3\text{O}^+ \) ToF-CIMS were dominated by small oxygenated compounds, especially C2-C4 photochemical products and methanol. Significant classes of hydrocarbon compounds detected included aromatics, cycloalkanes, and alkanes. The \( \text{H}_3\text{O}^+ \) ToF-CIMS measurements of aromatics, methanol, and \( \text{H}_2\text{S} \) agreed with independent measurements while methylcyclohexane and reactive nitrogen differed from independent measurement.

Between basins, there was large variation in the observed mixing ratios of aromatics, \( \text{H}_2\text{S} \), and methanol. In every basin, narrow, highly concentrated plumes with high mixing ratios of aromatics were measured, and average mixing ratios in many basins were comparable to concentrations observed downwind of large metropolitan areas. However, the profile of aromatics is different from that in urban air. I demonstrated the ability of \( \text{H}_3\text{O}^+ \) ToF-CIMS to detect hydrogen sulfide, and measured significantly enhanced \( \text{H}_2\text{S} \) in the Permian and Haynesville regions. Methanol was the single most abundant VOC observed by \( \text{H}_3\text{O}^+ \) ToF-CIMS and may have industrial sources.

Compared to the variability in aromatics, methanol, and \( \text{H}_2\text{S} \), photochemical compounds had similar mixing ratios in each basin. Additionally, the abundances of most oxygenates relative to acetone were similar between basins. This profile was also quite similar to that measured during a flight over the Los Angeles urban area during CALNEX 2010. The most highly variable compound was acetic acid, which can include primary emission from agriculture, especially in the Denver-Julesburg Basin.

The Permian Basin had the highest overall mixing ratios of all species reported here. This region is the largest oil field in the United States but has not been studied extensively from an air quality perspective. I conducted a detailed investigation of mass spectra recorded over Permian Basin. There are likely many chemically significant species, measureable by PTR-MS, in the atmosphere that are not currently routinely
reported. This includes both primary species such as pyrroline and early-generation secondary species, such as the oxidation products of cycloalkanes. Pyrroline (m/z 70.065, C₄H₇NH⁺) is especially interesting because it has not been previously reported as a VOC associated with oil and gas emissions, and may account for a substantial fraction of nitrate reactivity. The C₁₀H₁₆ measurement, which is most likely adamantane or an unusual monoterpane, indicates the presence of larger (C₁₀+) hydrocarbons emitted from oil and gas operations, which are currently underexplored in the literature. The most important aromatic oxidation product detected was benzaldehyde; other products, including phenol and two unidentified oxygenates, were present at much smaller concentrations. Several ion masses that could be cycloalkane oxidation products were detected. Finally, I report several new interpretations of PTR-MS ion masses previously described in the literature.
Chapter 5. Evaluation of NO$^+$ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds

Abstract

In the previous chapter, one serious limitation of the H$_3$O$^+$ ToF-CIMS measurements was that the H$_3$O$^+$ chemical ionization method did not allow chemically specific measurement of particular groups of compounds, such as alkanes and cyclic alkanes. NO$^+$ chemical ionization mass spectrometry (NO$^+$ CIMS) can achieve fast (1-Hz and faster) on-line measurement of trace atmospheric volatile organic compounds (VOCs) that cannot be ionized with H$_3$O$^+$ ions (e.g. in a PTR-MS or H$_3$O$^+$ CIMS instrument). Here I describe the adaptation of a high-resolution time-of-flight H$_3$O$^+$ CIMS instrument to use NO$^+$ primary ion chemistry. I evaluate the NO$^+$ technique with respect to compound specificity, sensitivity, and VOC species measured compared to H$_3$O$^+$. The evaluation is established by a series of experiments including laboratory investigation using a gas-chromatography (GC) interface, in-situ measurement of urban air using a GC interface, and direct in-situ measurement of urban air. The main findings are that (1) NO$^+$ is useful for isomerically resolved measurements of carbonyl species; (2) NO$^+$ can achieve sensitive detection of small (C4-C8) branched alkanes, but is not unambiguous for most; and (3) compound-specific measurement of some alkanes, especially iso-pentane, methylpentanes, and high mass (C12-C15) n-alkanes, is possible with NO$^+$. I also demonstrate fast in-situ chemically specific measurements of C12 to C15 alkanes in ambient air.


1. Introduction

Volatile organic compounds (VOCs) are central to the formation of ozone and secondary organic aerosol (SOA), and can have direct human health effects. Understanding the behavior of these species in
the troposphere presents several measurement challenges (Glasius and Goldstein, 2016). First, VOCs are highly chemically diverse. Second, many environmentally important species require measurement precision of better than 100 parts-per-trillion (pptv). Finally, numerous applications, such as eddy flux analyses or sampling from a mobile platform, require fast in-situ measurements, with 1 minute or faster time resolution.

$\text{H}_3\text{O}^+$ chemical ionization mass spectrometry ($\text{H}_3\text{O}^+$ CIMS), more commonly known as proton-transfer-reaction mass spectrometry (PTR-MS), is a well-established approach to measuring VOCs (de Gouw and Warneke, 2007; Jordan et al., 2009b). In $\text{H}_3\text{O}^+$ CIMS, air is mixed with hydronium ($\text{H}_3\text{O}^+$) ions in a drift tube region. VOCs are ionized by transfer of the proton from $\text{H}_3\text{O}^+$ to the VOC. These instruments are capable of VOC measurements that are fast, sensitive, and chemically detailed (Jordan et al., 2009b; Graus et al., 2010; Sulzer et al., 2014; Yuan et al., 2016a).

Despite these advantages, $\text{H}_3\text{O}^+$ CIMS has several limitations related to the reagent ion chemistry. For one, this technique generally cannot distinguish between isomers. For instance, this is a significant limitation when measuring aldehyde and ketone carbonyl isomers, which have very different behavior in the atmosphere. Separation of propanal and acetone with PTRMS has been explored using collision-induced dissociation with an ion-trap mass analyzer, but this technique negatively affects the instrument time resolution and sensitivity (Warneke et al., 2005). Additionally, some proton transfer reactions are dissociative. Large hydrocarbons (C8 and larger) fragment into common small masses, making spectra difficult to interpret (Jobson et al., 2005; Erickson et al., 2014; Gueneron et al., 2015). Alcohols and aldehydes can lose H$_2$O, lowering the sensitivity to the protonated parent mass; their product ion masses then coincide with those of hydrocarbons, making independent measurement difficult (Španěl et al., 1997; Buhr et al., 2002). Furthermore, $\text{H}_3\text{O}^+$ CIMS is not sensitive to small (~C8 and smaller) saturated alkanes, as their proton affinities are lower than or very close to that of water (Arnold et al., 1998; Gueneron et al., 2015). This is a serious limitation in studies of urban air or emissions from oil and natural gas extractions, where small alkanes can contribute a large fraction to the total gas phase carbon and chemical reactivity (Katzenstein et al., 2003; Gilman et al., 2013). Chemically specific, fast measurement of alkanes
and cyclic alkanes would have been especially valuable during the SONGNEX 2015 campaign described in Chapter 4, for example. Gas chromatography techniques avoid many of these limitations, but have much slower time resolution.

Use of NO$^+$ reagent ion chemistry may address some of the limitations of H$_3$O$^+$. Reaction of NO$^+$ with various VOCs has been extensively studied using selected-ion flow tube methods (SIFT-MS). SIFT methods use a quadrupole mass filter in between the ion source and ion-molecule reactor, which provides a very pure reagent ion source but limits the primary ion signal. SIFT studies have identified the major products of the reaction of NO$^+$ with VOCs representative of many different functional groups (Španěl and Smith, 1996, 1998a, b, 1999; Španěl et al., 1997; Arnold et al., 1998; Francis et al., 2007a; Francis et al., 2007b). Aldehydes and ketones are easily separable: ketones cluster with NO$^+$, forming mass ($m+30$) ions, whereas aldehydes react by hydride abstraction, forming mass ($m-1$) ions (where $m$ is the molecular mass of the species). Rather than losing H$_2$O, as in H$_3$O$^+$ CIMS, alcohols react by NO$^+$ adduct formation or hydride abstraction. And finally, NO$^+$ can be used to detect alkanes: small (>C4) branched alkanes and large (>C8) n-alkanes react by hydride abstraction, forming mass ($m-1$).

The application of SIFT methods to atmospheric analysis has been limited by relatively poor sensitivity (Smith and Španěl, 2005; Francis et al., 2007b; de Gouw and Warneke, 2007); although better sensitivities have been reported in recent years (Prince et al., 2010). The adaptation of an existing CIMS instrument to use the SIFT technique requires extensive instrument modification or the purchase of an external SIFT unit (Karl et al., 2012). Several groups have experimented with low-cost adaptation of H$_3$O$^+$ CIMS instruments to use NO$^+$ chemistry. Knighton et al. (2009) adapted an H$_3$O$^+$ CIMS instrument to measure 1,3-butadiene and demonstrated in-situ detection of this species in the atmosphere. Jordan et al. (2009a) have developed a hollow-cathode ion source capable of switchable reagent ion chemistry, and demonstrated laboratory measurement with NO$^+$ of several aromatics, chlorinated aromatics, and carbonyls, with sensitivities comparable to H$_3$O$^+$ CIMS. The NO$^+$ capability of the Jordan et al. instrument has been used in the laboratory by Inomata et al. (2013b) to investigate detection of n-tridecane and by Agarwal et
al. (2014) to measure picric acid, and by Liu et al. (2013) to investigate the behavior of MVK and methacrolein in a reaction chamber.

These studies suggest that an easy, low-cost adaptation of H$_3$O$^+$ CIMS instruments to NO$^+$ chemistry could greatly enhance our capability to measure VOCs in the atmosphere. However, the number of VOC species investigated to-date is small and few field measurements have been reported. The ability of a modified H$_3$O$^+$ CIMS instrument to separate carbonyl isomers in ambient air, and to measure small alkanes both in the laboratory and in ambient air, has not been evaluated. Finally, the lack of fragmentation of n-tridecane reported in Inomata et al. (2013b) is intriguing, but the use of an NO$^+$ CIMS instrument to measure similar high-mass alkanes in ambient air has not been demonstrated.

Here I evaluate the adaptation of an H$_3$O$^+$ CIMS instrument to use NO$^+$ reagent ion chemistry. I provide specifics on instrument set-up and operating parameters. I report the sensitivity and spectral simplicity of NO$^+$ CIMS, relative to H$_3$O$^+$ CIMS, for nearly 100 atmospherically relevant VOCs, including a wide range of functional groups, and provide product ion distributions for several representative compounds. I demonstrate, interpret, and evaluate measurements of separate aldehyde and ketone isomers, light alkanes, and several other species in ambient air. Finally, I investigate measurement of high-molecular-mass alkanes using NO$^+$. I extend the laboratory analysis of high-mass alkanes to C12-C15 n-alkanes and demonstrate fast, in-situ measurement of these species in ambient air.

2. Methods

2.1 Instrumentation

Two separate H$_3$O$^+$ CIMS instruments (referred to hereafter as PTR-QMS and H$_3$O$^+$ ToF-CIMS) were adapted to NO$^+$ chemistry in this work. Both instruments consist of (1) a hollow cathode reagent ion source, (2) a drift tube reaction region, (3) an ion transfer stage that transports from the drift tube to the mass analyzer and allows differential pumping, and (4) a mass analyzer. Both instruments have nearly identical hollow cathode ion sources and drift tube reaction regions, described in detail in de Gouw and Warneke (2007). The PTR-QMS (Ionicon Analytik) uses ion lenses to transfer ions from the drift tube to a
unit-mass-resolution quadrupole mass analyzer (Pfeiffer). This instrument is the same instrument used for the work described in Chapter 2, and is described further by de Gouw and Warneke (2007). The H$_3$O$^+$ ToF-CIMS uses RF-only segmented quadrupole ion guides to transfer ions from the drift tube to a time-of-flight mass analyzer with a mass resolution of 4000-6000 produced by Aerodyne Research Inc. / Tofwerk (Bertram et al., 2011). This instrument has been described in Chapter 3. A similar PTR-ToF instrument using quadrupole ion guides has also been recently described (Sulzer et al., 2014). ToF-CIMS data were analyzed using Tofware high-resolution peak-fitting software (Aerodyne Research Inc/ Tofwerk AG). A description of the algorithm is given in DeCarlo et al. (2006).

A gas chromatograph (GC) instrument was used both as an interface to the ToF-CIMS and as a separate instrument using an electron-impact quadrupole mass spectrometer. The GC collects VOCs in a liquid nitrogen cryotrap for a 5 minute period every 30 minutes. VOCs are then injected onto parallel Al$_2$O$_3$/KCl PLOT and semi-polar DB-624 capillary columns to separate C2-C11 hydrocarbons and heteroatom-containing VOCs. When used as an interface to the ToF-CIMS, the column eluant was directed to the inlet of the ToF-CIMS, where it was diluted with 50 sccm of clean air with controlled humidity. When operated as a separate instrument, the column eluant was directed to an electron-ionization quadrupole mass spectrometer (EIMS) operated in selected-ion mode. The response of this GC-EIMS instrument to various VOCs has been well characterized over a long period of field and laboratory applications, and further operational details have been reported elsewhere (Goldan et al., 2004;Gilman et al., 2010;Gilman et al., 2013).

### 2.2 Adaptation of H$_3$O$^+$ to NO$^+$ CIMS.

Ideally, both H$_3$O$^+$ and NO$^+$ reagent ion chemistry can be utilized with a single instrument. The fewest possible number of hardware parameters were changed to facilitate fast switching and instrument stability.

To achieve generation of NO$^+$ ions, the water reservoir was replaced with ultra-high purity air. The source gas flow (5 sccm), the hollow cathode parameters, and the drift tube operating pressure (2.4mbar)
were not changed. To optimize the generation of NO$^+$ ions relative to H$_3$O$^+$, O$_2^+$, and NO$_2^+$, and the generation of the desired VOC$^+$ ion products, the voltages of the intermediate chamber plates, $V_{IC1}$ and $V_{IC2}$, and the drift tube voltage $V_{DT}$ were adjusted. An instrument schematic showing the locations of $V_{IC1}$, $V_{IC2}$, and $V_{DT}$ can be found in the supplementary information (Figure A5.1). Optimization was performed sampling dry air.

It has been demonstrated that the quadrupole ion guides of the ToF-CIMS can significantly change the measured distribution of reagent and impurity ions (Yuan et al., 2016a). The PTR-QMS does not have that issue as strongly (modeled and measured cluster distributions are largely similar, as discussed by de Gouw and Warneke (2007)) and therefore we explored the effect of $V_{IC1}$, $V_{IC2}$, and $V_{DT}$ on reagent ion distribution using the PTR-QMS. As the PTR-QMS and ToF-CIMS have nearly identical ion source and drift tube design, we assume that ion behavior in these regions is the same for the two instruments.

First, $V_{DT}$ was held constant at 720 V (the original setting of the PTR-QMS instrument), and $V_{IC1}$ and $V_{IC2}$ were varied (Figure 5.1). The settings of $V_{IC1}$ (140 V) and $V_{IC2}$ (80 V) were selected as a compromise between high NO$^+$ ion count rate and low impurity ion count rates. The major impurity ions are H$_3$O$^+$, O$_2^+$, and NO$_2^+$, and it is desirable to limit the formation of these ions because they react with VOCs, complicating the interpretation of spectra. Next, several VOCs with different functional groups were introduced into the instrument, separately, and the drift tube electric potential scanned. A drift tube voltage of 350 V (electric field intensity relative to gas number density $E/N = 60$ Td) was selected to compromise between maximizing NO$^+$ ion count rate, minimizing H$_3$O$^+$, O$_2^+$, and NO$_2^+$, maximizing VOC ion count rates, minimizing alkane fragmentation, and promoting different product ions for carbonyls and aldehydes (Figure 5.2). This setting results in about $10 \times 10^6$ cps of NO$^+$ primary ions, while in typical PTR-MS settings we achieve about $30 \times 10^6$ cps of H$_3$O$^+$ primary ions.

We note that the $E/N$ of 60 Td used for the NO$^+$ CIMS is much lower than that used in typical PTRMS settings (circa 120 Td). In air, NO$^+$ will react with water to produce H$_3$O$^+$ and HNO$_2$ (Fehsenfeld et al., 1971). The electric field in the drift tube limits the formation of the NO$^+$ (H$_2$O)$_n$ intermediaries in this
reaction, promoting high NO\(^+\) count rates and VOC sensitivity. In PTRMS, the drift field is used to prevent the formation of analogous H\(_3\)O\(^+\) (H\(_2\)O)\(_n\) clusters. The bond energy of H\(_3\)O\(^+\) (H\(_2\)O)\(_n\) clusters is significantly higher than that of NO\(^+\) (H\(_2\)O)\(_n\) clusters (Keesee and Castleman, 1986), hence the need for a higher E/N in PTRMS settings.

The remainder of the work detailed in this manuscript was performed using the ToF-CIMS with the settings as described here. The ToF-CIMS has the advantages of high mass resolution, fast time resolution, and simultaneous measurement of all masses. Further small adjustments were made to the ToF-CIMS quadrupole ion guide voltages using Thuner software (Tofwerk AG) to promote sensitivity to VOCs and separate carbonyl isomers. The two most important such adjustments decreased the electric potentials immediately upstream of each quadrupole ion guide (Figure A5.2). These adjustments reduced declustering at these locations, which improved the transmission of VOC NO\(^+\) clusters. In this chapter, all work with the ToF-CIMS instrument was conducted with the small segmented quadrupole (SSQ). (The SSQ was removed before the work described in Chapter 6; after the removal of the SSQ, the BSQ voltages were re-tuned and the NO\(^+\) CIMS response to VOCs was checked for consistency with the un-modified instrument).

Figure 5.1. Dependence of NO\(^+\), H\(_3\)O\(^+\), NO\(_2\)\(^+\), and O\(_2\)\(^+\) on intermediate chamber voltages.
The arrow denotes the selected operating conditions. Experiment conducted in dry air (H\(_3\)O\(^+\) is from residual water in the instrument and in commercial ultrazero air.)
Figure 5.2. VOC and primary product ion dependence on drift tube voltage. Traces are labeled by the nominal product ion m/z in Th. (a) Methyl vinyl ketone. (b) Methacrolein. (c) 2,2-dimethylbutane. (d) Methylcyclohexane. (e) Primary ions and clusters. The dashed line indicates the selected operating voltage. Experiment conducted in dry air (H$_3$O$^+$ is from residual water in the instrument and in commercial ultrazero air.)
3. Results and Discussion

3.1 Laboratory experiments

3.1.1 Sensitivity and simplicity of the NO$^+$ reagent ion chemistry

VOCs from several calibration cylinders (VOCs listed in Table A5.1) were diluted with high purity air to mixing ratios of approximately 10 ppbv, and introduced into the sampling inlet of the GC interface. Eluant from the column was directed into the ToF CIMS as described above. A relative humidity of 20% was used for this experiment. This humidity condition is similar to that expected for ambient measurements discussed in Section 3.2; this condition was chosen to aid interpretation of ambient air data. Humidity effects are discussed in Section 3.1.5. Several species co-elute with another compound (m- and p- xylenes; myrcene and camphene; 1-ethyl,3-methylbenzene and 1-ethyl,4-methylbenzene); reported sensitivities and product ions are an average of the two co-eluting species.

Each VOC mixture was sampled twice, once with H$_3$O$^+$ and once with NO$^+$ reagent ion chemistry and instrument settings. Based on the results we evaluated the utility of NO$^+$ CIMS relative to H$_3$O$^+$ CIMS using two metrics. The first metric is sensitivity for individual VOCs. To determine the sensitivity ($S$), the signals (counts per second) of all product ions were integrated over the width of the chromatographic peak and sensitivities for the measured VOCs using NO$^+$ chemistry were calculated relative to the sensitivity using H$_3$O$^+$ chemistry ($S_{NO^+}/S_{H3O^+}$). For several VOCs, we also calculated the relative sensitivity if only the most abundant product ion (the quantitation ion) is measured. Because only one concentration was sampled, this metric relies on sensitivity being linear with concentration. Linear sensitivity is a reasonable assumption for the NO$^+$ and H$_3$O$^+$ ToF-CIMS because separate multiple-point calibrations for select VOCs showed a linear response (Section 3.1.4, Figure A5.3), H$_3$O$^+$ CIMS has demonstrated linear sensitivity over a wide range of concentration (de Gouw and Warneke, 2007; Sulzer et al., 2014; Yuan et al., 2016a), and the NO$^+$ CIMS agrees well with an independent technique over a range of atmospheric concentrations (Section 3.2.2).
The second metric is the simplicity of spectra. In an ideal instrument, each VOC would produce only one product ion, and each ion mass would be produced by only one VOC. However, using NO\(^+\) and H\(_3\)O\(^+\) reagent ions, fragmentation of product ions does occur. As a metric for the complexity of the product ion distribution resulting from particular VOCs, we determined the fraction of the most abundant ion to the total signal from this VOC (\(F\)) and discuss (\(F_{\text{NO}^+}\)) relative to (\(F_{\text{H}_3\text{O}^+}\)). Figure A5.4 contains a comparison of \(F_{\text{NO}^+}\) and \(F_{\text{H}_3\text{O}^+}\), and an example product ion distribution. A larger value of this ratio means that NO\(^+\) reagent ion chemistry creates a simpler product ion distribution for that particular VOC. This metric does not indicate whether a particular product ion is produced by only one VOC. Uniqueness of product ions is discussed in Sect. 3.1.2. The NO\(^+\) CIMS product ion distributions of 25 atmospherically relevant VOCs are reported in Table 2.

Figure 5.3 summarizes the comparison between NO\(^+\) and H\(_3\)O\(^+\) reagent ion chemistry for the two metrics. On the y-axis the spectrum simplicity metric and on the x-axis the sensitivity metric are shown.

Figure 5.3. Comparison of production ion distribution and sensitivity of VOCs using NO\(^+\) and H\(_3\)O\(^+\) reagent ion chemistry, at a relative humidity of 20%.
Branched alkanes and most cyclic alkanes are detected with far greater sensitivity using NO\textsuperscript{+} chemical ionization than with H\textsubscript{3}O\textsuperscript{+} chemical ionization. Aromatics and alkenes are detected slightly more sensitively, and, on average, ketones are detected slightly less sensitively. Alcohols are detected more sensitively, by at least a factor of two, with the exception of methanol. The lower sensitivity to methanol is consistent with slower reaction kinetics reported in the literature (Španěl and Smith, 1997). Monoterpenes and acetonitrile are detected substantially less sensitively.

In comparing the simplicity of the product ion distribution between H\textsubscript{3}O\textsuperscript{+} and NO\textsuperscript{+} chemistry, most branched and cyclic alkanes, ketones, and monoterpenes have a higher fraction of signal on a single product ion (simpler spectra). I also highlight that many alkyl substituted aromatics fragment substantially with H\textsubscript{3}O\textsuperscript{+} chemistry but do not with NO\textsuperscript{+} chemistry. The few exceptions (notably, benzene) create more complicated spectra because an NO\textsuperscript{+} cluster product is also present (m+30).

### 3.1.2 Distribution of product ions

It is somewhat more difficult to predict the ionized VOC products of NO\textsuperscript{+} CIMS compared to H\textsubscript{3}O\textsuperscript{+} CIMS, because NO\textsuperscript{+} has three common reaction mechanisms: charge transfer, hydride abstraction, and cluster formation. Groups of VOCs that have similar charge transfer and hydride abstraction enthalpies tend to react with similar ionization mechanisms (Figure 5.4). Figure 5.4 uses thermodynamic information from Lias et al. (1988), and mechanistic information from this work (see Table A5.1 for a list of species) and from SIFT studies (Španěl and Smith, 1996, 1998a, b, 1999;Španěl et al., 1997;Arnold et al., 1998;Francis et al., 2007a;Francis et al., 2007b). Charge transfer occurs if the reaction enthalpy is favorable, regardless of the hydride transfer enthalpy. If the charge transfer enthalpy is close to zero, then NO\textsuperscript{+} clustering occurs; and if charge transfer is not favorable but hydride transfer is, then hydride transfer will occur. In terms of VOC families, this means that carbonyls participate in two mechanisms: ketones cluster with NO\textsuperscript{+}, and aldehydes hydride transfer. Branched alkanes exclusively undergo hydride transfer. Aromatics undergo charge transfer and benzene also clusters; alcohols undergo hydride transfer, and alkenes charge transfer, cluster, or hydride transfer depending on the size of the molecule and the location of the double bond.
VOC identification is indicated by the small numbers and is listed in Table 5.1. Hydride abstraction enthalpies for ketones are not known, but can be assumed to be positive based on structural considerations (lack of tertiary hydrogen). Ion thermodynamic information is available for several species whose reaction mechanism was not experimentally verified in this or previous work; an expected mechanism was determined by analogy with a VOC of similar structure:

17 1-butanol; by analogy with 1-propanol.
18 2-methylpropanol; by analogy with 1-propanol.
19 2-butanol; by analogy with 2-propanol.
20 1,4-pentadiene; by analogy with isoprene.
34 4-methyl-2-pentene; by analogy with 2-pentene.
35 3-methyl-1-pentene; by analogy with 1-hexene.
36 2,3-dimethyl-1-butene; by analogy with iso-butene.
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Table 5.1. VOC species in Figure 5.4 and their charge transfer and hydride transfer reaction enthalpies.

Although Figure 5.4 provides a general way to predict the possible mechanisms for a particular VOC, it provides no information about the distribution of the signal between different mechanisms or the degree of fragmentation. The distribution depends strongly on instrumental conditions, which include E/N settings in the ion-molecule reaction region (by far the most important effect), fragmentation and clustering in the ion optics, presence of impurity ions such as O₂⁺ from the converted hollow cathode ion source, and relative humidity (Section 3.1.5).
In Figure 5.5 the product ion distributions of several VOCs determined in this work are compared to three others using NO\(^+\). Studies by the University of Leicester used a much higher E/N ratio in the drift tube, leading to higher fragmentation and lower NO\(^+\) adduct formation compared to this work (Wyche et al., 2005; Blake et al., 2006). Investigation of higher-mass alkanes by Yamada et al. (2015) used similar E/N, but achieved lower contaminant O\(_2^+\), which is a likely explanation for the higher degree of fragmentation of tridecane seen in this work. In SIFT-MS studies, without an electric field, fragmentation is minimized and preselection of NO\(^+\) primary ions eliminates contaminant H\(_3^+\)O\(^+\) and O\(_2^+\) and therefore SIFT product ion distributions are generally simpler. These differences highlight the importance of selection of drift tube operating conditions and instrument characterization.

![Comparison of product ion distributions between four sets of instrumental and environmental conditions.](chart.png)

<table>
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<tr>
<th>Ions</th>
<th>Study</th>
<th>E/N</th>
<th>H(_2)O</th>
<th>O(_2^+)</th>
</tr>
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<tr>
<td>charge transfer</td>
<td>this work</td>
<td>60</td>
<td>20% RH</td>
<td>4% of NO(^+)</td>
</tr>
<tr>
<td>NO(^+) adduct</td>
<td>SIFT-MS</td>
<td>N/A</td>
<td>0</td>
<td>0</td>
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<tr>
<td>hydride abstraction</td>
<td>U. of Leicester 148-165</td>
<td>residual</td>
<td>negligible</td>
<td></td>
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<tr>
<td>residual H(_3)O(^+) product</td>
<td>NIES/NTSEL Japan 67</td>
<td>0</td>
<td>1.5% of NO(^+)</td>
<td></td>
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</table>

Figure 5.5. Comparison of product ion distributions between four sets of instrumental and environmental conditions. 

a. Španěl and Smith (1998a); b. Blake et al. (2006); c. Španěl et al. (1997); d. Wyche et al. (2005); e. Yamada et al. (2015)
3.1.3 Alkane fragmentation

Small (C4-C10) branched alkanes cannot be measured by H$_3$O$^+$ CIMS. With NO$^+$ CIMS, these VOCs are detectable but generally fragment to produce several ionic fragments that are common to different species. These masses (for example, m/z 57 C$_4$H$_9^+$) are produced by many different compounds and are likely not useful for chemically resolved atmospheric measurements. A few masses (e.g. m/z 71 C$_5$H$_{11}^+$ and m/z 85 C$_6$H$_{13}^+$) are only produced by a few compounds and were therefore targeted for further investigation in ambient air measurements. Conversely, cyclic alkanes fragment very little. Figure A5.5 shows the product ion distributions of several representative aliphatic compounds. We note that the major product ions of cyclic alkanes (M-H) are the same with H$_3$O$^+$ and with NO$^+$ chemistry. However, the mechanism is different: NO$^+$ ionizes by hydride abstraction, while H$_3$O$^+$ ionizes by protonation followed by loss of H$_2$ (Midey et al., 2003). The H$_3$O$^+$ ionization mechanism has a secondary channel consisting of protonation followed by elimination of CH$_4$ or C$_n$H$_{2n}$ (Midey et al., 2003). The difference in ionization mechanism is a likely explanation for the lower degree of fragmentation observed using NO$^+$ chemistry.

Compared to small (C8 and smaller) alkanes, large (C12 and higher) n-alkanes show little fragmentation, with at least 50% of the total ion signal accounted for by the expected parent mass (m-l) (Figure 5.6). Additionally, the degree of fragmentation decreases with increasing carbon chain length. It is quite difficult to measure these compounds with H$_3$O$^+$ CIMS because they fragment extensively and are not detected sensitively (Erickson et al., 2014). NO$^+$ CIMS could provide a fast, sensitive, chemically specific measurement of these compounds. It should be mentioned that large n-alkanes (C10 and larger) are not measureable with the GC interface. Dodecane (C$_{12}$H$_{26}$), tridecane (C$_{13}$H$_{28}$), tetradecane (C$_{14}$H$_{30}$), and pentadecane (C$_{15}$H$_{32}$) were sampled directly with the NO$^+$ ToF-CIMS and product ions were identified by correlation with the expected major product ion (m-l). The NO$^+$ ToF-CIMS sensitivity to pentadecane was determined using a permeation source (Veres et al., 2010). Contaminant O$_2^+$ could potentially reduce the measured parent ion ([M-H]+) through fragmentation; an alkane measurement corrected for O$_2^+$ interference would have higher sensitivity and a simpler product ion distribution (eg. Yamada et al. (2015)).
3.1.4 Instrument response factor for select compounds

A calibration factor was determined for various VOCs by (1) direct calibration, (2) estimation from sensitivity relative to H$_3$O$^+$ CIMS, or (3) estimation from correlation with GC-EIMS (Table 5.2). Direct calibrations were performed by mixing a known concentration of a VOC from either a permeation cell (pentadecane) or a calibration gas cylinder (other VOCs) into an ambient humidity (~20%) high-purity air dilution stream. Calibration factors estimated from sensitivity relative to H$_3$O$^+$ CIMS were calculated using H$_3$O$^+$ ToF-CIMS calibration factors and results from laboratory GC-CIMS experiments (Sect. 3.1.1). Calibration factors for H$_3$O$^+$ ToF-CIMS were determined in previous work (Yuan et al., 2016a).

Figure 5.6. Large (C12-C15) n-alkane product ion distribution, using relative humidity of 20%. The expected largest mass resulting from hydride abstraction (m-1) is highlighted in red. N-octane (C8) is shown for comparison.
Table 5.2. Sensitivities and detection limits of NO\textsuperscript{+} ToF-CIMS for VOCs. Product ions not used to establish sensitivity are listed in gray text. The H\textsubscript{3}O\textsuperscript{+} ToF-CIMS detection limits in the farthest right column are from Chapter 3. * Product from residual H\textsubscript{3}O\textsuperscript{+}. † Both product ions can be unambiguously assigned to benzene. We therefore report also the counting statistics and limit of detection for the sum of the two ions. ‡ For technical reasons, pentadecane sensitivity was determined in dry air.

<table>
<thead>
<tr>
<th>VOC species</th>
<th>Ion formula (% of total signal)</th>
<th>NO\textsuperscript{+} sensitivity (cps/ppb)</th>
<th>NO\textsuperscript{+} detection limit (ppb)</th>
<th>H\textsubscript{3}O\textsuperscript{+} CIMS 1s detection limit (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>CH\textsubscript{3}ONO\textsuperscript{+} M+NO\textsuperscript{+} 12% 62.024 0.7 0.07</td>
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<td>0.397 ppb</td>
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<tr>
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<td>CH\textsubscript{3}OH\textsuperscript{**} M+H\textsuperscript{+} 49% 33.034 1.23 0.67</td>
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<tr>
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<tr>
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<td>CH\textsubscript{3}O\textsubscript{2}+ M+H\textsubscript{3}O\textsuperscript{+} 8% 60.044</td>
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<tr>
<td>Acetotinirile</td>
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<td>45 ppt</td>
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<td>C\textsubscript{6}H\textsubscript{5}NH\textsuperscript{**} M+H\textsuperscript{+} 44% 42.034</td>
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<tr>
<td></td>
<td>C\textsubscript{6}H\textsubscript{5}NO\textsuperscript{**} M+H\textsubscript{3}O\textsuperscript{+} 8% 60.044</td>
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<td>C\textsubscript{10}H\textsubscript{12} fragment 3% 127.148</td>
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<td>C\textsubscript{10}H\textsubscript{12} fragment 3% 141.164</td>
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<td>C\textsubscript{10}H\textsubscript{12} fragment 3% 113.132</td>
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### Table 5.2 (continued)

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<th>Mechanism</th>
<th>(% of total signal)</th>
<th>Exact m/z (Th)</th>
<th>Relative (NO^+cps/ H_3O^+cps)</th>
<th>Background cps</th>
<th>Noise scale factor α</th>
<th>NO^+ sensitivity (ncps/ppb)</th>
<th>NO^+ detection limit</th>
<th>H_3O^+ 1-s detection limit</th>
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<td>100.039</td>
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<td>C_5H_10OH^+</td>
<td>M+H^+</td>
<td>7%</td>
<td>87.08</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
<td>C_10H_16^+</td>
<td>M^+</td>
<td>59%</td>
<td>136.125</td>
<td>0.28</td>
<td>0.39</td>
<td>1.69</td>
<td>7.3</td>
<td>73</td>
<td>233 ppt</td>
</tr>
<tr>
<td></td>
<td>C_7H_8^+</td>
<td>fragment</td>
<td>24%</td>
<td>92.062</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C_7H_9^+</td>
<td>fragment</td>
<td>11%</td>
<td>93.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C_10H_16H^++</td>
<td>M+H^+</td>
<td>7%</td>
<td>137.132</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
C. Sensitivity estimated via correlation with GC-EIMS; ambient (20%) relative humidity

<table>
<thead>
<tr>
<th>VOC species</th>
<th>Ion formula ( % of total signal)</th>
<th>Exact m/z (Th)</th>
<th>Correlation with GC (R²)</th>
<th>Background cps</th>
<th>Noise scale factor α</th>
<th>NO⁺ sensitivity (ncps/ppb)</th>
<th>NO⁺ sensitivity (cps/ppb)</th>
<th>1-s detection limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanal</td>
<td>C₃H₅O⁺, C₃H₅O₂⁺, C₃H₅OH⁺⁺</td>
<td>M-H, M-H+H₂O, M+H⁺</td>
<td>57.033, 75.044, 59.049</td>
<td>0.928, 11</td>
<td>1.40</td>
<td>170, 1057</td>
<td>26 ppt</td>
<td></td>
</tr>
<tr>
<td>Methacrolein +</td>
<td>C₅H₁₀O⁺, C₅H₁₀ONO⁺, C₅H₉⁺</td>
<td>M-H, M+NO⁺, fragment</td>
<td>69.033, 100.039, 41.039</td>
<td>0.984, 4.1</td>
<td>1.37</td>
<td>48, 325</td>
<td>60 ppt</td>
<td></td>
</tr>
<tr>
<td>iso-Pentane</td>
<td>C₅H₁₁⁺, C₅H₁₀⁺, fragment</td>
<td>M-H, fragment</td>
<td>71.086, 43.054</td>
<td>0.888, 23</td>
<td>1.36</td>
<td>101, 706</td>
<td>49 ppt</td>
<td></td>
</tr>
<tr>
<td>Methylocyclopentane</td>
<td>C₅H₁₁⁺</td>
<td>M-H</td>
<td>83.086</td>
<td>0.961, 7.4</td>
<td>1.34</td>
<td>154, 1225</td>
<td>18 ppt</td>
<td></td>
</tr>
<tr>
<td>C5 aldehydes</td>
<td>C₅H₁₀O⁺, C₅H₉⁺, C₅H₁₂O⁺⁺</td>
<td>M-H, fragment, M+H₂O</td>
<td>85.065, 57.07, 103.075</td>
<td>0.936, 9.8</td>
<td>1.38</td>
<td>119, 904</td>
<td>28 ppt</td>
<td></td>
</tr>
<tr>
<td>2- and 3- methylpentane</td>
<td>C₆H₁₀⁺, C₆H₁₀⁺, C₆H₁₂⁺⁺</td>
<td>M-H, fragment, M+H₂O</td>
<td>85.101, 43.054, 57.07</td>
<td>0.978, 16</td>
<td>1.34</td>
<td>122, 981</td>
<td>30 ppt</td>
<td></td>
</tr>
<tr>
<td>Hexanal</td>
<td>C₆H₁₁O⁺, C₆H₁₁O₂⁺⁺</td>
<td>M-H, M+H₂O, fragment</td>
<td>99.08, 117.091, 71.086</td>
<td>0.945, 10</td>
<td>1.47</td>
<td>160, 1270</td>
<td>22 ppt</td>
<td></td>
</tr>
<tr>
<td>Styrene</td>
<td>C₆H₁₂⁺</td>
<td>M⁺</td>
<td>104.062</td>
<td>0.949, 0.62</td>
<td>1.47</td>
<td>112, 966</td>
<td>15 ppt</td>
<td></td>
</tr>
<tr>
<td>Benzaldehyde</td>
<td>C₆H₁₃O⁺</td>
<td>M-H</td>
<td>105.033</td>
<td>0.923, 12</td>
<td>1.37</td>
<td>75, 621</td>
<td>43 ppt</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2 (continued)
These calibration factors were multiplied by the relative peak areas determined in Sect. 3.1.1 to obtain estimated NO$^+$ ToF-CIMS calibration factors. (An example chromatogram and calculation is shown in Figure A5.6). Calibration factors estimated from correlation with GC-EIMS were calculated from the slope of NO$^+$ ToF-CIMS measurements against GC-EIMS measurements in ambient air (discussed in further detail in Section 3.2.2).

In the following discussion we use two metrics of instrument response: counts-per-second (cps) and normalized counts-per-second (ncps). This treatment is analogous to that discussed in Chapter 3. Counts-per-second (cps) is the raw ion count rate of the instrument. Two operations were applied to cps measurements to obtain ncps. First, a duty cycle correction (d.c.c.) was applied (Chernushevich et al., 2001):

$$I_{corr} = cps \times \sqrt{\frac{m/z_{reference}}{m/z}}$$  \hspace{1cm} (1)

where $I_{corr}$ is the duty-cycle corrected ion count rate and $m/z_{reference}$ is an arbitrary reference mass (in this work $m/z_{reference} \equiv 55$). The duty-cycle correction accounts for differences in ion residence time in the extraction region of the ToF and eliminates a mass-dependent sensitivity bias. Then, measurements were normalized to the duty-cycle corrected NO$^+$ (primary ion) measurement, which typically has count rates on the order of $10^6$ above that of VOCs:

$$ncps = 10^6 \frac{I_{corr}}{NO^+_{corr}}$$  \hspace{1cm} (2)

The normalization removes variability due to fluctuations in the ion source and detector. In calculating limits of detection, we use duty-cycle uncorrected cps, as this best reflects the fundamental counting statistics of the instrument. In reporting ambient air measurements, we use ncps. The ncps measurement reduces several significant instrumental biases and better reflects VOC abundances in air.

Limits of detection at 1Hz measurement frequency were calculated by finding the mixing ratio at which the signal-to-noise ratio (S/N) is equal to 3. The calculation can be expressed by (Bertram et al., 2011; Yuan et al., 2016a):
where $C_f$ is the instrument response factor, in cps per ppb; $[X]_{lod}$ is the limit-of-detection mixing ratio of species X in ppb; $t$ is the sampling period of 1 second; $\alpha$ is the scaling factor of noise compared to expected Poissonian counting statistics; and $B$ is the background count rate in cps. The scaling factor $\alpha$ is generally greater than 1 because high-resolution peak overlap and fitting algorithms create additional noise (Cubison and Jimenez, 2015). For comparison, H$_3$O$^+$ ToF-CIMS limits of detection, using the same ToF-CIMS instrument, are included where available.

Aliphatics and aromatics are generally detected quite sensitively. Aromatics have sub-100 ppt detection limits and are detected slightly more sensitively with NO$^+$ CIMS than with H$_3$O$^+$ CIMS, with NO$^+$ detection limits generally about 30% lower. Aliphatic species are detected with quite low detection limits (less than 50 ppt) and with substantially better sensitivity than H$_3$O$^+$: the detection limit of methylcyclohexane using NO$^+$ is a factor of 27 lower than with H$_3$O$^+$.

Aldehydes and ketones also have detection limits of around 100 ppt or less, with the exception of acetaldehyde (l.o.d. = 355 ppt). The higher detection limit of acetaldehyde is due to a somewhat higher instrumental background and a lower response factor that is consistent with reaction kinetics (Španěl et al., 1997). Methanol has a very high detection limit (19 ppb); this is expected from the anomalously low rate constant of the methanol-NO$^+$ reaction (Španěl and Smith, 1997). In contrast, ethanol is detected far more sensitively with NO$^+$ than with H$_3$O$^+$, with a detection limit of 105 ppt (compared to 1600 ppt for H$_3$O$^+$).

### 3.1.5 Humidity dependence

Humidity-dependent behaviors of primary ions and selected VOCs (acetaldehyde, acetone, isoprene, 2-butane, benzene, toluene, o-xylene, and 1,3,5-trimethylbenzene) were determined by diluting a VOC calibration standard into humidified air to reach approximately 10ppb mixing ratio, then sampling directly with the NO$^+$ ToF-CIMS. Air temperature was 27°C. Product ion and signal dependences on humidity for selected primary ions and VOCs are shown in Figure 5.7 (additional species are included in
As relative humidity increases, \( \text{NO}^+ \) (m/z 30) remains relatively constant, while protonated water and protonated water clusters (especially m/z 37, \( \text{H}_2\text{O}_2^+ \)) increase. As the abundance of \( \text{H}_2\text{O}^+ \) in the drift tube increases, one might expect to see increased products of VOC reaction with \( \text{H}_2\text{O}^+ \) with a corresponding decrease in \( \text{NO}^+ \) products. Although an increase of \( \text{H}_3\text{O}^+ \) product is seen for some species (e.g. MEK), it is not universally true. For many species, the major effect is that the \( \text{NO}^+ \) adduct product increases relative to other \( \text{NO}^+ \) product ions. This effect is especially intense for isoprene, where the isoprene-\( \text{NO}^+ \) cluster (m/z 98, \( \text{C}_5\text{H}_8\text{NO}^+ \)) increases by a factor of 10 from 0 to 70% relative humidity. A similar humidity effect, observed during SIFT measurements of alkenes, has been reported previously by Diskin et al. (2002), who attributed the effect to better stabilization of excited intermediary (\( \text{NO}^+ \text{R}^* \)) ions by \( \text{H}_2\text{O} \). A full theoretical investigation of this effect is beyond the scope of this work. For \( \text{NO}^+ \) measurements of ambient air reported in Chapter 5, I applied an experimentally-determined humidity correction similar to that used for \( \text{H}_3\text{O}^+ \) data (Chapter 3).

Figure 5.7. Humidity dependence of primary ions and selected VOCs.
(a) \( \text{NO}^+ \) and water clusters. (b) isoprene. (c) methyl ethyl ketone (MEK). (d) benzene.
3.2 Measurements of urban air

3.2.1 GC-NO$^+$ CIMS measurements

Measurement of ambient air using the GC interface allowed us to determine which compounds in ambient air produce which masses. This is the essential link between laboratory measurements of calibration standards, and interpretation of ambient NO$^+$ ToF-CIMS measurements. Ambient air from outside the laboratory was sampled from Oct. 27, 2015-Oct. 30, 2015 through an inlet three meters above ground level, and directed through 10 meters of $\frac{1}{2}''$ diameter Teflon tubing at a flow rate of 17 slpm (residence time approximately 4 seconds). The GC interface subsampled this stream. Eluant from the column was directed into the NO$^+$ ToF CIMS as described in Sect. 2.1. The laboratory is in an urban area (Boulder, CO) and the inlet was located near a parking lot and loading dock. Absolute instrument background (including the GC interface) was determined by sampling zero air at the beginning and end of the three-day measurement period. Instrument performance and stability, retention times of selected compounds, and instrument background were checked at least once per day by sampling a 56-component hydrocarbon calibration standard.

Figure 5.8 shows several masses from a typical chromatogram. In this chromatogram, it is clear, for instance, that the majority of signal from m/z 83 (C$_6$H$_{11}^+$) can be attributed to one compound (methylcyclopentane). On the other hand, m/z 57 (C$_4$H$_9^+$) is produced from many different compounds with comparable intensities. Aldehydes and ketones appear to be well separated, as expected from the laboratory experiments. Figure 5.9 summarizes the contributions of different VOCs to several ions (m/z 57, C$_4$H$_9^+$ and m/z 83 C$_6$H$_{11}^+$) during the entire three-day measurement period. M/z 57 (C$_4$H$_9^+$) has contributions from many different VOCs, and the relative proportions are highly variable. Conversely, m/z 83 (C$_6$H$_{11}^+$) is mostly attributable to methylcyclopentane during the majority of the three-day measurement period. M/z 57 (C$_4$H$_9^+$) does not provide a useful measurement of alkanes, while m/z 83 (C$_6$H$_{11}^+$) may possibly provide a useful measurement of methylcyclopentane. Corresponding figures for other masses can be found in the Appendix for this chapter (Figure A5.8). Table 5.3 summarizes my assessment of key ions.
Figure 5.8. Example GC-CIMS chromatogram of ambient air sample. Masses have been split between two panels for clarity. Top: select masses corresponding to branched and cyclic alkanes. Bottom: select masses corresponding to aldehydes and ketones.
Figure 5.9. Contributions to two masses based on GC-CIMS measurements of ambient air. “Total signal” is normalized counts per chromatogram. (a) m/z 57 C$_4$H$_9^+$. (b) m/z 83 C$_6$H$_{11}^+$.

<table>
<thead>
<tr>
<th>Ion formula</th>
<th>Exact mass (Th)</th>
<th>Assessment from series GC-NO$^+$ ToF-CIMS</th>
<th>Correlation with parallel GC-EIMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_5^+$</td>
<td>41.039</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_3$O$^+$</td>
<td>43.018</td>
<td>acetaldehyde</td>
<td>R$^2$ = 0.942, 0.892</td>
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<tr>
<td>C$_3$H$_7^+$</td>
<td>43.054</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$O$^+$</td>
<td>45.033</td>
<td>ethanol</td>
<td>R$^2$ = 0.998</td>
</tr>
<tr>
<td>C$_4$H$_9^+$</td>
<td>54.046</td>
<td>1,3-butadiene$^1$</td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_6$O$^+$</td>
<td>56.062</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_7^+$</td>
<td>57.033</td>
<td>propanal</td>
<td>R$^2$ = 0.928</td>
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<tr>
<td>C$_5$H$_6$O$^+$</td>
<td>57.070</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_5$O$^+$</td>
<td>59.049</td>
<td>interference from acetone; if accounted for, sum of C3 alcohols</td>
<td></td>
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<tr>
<td>CH$_2$NO$_2^+$</td>
<td>62.024</td>
<td>methanol, but poor sensitivity</td>
<td>R$^2$ = 0.904, 1.25</td>
</tr>
<tr>
<td>C$_5$H$_8^+$</td>
<td>66.046</td>
<td>interference from benzene; if accounted for, cyclopentadiene</td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_9$O$^+$</td>
<td>68.026</td>
<td>furan$^2$</td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_8^+$</td>
<td>68.062</td>
<td>possibly: isoprene$^3$</td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_8$O$^+$</td>
<td>69.033</td>
<td>methacrolein + crotonaldehyde$^4$</td>
<td>R$^2$ = 0.984</td>
</tr>
<tr>
<td>C$_6$H$_9^+$</td>
<td>69.070</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_5$H$_9$O$^+$</td>
<td>70.078</td>
<td>possibly: sum of 2-pentenes$^5$</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_8$O$^+$</td>
<td>71.049</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_8$O$^+$</td>
<td>71.086</td>
<td>iso-pentane</td>
<td>R$^2$ = 0.888</td>
</tr>
<tr>
<td>C$_5$H$_8$O$^+$</td>
<td>73.065</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>C$_6$H$_9^+$</td>
<td>78.046</td>
<td>benzene$^6$</td>
<td>R$^2$ = 0.987, 0.847</td>
</tr>
<tr>
<td>C$_5$H$_7$O$^+$</td>
<td>82.041</td>
<td>possibly: sum of 2- and 3-methylfuran$^7$</td>
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</tr>
<tr>
<td>Mass</td>
<td>Formula</td>
<td>Assignment</td>
<td>R²</td>
</tr>
<tr>
<td>-------</td>
<td>--------------------</td>
<td>-------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>83.086</td>
<td>C₆H₁₁O⁺</td>
<td>methylcyclopentane</td>
<td>0.961</td>
</tr>
<tr>
<td>85.065</td>
<td>C₅H₁₀O⁺</td>
<td>sum of C₅ aldehydes</td>
<td>0.936</td>
</tr>
<tr>
<td>85.101</td>
<td>C₆H₁₃⁺</td>
<td>sum of 2- and 3-methylpentane</td>
<td>0.978</td>
</tr>
<tr>
<td>86.060</td>
<td>C₅H₁₀NO⁺</td>
<td>several non-correlated species</td>
<td></td>
</tr>
<tr>
<td>87.080</td>
<td>C₅H₁₁O⁺</td>
<td>C₅ alcohols and ethers; significant interference from minor carbonyl product ions</td>
<td></td>
</tr>
<tr>
<td>88.039</td>
<td>C₅H₁₀NO⁺</td>
<td>acetone</td>
<td>0.978</td>
</tr>
<tr>
<td>90.019</td>
<td>C₅H₁₀O⁺</td>
<td>possibly: acetic acid (chromatography too poor to determine)</td>
<td>1.13</td>
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<tr>
<td>92.062</td>
<td>C₇H₁₄⁺</td>
<td>toluene</td>
<td>0.999</td>
</tr>
<tr>
<td>97.101</td>
<td>C₇H₁₃⁺</td>
<td>sum of C₇ cyclic alkanes</td>
<td>0.917</td>
</tr>
<tr>
<td>99.080</td>
<td>C₆H₁₃O⁺</td>
<td>hexanal</td>
<td>0.945</td>
</tr>
<tr>
<td>99.117</td>
<td>C₇H₁₅⁺</td>
<td>possibly: sum of 2- and 3-methylhexane, but poor sensitivity</td>
<td></td>
</tr>
<tr>
<td>100.039</td>
<td>C₇H₁₀NO⁺</td>
<td>MVK</td>
<td>0.950</td>
</tr>
<tr>
<td>100.076</td>
<td>C₅H₁₀NO⁺</td>
<td>possibly: sum of C₅ terminal alkenes, but poor sensitivity</td>
<td></td>
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<tr>
<td>102.055</td>
<td>C₇H₁₀NO₂⁺</td>
<td>MEK</td>
<td>0.971</td>
</tr>
<tr>
<td>104.062</td>
<td>C₆H₁₂⁺</td>
<td>styrene (vinyl benzene)</td>
<td>0.949</td>
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<td>105.033</td>
<td>C₇H₁₃O⁺</td>
<td>benaldehyde</td>
<td>0.923</td>
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<tr>
<td>106.078</td>
<td>C₈H₁₀⁺</td>
<td>sum of C₈ aromatics</td>
<td>0.952</td>
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<tr>
<td>108.044</td>
<td>C₉H₁₀NO⁺</td>
<td>benzene</td>
<td>0.746</td>
</tr>
<tr>
<td>111.117</td>
<td>C₈H₁₁NO⁺</td>
<td>possibly: sum of C2 alkyl-substituted cyclohexanes</td>
<td>0.761</td>
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<tr>
<td>113.096</td>
<td>C₈H₁₀O⁺</td>
<td>heptanal</td>
<td></td>
</tr>
<tr>
<td>113.132</td>
<td>C₉H₁₅⁺</td>
<td>possibly: sum of methylheptanes, but poor sensitivity</td>
<td></td>
</tr>
<tr>
<td>116.071</td>
<td>C₉H₁₀NO₂⁺</td>
<td>sum of C₅ ketones</td>
<td>0.945</td>
</tr>
<tr>
<td>118.078</td>
<td>C₉H₁₀⁺</td>
<td>possibly: sum of methylstyrene isomers³</td>
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</tr>
<tr>
<td>120.093</td>
<td>C₉H₁₅⁺</td>
<td>sum of C₉ aromatics; scatter possibly due to disparity in response factors</td>
<td>0.600</td>
</tr>
<tr>
<td>127.112</td>
<td>C₈H₁₆O⁺</td>
<td>octanal</td>
<td></td>
</tr>
<tr>
<td>130.086</td>
<td>C₉H₁₀NO₂⁺</td>
<td>possibly: sum of C6 ketones³</td>
<td></td>
</tr>
<tr>
<td>134.109</td>
<td>C₁₀H₁₄⁺</td>
<td>possibly: sum of C₁₀ aromatics</td>
<td></td>
</tr>
<tr>
<td>136.125</td>
<td>C₁₀H₁₆⁺</td>
<td>monoterpenes plus unknown interference; possibly adamantane from vehicle exhaust</td>
<td>0.584</td>
</tr>
<tr>
<td>144.102</td>
<td>C₉H₁₆NO₂⁺</td>
<td>heptanone</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3. Assessment of significant product ions investigated by GC-NO⁺ CIMS and parallel GC-EIMS and NO⁺ CIMS measurement of ambient air. Masses in bold can be unambiguously assigned to a single VOC or a structurally related, correlated group of VOCs.

1 Cross-comparison with independent GC-EIMS not possible due to chromatographic quantitation ion overlap with neighboring peaks.
2 Cross-comparison with independent GC-EIMS not possible due to EIMS quadrupole SIS (selected ion scan) window restrictions.
3 Concentrations too low in ambient air to determine.
4 Winter urban air sampled was likely influenced by local domestic biomass burning; crotonaldehyde may be a smaller fraction of signal in other environments.
5 Benzene correlation using sum of m108 C₆H₆NO⁺ and m78 C₆H₆⁺.
6 With exclusion of single outlier, R² = 0.831.
3.2.2 NO⁺ CIMS vs. GC-EIMS Measurement Comparison

Measurements using the GC interface do not provide any information about the fast time response capability of the NO⁺ ToF-CIMS. Additionally, not all compounds detectable by NO⁺ CIMS and present in ambient air can be transmitted through the GC interface. Simultaneous GC-EIMS and NO⁺ ToF-CIMS measurements were conducted to investigate fast NO⁺ measurements, determine if there are any significant interferences to key NO⁺ masses, and explore NO⁺ CIMS response to VOCs not transmittable through the GC interface.

Ambient air was sampled into the laboratory as described in the previous section. The GC-EIMS and the NO⁺ ToF-CIMS were run as separate instruments and subsampled the 17 SLPM flow at the same point. Measurements were taken from Nov. 4, 2015 through Nov. 6, 2015. The GC-EIMS instrument was operated on a 30-minute schedule. GC-EIMS instrument background was determined from zeros taken at the beginning and end of the three-day measurement period. The 56-component hydrocarbon calibration standard was sampled once per day. The NO⁺ ToF-CIMS measured at 1 Hz frequency. Instrument zeros were taken for a two minute period once every hour (example time series with zeros in Figure A5.3). Calibration gas from a 10-component hydrocarbon standard was sampled for two minutes once every three hours. At the end of the three-day measurement period, both instruments were disconnected from the ambient air line and sampled air from inside the laboratory for 1.5 hours (three GC samples), to investigate the NO⁺ ToF-CIMS response to air with a VOC composition substantially different from urban air.

For all comparisons between the two instruments, the 1Hz NO⁺ ToF-CIMS measurements were averaged over the 5-minute GC-EIMS collection period. The NO⁺ ToF-CIMS was calibrated using air with ambient humidity (approximately 20%) for the 10 species listed in Table 5.2A, and no further humidity correction was applied. Correlations between independent GC and calibrated CIMS measurements generally show high correlation coefficient ($R^2 > 0.9$) and slopes close to 1 (examples in Figure 5.10a, b). This demonstrates that an adapted NO⁺ CIMS instrument retains sensitive measurement of atmospherically important species such as aromatics that are often targeted using PTRMS and in addition can detect
compounds such as iso-pentane, sum of 2- and 3-methylpentanes, methylcyclopentane, and sum of C7 cyclic alkanes (Figure 5.10c-f) that are usually not detected with PTR-MS. Slopes for calibrated VOCs, and correlation coefficients ($R^2$) for all VOCs investigated, are included in Table 5.3. The good agreement also indicates that humidity-dependence of sensitivity is likely not a severe effect for most species. (This was indeed the case for humidity correction factors that were later experimentally determined and applied to measurements in Chapter 6.)

Figure 5.10. Correlations between VOCs measured with GC-EIMS and NO+ ToF-CIMS in ambient air. The 1Hz NO+ ToF-CIMS measurement is averaged to the 5 minute GC collection period. Orthogonal least-squares linear best fits (ODR best fit) are shown with dashed lines. The lines appear curved due to log scale axes. For several compounds (e.g. methylcyclopentane, 2-and 3 methylpentanes), the single high outlier pulls the best fit slightly away from the data points at low mixing ratios. (a) Toluene. (b) C8 aromatics: sum of ethylbenzene, o-xylene, m-xylene, and p-xylene. (c) Iso-pentane. (d) Sum of 2-methylpentane and 3-methylpentane. (e) Methylcyclopentane. (f) C7 cyclic alkanes: sum of methylcyclohexane, ethylcyclopentane, and dimethylcyclopentanes.
To assess the ability of the NO$^+$ Tof-CIMS to separate ketones and aldehydes, I explore measurements of propanal and acetone. The separate measurement of these two species is a good test case because the two peaks are chromatographically well resolved on the GC-EIMS, there are few isomers of C$_3$H$_6$O (of which acetone and propanal are likely the only atmospherically relevant species), and independent measurements of these two species are interesting for scientific reasons: aldehydes are generally much more reactive with OH than their ketone isomers and may have significantly different behavior in the atmosphere (Atkinson and Arey, 2003).

A time-series of propanal and acetone is shown in Figure 5.11a. The two compounds have clearly different behavior in the atmosphere: there is fast (seconds to minutes), high variability in the acetone measurement that is not seen in the propanal measurement, and the longer term (~hours) variability of acetone and propanal is not the same. The fast, high spikes in acetone may come from local sources such as exhaust from chemistry labs in the building. The acetone comparison between the GC-EIMS and the NO$^+$ ToF-CIMS has a slope of 1.13, a correlation coefficient $R^2$ of 0.978 and negligible offset. The comparison between the GC and CIMS propanal measurements has an $R^2$ of 0.928 (Figure 5.11b, c).
Several episodes occurred with elevated high-mass n-alkane masses (m/z 169 C$_{12}$H$_{25}^+$, dodecane; m/z 183 C$_{13}$H$_{27}^+$, tridecane; m/z 197 C$_{14}$H$_{29}^+$, tetradecane; m/z 211 C$_{15}$H$_{31}^+$, pentadecane). Two examples are shown in Figure 5.12. The episodes show high temporal and compositional variability. The inlet was downwind from a parking lot, and next to a loading dock and electric power generator for the building, and it is likely that the elevated C12-C15 alkanes are from any or all of these sources. An ambient air measurement of these species is particularly interesting because they have been implicated in efficient secondary organic aerosol production from diesel fuel exhaust (Gentner et al., 2012).

4. Conclusions

In summary, an H$_3$O$^+$ ToF-CIMS (PTR-MS) instrument was easily and inexpensively converted into an NO$^+$ CIMS by replacing the reagent source gas and modifying the ion source and drift tube voltages. The usefulness of NO$^+$ CIMS for atmospheric VOC measurement was then evaluated by (1) using a GC interface to determine product ion distributions for nearly 100 VOCs and compare the sensitivity and
simplicity of spectra to H$_3$O$^+$ CIMS, (2) measuring ambient air with a GC interface, to map product ions to their VOC precursors and determine which ions may be useful for chemically specific measurement, and (3) measuring ambient air directly, to evaluate chemical specificity and investigate fast (1Hz) time measurement of new compounds. Additionally, the NO$^+$ CIMS response to C12-C15 n-alkanes, and to variable humidity was determined in some detail.

NO$^+$ CIMS is a valuable technique for atmospheric measurement because it can separate small carbonyl isomers, it can provide fast and chemically specific measurement of cyclic and a few important branched alkanes (notably, isopentane and methylpentanes) that cannot be detected by PTR-MS, it can measure alkyl-substituted aromatics with less fragmentation than H$_3$O$^+$ CIMS, and it can detect larger (C12-C15) alkanes. With NO$^+$ CIMS significant fragmentation of most small alkanes does occur, making them difficult to measure quantitatively. There are also interferences on many alcohols (with the exception of ethanol) and butanal. Additionally, it is worth considering that VOC NO$^+$ cluster formation moves certain species into a higher mass range. This may be a drawback because the number of possible isobaric compounds increases with mass, and it may be more difficult for high-resolution peak-fitting algorithms to separate species of interest from isobaric interferences (example in Figure A5.9). Finally, because there are three different ionization mechanisms, (hydride transfer, charge transfer, and NO$^+$ adduct formation), it may be difficult to determine which VOC precursors correspond to particular ions. NO$^+$ CIMS may be an extremely useful supplementary approach for specific applications such as studying secondary organic aerosol precursors in vehicle exhaust, investigating emissions from oil and natural gas extraction, identifying additional species in complex emissions such as biomass burning, measuring emissions of oxygenated consumer products and solvents in urban areas, and investigating photochemistry of biogenic VOCs. In the next chapter, I describe the application of NO$^+$ ToF-CIMS to measuring VOCs in vehicle exhaust.
Chapter 6. Direct measurement of on-road VOC emissions from vehicles using NO$^+$ ToF-CIMS

Abstract

VOCs emitted from vehicles on a Denver Metro freeway ramp were measured using NO$^+$ ToF-CIMS for several hours in summer of 2016. Fast time resolution allowed characterization of individual emission plumes. Application of positive matrix factorization (PMF) discovered two major and two minor VOC sources: gasoline exhaust, gasoline vapor, diesel exhaust, and an unidentified isopropanol-containing source. The VOC profiles of gasoline exhaust, gasoline vapor, and diesel exhaust agree well with literature and laboratory samples. Emissions from gasoline vapor were quite important relative to gasoline exhaust (20% and 60% of total instrument signal, respectively) and were larger than emissions from diesel exhaust (11% of total instrument signal). Plumes of gasoline vapor and exhaust were very distinct in our measurements and rarely overlapped in time. The relative contributions of gasoline exhaust, gasoline vapor, and diesel to various VOCs were calculated for the measured on-road Colorado vehicle emissions and for emissions in Los Angeles (CalNex). The comparison to the CalNex data also highlighted which VOCs can be explained by vehicle sources (aromatics, alkanes, alkenes, and some carbonyls) and which cannot (ethanol, isopropanol, hexanals, benzaldehyde, acetone, and MEK). The pilot study described in this chapter demonstrates the use of the NO$^+$ ToF-CIMS technique. The method described here could close the gap between dynamometer studies, which provide high chemical detail for a limited number of specific vehicles, and tunnel studies, which provide a fleet-averaged emissions profile.

1. Introduction

On-road vehicles are a major source of VOC pollution, accounting for 13% of US anthropogenic VOC emissions (EPA Air Pollutant Emissions Trends Data). These emissions are not only significant, but have also changed dramatically over time due to regulatory pressure and new technology. US on-road vehicle VOC emissions decreased by nearly 75% from 1990 to 2011 (EPA Report on the Environment), and the effects of this trend are evident in long-term measurements of VOC content and composition in the
atmosphere (Warneke et al., 2012). It is important to have detailed, up-to-date measurements of this emission source.

Several current challenging questions about vehicle emissions could benefit from improved observations. One unresolved question is the relative contributions of diesel and gasoline fuel usage to the formation of secondary organic aerosol. Several field studies disagree (Samy and Zielinska, 2010; Bahreini et al., 2012; Gentner et al., 2012) and chamber studies have suggested that a detailed picture of the chemical composition of emissions is necessary to resolve this question (Chirico et al., 2010; Nordin et al., 2013; Gordon et al., 2014; May et al., 2014). Measurement of higher mass, semivolatile hydrocarbons may be especially important to the resolution of this issue (Gentner et al., 2012; Gentner et al., 2013). Other important questions involve the accuracy of regulatory inventories and the effectiveness of regulations. Inventories do not always agree with measurements (e.g. Kim et al. (2011)); measurements can help highlight inaccuracies, provide emission factors, and quantify the relative contributions of various sources to particular VOCs or families of VOCs. Finally, field measurements supply data crucial to assessing the effectiveness of regulations. A number of previous studies have characterized VOC composition from vehicles in the laboratory or using in-situ techniques. Table 6.1 lists a few of the most pertinent studies to this work.

Chemically-detailed measurements of VOC emissions from individual vehicles, in a real-world conditions along a roadway, are challenging because they require an instrument that is portable, has time resolution high enough to capture narrow plumes of emissions, and can measure many species simultaneously. Chemical ionization mass spectrometry (CIMS) meets these requirements, and a number of studies, mostly in the laboratory, have investigated vehicle exhaust using PTR-MS (Jobson et al., 2005; Rogers et al., 2006; Inomata et al., 2013a; Erickson et al., 2014; Yamada et al., 2015; Gueneron et al., 2015). A recent review of online MS techniques for studying vehicle exhaust in laboratory situations has been given by Inomata et al. (2016).
<table>
<thead>
<tr>
<th>Citation</th>
<th>Measurement location/ type of vehicle</th>
<th>VOCs measured</th>
<th>Analytical technique</th>
<th>Time resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kirchstetter et al. (1999)</td>
<td>Caldecott tunnel (USA) light duty vehicles</td>
<td>Benzene, Aldehydes (limited), 1,3-butadiene, MTBE</td>
<td>Canister collection/ GC-FID; cartridge collection/ HPLC</td>
<td>2 hours</td>
</tr>
<tr>
<td>Kean et al. (2001)</td>
<td>Caldecott tunnel (USA) light duty vehicles</td>
<td>Ketones, Aldehydes (extensive)</td>
<td>Cartridge collection/ LCMS</td>
<td>2 hours</td>
</tr>
<tr>
<td>Schauer et al. (2002)</td>
<td>Laboratory: dynamometer light duty trucks gasoline vehicles</td>
<td>Alkanes, Alkenes, Cycloalkanes, Aromatics, Aldehydes, Acids (extensive) Ketones (limited)</td>
<td>Canister collection/ GC-FID; cartridge collection/LCUV</td>
<td></td>
</tr>
<tr>
<td>Legreid et al. (2007)</td>
<td>Gubrist tunnel (CHE) all vehicle fleet</td>
<td>Small aromatics, Aldehydes, Small ketones, Alcohols, Esters Alkenes (limited)</td>
<td>Sorbent collection/ GCMS</td>
<td>50 minutes</td>
</tr>
<tr>
<td>Ban-Weiss et al. (2008)</td>
<td>Caldecott tunnel light duty vehicles</td>
<td>Ketones, Aldehydes (extensive)</td>
<td>Cartridge collection/ LCMS</td>
<td>2 hours</td>
</tr>
<tr>
<td>Gentner et al. (2012)</td>
<td>Laboratory: diesel and gasoline fuel composition; Caldecott tunnel (all vehicles); Bakersfield (USA) (ambient)</td>
<td>Alkanes, Alkenes, Cycloalkanes, Aromatics (extensive)</td>
<td>In-situ: GC-MS - FID; Lab: GC/VUV-MS</td>
<td>1 hour</td>
</tr>
<tr>
<td>May et al. (2014)</td>
<td>Laboratory: dynamometer Gasoline vehicles Medium &amp; heavy duty diesel vehicles</td>
<td>Aldehydes, Ketones, Alkenes, Alkanes, Cycloalkanes, Aromatics (extensive)</td>
<td>Teflon bag/GC; Cartridge collection /LC</td>
<td></td>
</tr>
<tr>
<td>Gentner et al. (2013)</td>
<td>Laboratory: diesel and gasoline fuel composition; Caldecott tunnel (all vehicles)</td>
<td>Alkanes, Alkenes, Cycloalkanes, Aromatics (extensive) Ethanol, carbonyls (limited)</td>
<td>In-situ: GC-MS - FID; Lab: GC/VUV-MS</td>
<td>1 hour</td>
</tr>
<tr>
<td>Smit et al. (2017)</td>
<td>Brisbane CLEM7 tunnel (AUS); all vehicle fleet</td>
<td>Alcohols, Aromatics, Alkanes (limited) 1,3-butadiene, cyclohexane, MTBE</td>
<td>Canister collection/GCMS</td>
<td>24 hours</td>
</tr>
<tr>
<td>Yamada et al. (2015)</td>
<td>Laboratory: gasoline vehicle evaporative emissions</td>
<td>Alkanes, aromatics, alkenes (limited)</td>
<td>NO+ CIMS</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1 Literature VOC composition measurements referenced in this chapter.

NO+ CIMS is an especially suitable technique because, unlike PTRMS, it retains high sensitivity and relatively low fragmentation of many important VOCs found in vehicle exhaust, especially ethanol, alkanes, and cyclic alkanes. NO+ CIMS has not been used nearly as extensively as PTRMS, but a few laboratory studies have explored its application to fossil fuel emissions. Smith et al. (2002) demonstrated the detection of alkanes and aldehydes in vehicle exhaust using NO+ selected-ion flow tube mass.
spectrometry (SIFT-MS). NO+ CIMS using a switchable-reagent-ion PTRMS instrument has also been used to study evaporative emissions from gasoline vehicles (Yamada et al., 2015).

In the previous chapter, I described the development of NO+ CIMS capability with an H_3O+ ToF-CIMS instrument, and established a framework for interpreting the measurements (Koss et al., 2016). The experiment described here was designed as a pilot study to evaluate and demonstrate the utility of NO+ CIMS for in-situ measurement of VOCs from individual vehicles. Using the NO+ CIMS technique, I am able to distinguish and provide detailed VOC profiles for several major on-road emission sources. More extensive measurements will be needed to determine fleet averages and reliable statistics for different vehicle characteristics.

2. Methods

2.1. Field measurement

Field measurements were performed adjacent to a freeway exit ramp (NB I-25 to WB Sixth Ave) in the Metro Denver area. The ramp has an uphill grade of 4.6° and a high traffic volume. This location has been the site of many years of previous studies and is described most recently in Bishop and Stedman (2014). Measurements were conducted on June 27 and 28, 2016 from 10:00-14:00 MST. The ambient temperature increased steadily from 28.5°C to 36.5°C during this time. Wind speeds were light and variable (0-6 m/s) and generally from the northwest (crossing the roadway, towards the instrumentation).

Measurements were conducted using the NOAA mobile laboratory. The mobile laboratory has been recently described by Eilerman et al. (2016). The mobile laboratory was equipped with a range of chemical and meteorological instrumentation, all of which operated at 1Hz time resolution (Table 6.2). The mobile laboratory was parked to the southwest of the exit ramp. A 4m, 1/4” ID teflon line was installed on the guard rail (approx. 1m height); the line was subdivided to the various instruments inside the mobile lab.

<table>
<thead>
<tr>
<th>Measured parameter</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>VOCs</td>
<td>NO+ ToF-CIMS</td>
</tr>
<tr>
<td>N_2O, CO, H_2O</td>
<td>Integrated cavity output spectroscopy</td>
</tr>
<tr>
<td>CO_2, CH_4</td>
<td>Wavelength scanned cavity ring-down spectroscopy</td>
</tr>
<tr>
<td>NH_3, H_2O</td>
<td>Cavity ring-down spectroscopy</td>
</tr>
<tr>
<td>Position and met data</td>
<td>Differential GPS and Airmar Wx</td>
</tr>
</tbody>
</table>

Table 6.2 Mobile laboratory instrumentation
VOC measurements were made using a ToF-CIMS instrument equipped with both H$_3$O$^+$ and NO$^+$ reagent ion capability. On June 27 H$_3$O$^+$ reagent ion chemistry was used, and on June 28 NO$^+$ reagent ion chemistry was used. The data from June 28 obtained using NO$^+$ CIMS were more relevant to this study and will be analyzed in detail here.

The NO$^+$ ToF-CIMS instrument used in this work has been described previously in detail in the previous chapter and in the literature (Koss et al., 2016). This instrument generates NO$^+$ reagent ions in a hollow cathode ion source using ultrapure air. The NO$^+$ ions are then mixed with ambient air containing VOCs in a drift tube region. NO$^+$ ionizes VOCs through a number of mechanisms, which depend on the size and functional groups of the VOC molecule. The ionized VOCs are then transferred through several ion guides and separated using a high-resolution time-of-flight mass analyzer (Aerodyne Research Inc./Tofwerk). The instrument has a mass resolution of approximately 3900-5900 (HWHM m/Δm) over mass range m/z 12-200, which is sufficient to distinguish the isobaric compounds reported in this work and to calculate their elemental formulas. The instrument was directly calibrated for a number of VOCs using permeation sources and standard cylinders. Sensitivity factors of several other compounds were estimated by laboratory comparison to PTR-MS and GC-MS instruments, or from VOCs with similar functionality (Table 6.3). One-second 3σ detection limits range from about 20 ppt (aromatics) to 300 ppt (acetaldehyde). Data were corrected for humidity-dependent sensitivity using correction factors determined from laboratory calibration. All reported values are VOC enhancement above background.

Additionally, a remote sensing system operated by the University of Denver was deployed at the site. This system uses collinear IR and UV beams directed across the roadway to measure the ratios of CO, HC, NO, and NO$_2$ to CO$_2$ in exhaust from individual vehicles (Burgard et al., 2006; Popp et al., 1999). The instrument additionally takes an image of the vehicle license plate, which can be used to determine vehicle type and age. Long-term measurements from this instrument have been included in a number of publications (Bishop and Stedman, 2008). Although measurements from this system are not included in this experimental summary, they are discussed in our assessment of the pilot study (section 3.4).
<table>
<thead>
<tr>
<th>VOC name</th>
<th>Quantification ion (m/z Th, formula)</th>
<th>Calibration method</th>
<th>Uncertainty estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>45.034 C₂H₅O</td>
<td>directly calibrated, permeation source</td>
<td>20%</td>
</tr>
<tr>
<td>isopropanol</td>
<td>59.049 C₃H₇O</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>43.054 C₂H₃O</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>propanal</td>
<td>57.034 C₃H₇O</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>butanals</td>
<td>71.050 C₄H₉O</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>pentanals</td>
<td>85.065 C₅H₁₁O</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>hexanals</td>
<td>99.080 C₆H₁₃O</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>Methacrolein + crotonaldehyde</td>
<td>69.034 C₅H₉O</td>
<td>GC comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>benzaldehyde</td>
<td>105.033 C₅H₇O</td>
<td>GC comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>acetone</td>
<td>88.039 C₆H₁₂NO₂</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>MEK</td>
<td>102.055 C₇H₁₄NO₂</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>pentanones</td>
<td>116.071 C₈H₁₄NO₂</td>
<td>PTRMS comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>MVK</td>
<td>100.039 C₇H₁₄NO₂</td>
<td>PTRMS comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>butanediene</td>
<td>116.034 C₈H₁₄NO₃</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>benzene</td>
<td>78.046+ C₆H₆⁺</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>toluene</td>
<td>108.044 C₆H₈NO</td>
<td>GC comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>C₈ aromatics</td>
<td>92.062 C₇H₈</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>C₉ aromatics</td>
<td>106.078 C₈H₁₀</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>styrene</td>
<td>120.093 C₉H₁₂</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>Methylstyrene + indane</td>
<td>118.078 C₈H₁₀</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>isopentane</td>
<td>71.086 C₅H₁₁</td>
<td>GC comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>methylpentanes</td>
<td>85.101 C₆H₁₃</td>
<td>GC comparison</td>
<td>factor of 2</td>
</tr>
<tr>
<td>methylheptanes</td>
<td>99.117 C₇H₁₅</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>undecane</td>
<td>155.179 C₁₁H₂₃</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>dodecane</td>
<td>169.195 C₁₂H₂₅</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>tridecane</td>
<td>183.211 C₁₃H₂₇</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>pentadecane</td>
<td>211.242 C₁₅H₃₁</td>
<td>directly calibrated, permeation source</td>
<td>factor of 2</td>
</tr>
<tr>
<td>methylcyclopentane</td>
<td>83.086 C₇H₁₁</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>97.101 C₇H₁₃</td>
<td>directly calibrated, standard cylinder</td>
<td>20%</td>
</tr>
<tr>
<td>C₈ cycloalkanes</td>
<td>111.117 C₈H₁₅</td>
<td>average of functional group</td>
<td>factor of 2</td>
</tr>
<tr>
<td>1,3-butadiene</td>
<td>54.046 C₄H₆</td>
<td>From (Knighton et al., 2009), scaled to benzene</td>
<td>factor of 2</td>
</tr>
</tbody>
</table>

Table 6.3 NO⁺ ToF CIMS calibration information.

2.2 Laboratory measurement

To support my interpretation of field measurements, regular E10 gasoline, diesel, and windshield fluid were purchased from local gas stations and sampled in the lab with the same NO⁺ ToF-CIMS instrument. Gasoline and diesel were obvious candidates for vehicle-related emissions, and the windshield fluid was a possible source of isopropanol-enriched emissions (see section 3.1). The headspace of gasoline and diesel fuel, and of windshield fluid were sampled after warming the sealed sample containers to 25°C.
The whole composition of gasoline was measured by heating a ~100 μL sample in a closed vial at 250°C until no liquid remained, and sampling the resulting vapor.

Additionally, we sampled the tailpipe exhaust of three passenger vehicles: a 2014 Ford Fusion (gasoline), a 2014 Chevrolet Equinox (E85 flex fuel gasoline), and a 2000 Volkswagen Jetta (diesel). A 3/8” OD Teflon sampling line was extended from the NO+ ToF-CIMS to within 20 cm of the tailpipe of each vehicle. Each vehicle was parked with the engine off for at least an hour before the exhaust was sampled. The ambient temperature was approximately 16 °C. Each vehicle was idled for several minutes, then the running speed of the engine was temporarily increased for several seconds. I observed minor differences in VOC composition between the two engine modes, but these differences were too small to affect the qualitative use of the exhaust profiles described in this work. Profiles were determined by integrating the signal of each ion over the time period of the exhaust sample.

2.3 Application of positive matrix factorization (PMF)

Several hundred 1-10 seconds-wide high-concentration peaks from emissions of individual vehicles dominate the measured VOCs time series. These peaks were generally well separated in time and clearly included several different compositions, which makes Positive Matrix Factorization (PMF) an ideal tool to determine and identify major categories of VOC emissions from individual vehicles (Figure 6.1).

Time-series data of 183 VOC product ions were analyzed using the PMF Evaluation Tool v. 2.08A. The exact mass and ion formula of these ions are provided in Table A6.1. PMF is a mathematical analysis technique that can be applied to a data matrix in which the columns are time series of VOC product ions. PMF separates the data matrix into several time series of VOC source intensities (“factor time series”), each of which has a distinct VOC composition profile (“factor profiles”). This section includes details regarding the PMF implementation, selection of the PMF solution, and related quality checks.

The basic principles of PMF, the application of PMF to atmospheric chemistry measurements, and the PMF Evaluation Tool have been described extensively elsewhere (Paatero and Tapper, 1994; Paatero,
I briefly restate here several terms necessary to describe the PMF set-up and results. A more thorough description of each term can be found in Ulbrich et al. (2009):

<table>
<thead>
<tr>
<th>Term/symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q/Q_{\text{exp}}$</td>
<td>A quality-of-fit parameter which depends on the total residual error between the PMF best-fit and the original data. As the best fit improves, $Q/Q_{\text{exp}}$ decreases to near 1.</td>
</tr>
<tr>
<td>Data matrix</td>
<td>Matrix containing measured normalized-counts-per-second instrument signal; columns are different ion masses and the rows are time series.</td>
</tr>
<tr>
<td>Error matrix</td>
<td>Matrix containing estimated measurement uncertainty for each data point.</td>
</tr>
<tr>
<td>Seed</td>
<td>Randomized starting point used to initialize the PMF algorithm.</td>
</tr>
<tr>
<td>FPEAK</td>
<td>A parameter that allows exploration of the effect of rotation or factor mixing on the PMF solution.</td>
</tr>
</tbody>
</table>

The PMF Evaluation Tool requires as input a data matrix of measured VOC intensities, and a data matrix of the estimate of uncertainty for each VOC at each time point (“error matrix”). The data matrix was built by concatenating normalized counts-per-second (ncps) VOC ion signals with visible enhancement above background. Instrument signals were chosen (rather than calibrated ppb enhancements) because not every ion mass can be unambiguously assigned to a single VOC, but these masses still contain useful information.

It has been previously demonstrated that noise (error) in the ToF CIMS instrument is proportional to the square root of the signal (Koss et al., 2016; Yuan et al., 2016a). From the time series of each ion mass included in the data matrix, several blocks were selected from background measurements, calibration, or other short time periods with stable concentration; and the average (μ) and standard deviation (σ) were calculated for each block. A best fit of $\sigma = A \sqrt{\mu} + B$ was applied to each set of μ and σ, and the scaling factors A and B were determined for each ion mass. The equation $\sigma(t) = A \sqrt{x(t)} + B$ was then applied to the time series of each ion mass ($x(t)$) to determine the error as a function of time ($\sigma(t)$). The error matrix represents the estimated 1σ standard deviation of each VOC ion mass at each time point. The resulting lowest values of $Q/Q_{\text{exp}}$ in the chosen solution are slightly below 1, indicating that the error is not significantly over or under-estimated.
I first explored the PMF solution by varying the seed. I explored 10 possible seeds. The range of $Q/Q_{\text{exp}}$ across seeds was very small, and time series of various factors were extremely similar, regardless of number of chosen factors (Figure A6.1). This qualitative assessment based on seed gives me confidence that there are no significant local minima in the space of solutions.

I also explored a range of values of fPeak, which allowed me to assess the effect of solution rotation and factor “mixing”. “Mixing” occurs when PMF presents a solution that is a linear combination of the factors of the actual (physically realistic) solution. Negative fPeak values rotate, mix, or unmix, factors by making time series less correlated and mass spectra (compositional profile) more correlated; and positive fPeak values increase the correlation in time series and decrease the correlation in mass spectra.

From previous work on the VOC composition of vehicle emissions (Gentner et al., 2012), and the behavior of emission plumes at our roadside sampling site (Bishop and Stedman, 2008), I anticipated that factor composition profiles may be somewhat correlated (sources contain many of the same VOCs), but the factor time series should be highly uncorrelated (emissions from no more than one source are sampled at any one time). I therefore selected a range of fPeak values, -3 to 1, to help me explore solutions with uncorrelated time series and correlated mass spectra.

$Q/Q_{\text{exp}}$ shows a clear minimum between fPeak of about -1 and 0.6 (the width of the minimum $Q/Q_{\text{exp}}$ well is somewhat dependent on the number of factors chosen). I selected an fPeak value of -0.4, which, for our selected number of factors, was the most negative fPeak value for which $Q/Q_{\text{exp}}$ did not increase significantly (Figure A6.2). Within the range of fPeak values for which $Q/Q_{\text{exp}}$ is similarly low, there is a range of significantly diverse PMF solutions. This indicates that the PMF solution is quite sensitive to “mixing” or to rotational ambiguity. However, in the selected fPeak=-0.4 solution, the correlation between time-series of non-background factors is very low (R<0.2), suggesting that spikes from different emission sources were effectively separated (Figure A6.3). Factors with overall low intensity may still be susceptible to “mixing” and have a higher degree of uncertainty.
Choice of the number of PMF factors is subjective (Ulbrich et al., 2009). To choose the number of factors, I assessed $Q/Q_{exp}$ as a function of the number of factors (Figure A6.4); degree of “splitting” of factors (Figure A6.5); and allocation of key VOC ion masses of scientific interest. “Splitting” occurs when one physically meaningful factor is divided into two highly correlated factors; the division is not physically meaningful and is not desirable in a PMF solution. I ultimately selected a six-factor solution that includes four emission sources and two (split) background factors. With this solution, the only significant VOC variability unaccounted for is a single large spike of methanol that occurred in the middle of the experiment. This isolated enhancement may be from local industry and is not relevant to my analysis.

At least three factors are needed to reduce $Q/Q_{exp}$ to acceptable levels. The three factors include two vehicle emission sources (characterized by spikes and enhancements of alkanes) and a “background” source characterized by enhanced photochemical species and a gradual variation over the course of the experiment. These two vehicle emission factors are highly robust and are retained regardless of the number of factors chosen. A four-factor solution splits the “background” factor into two factors with highly correlated mass spectra and time series; the two split factors sum to the original background factor. A five-factor solution is able to account for spikes containing long-chain alkanes, which are particularly interesting. Six factors introduces a final isopropanol-containing factor. With more than six factors, the vehicle emission, long-chain alkane, and isopropanol factors are successively split. With eight factors, the long-chain alkane factor is split into two factors that have different mass spectra and time series, but the number of spikes in each factor is quite small and I was not confident that it would lead to a statistically supportable analysis. A larger data set would help to establish the robustness of such factors, and to distinguish between compositionally similar emission sources that in this analysis may be grouped into a single factor.
3. Results and discussion

3.1 PMF results and identification of factors

The selected PMF solution returned four factors of interest. Periods of high concentration in each of the four factors rarely overlap in time, and have significantly different chemical composition. A time series of the four factors and a few representative VOCs is shown in Figure 6.1. Factor profiles returned by PMF, and comparisons to laboratory measurements and literature profiles, are shown in Figure 6.2.

![Figure 6.1 Time series of selected VOCs (top), and PMF factors (bottom). For clarity only a portion of the time series is shown (full time series is approximately 4 hours).](image)

The factors were identified as (Factor 1) diesel exhaust; (Factor 2) gasoline exhaust; (Factor 3) gasoline vapor; and (Factor 4) unknown isopropanol-containing source. The first three factors were identified by comparison to NO$^+$ ToF-CIMS laboratory samples of fuels and vehicle exhaust, and to profiles published by Gentner et al. (2013). A description of the Gentner et al. (2013) profiles and their conversion to approximate NO$^+$ ToF-CIMS mass spectra is given in the appendix (A6.1).
Figure 6.2 Profile comparisons, shown as mass spectra, of different emission sources.
The four factors returned by PMF are shown in the top row. The second two rows show laboratory samples, using NO⁺ CIMS, of fuel composition and vehicle exhaust. The bottom row includes literature profiles from Gentner et al. (2013), converted to NO⁺ CIMS m/z space using approximate calibration factors.
The gasoline exhaust (factor 2) and gasoline vapor (factor 3) factors account for the majority of non-background VOC signal (60% and 20% of total ncps signal, respectively), which is consistent with the predominance of hydrocarbon emissions from gasoline vehicles in the Denver Metro Area (Pokharel et al., 2002). The Factor 2 gasoline exhaust profile is quite similar to the gasoline exhaust profile reported by Gentner et al. (2013), and is differentiated from Factor 3 (gasoline vapor) by high aromatic signal relative to alkane signal. The two gasoline vehicles sampled in the lab had profiles that differed from one another, and from the PMF gasoline exhaust factor. The 2014 Chevrolet Equinox emitted very high ethanol compared to other VOCs, while the 2014 Ford Fusion emitted little ethanol. The PMF gasoline exhaust factor has elements of both: relatively high ethanol, and a range of aromatics and small alkanes. The Factor 3 gasoline vapor profile is quantitatively similar ($R^2 = 0.97$) to our laboratory measurement of evaporated gasoline. I highlight that plumes of these two sources (gasoline exhaust and vapor) are well separated and rarely overlap.

Factor 1, which I have identified as diesel exhaust, accounts for 11% of non-background instrument signal and is distinguished from the gasoline sources by a series of high-mass alkanes extending to m/z greater than 200. These high-mass alkanes can also be seen in the laboratory sample of diesel headspace, in the Gentner et al. (2013) literature profile, and in the laboratory sample of the 2000 VW Jetta passenger diesel vehicle, and are characteristic of diesel fuel (Gentner et al., 2012). The distribution of high-mass (<C10) alkanes is qualitatively very similar between the Factor 1 PMF, diesel headspace, and VW Jetta samples. I identified this factor as diesel exhaust, rather than headspace, because it includes relatively high signal of a number of oxygenates, especially acetone, that are present in the “on-road” diesel profile from Gentner et al. (2013) but not in my laboratory headspace sample and published composition samples. The 2000 VW Jetta emitted relatively high amounts of acetone, but also emitted significant quantities of small aldehydes, especially acetaldehyde and propanal, that are missing from the Factor 1 PMF profile. There were not enough diesel vehicles sampled for the PMF tool to separate contributions from diesel vapor, diesel exhaust, or different types of diesel vehicles, so it is likely that this factor includes several types of
diesel vehicles with a variety of VOC emission profiles.

The fourth factor is dominated by isopropanol. Although windshield fluid has been reported as a source of alcohols (Legreid et al., 2007), our laboratory measurement of windshield fluid is quite different from the PMF isopropanol factor. I was not able to identify this factor. Some possible sources are windshield fluid with different composition from the laboratory sample, other vehicle-related product (e.g. gas line antifreeze), or a non-vehicle source from local industry.

3.2 Emission source correlation with other chemical measurements

Figure 6.3 (next page) shows the correlation of different PMF vehicle emission factors with other chemical measurements that were not included in the PMF analysis: CH₄, CO, CO₂, and N₂O. The gasoline exhaust factor correlates with CO with $R^2=0.89$, which further supports my interpretation of this factor. There is also positive correlation with $R^2 = 0.14$ between the gasoline exhaust factor and CH₄, and between gasoline exhaust and N₂O with $R^2= 0.59$. No enhancements were seen in the NH₃ measurement, possibly due to wall loss in the inlet (4 m of $\frac{1}{4}$" ID teflon line).

3.3 Relative ppb enhancements in source profiles compared to literature

In section 3.1, I qualitatively compared the PMF profiles, in units of instrument signal (normalized counts per second, or “ncps”), to laboratory and literature profiles. This was to identify the source of each PMF factor. However, NO$^+$ CIMS does not detect all VOCs with equal sensitivity (Koss et al., 2016), and it is difficult to use “ncps” profiles to quantitatively compare to the literature, or to use in modeling. Therefore, we calculated the mixing ratio (ppb) enhancements of 31 VOCs in each profile.

To calculate the relative mixing ratios of each VOC from each source, I did not rely solely on the factor profiles provided by PMF. The factor profiles from PMF work well for the qualitative identification described in section 3.1, but emission factors from PMF profiles can be problematic especially for compounds with low enhancements. Issues occur because rotational “mixing” between PMF factors cannot be entirely eliminated (section 2.3), and because small errors in estimating measurement uncertainty (noise) can lead to inaccuracy in the PMF profile enhancement.
I used the PMF time series of each source factor to create a “mask” for times during which that source was especially enhanced, and did not overlap with contributions from other sources. Then, using the mask, I determined the orthogonal-distance-regression (ODR) slope and correlation coefficient ($R^2$) between each VOC and the total VOC signal from that emission source. The slope gives the per-mol emission of that VOC species relative to other VOCs (detected by NO$^+$ CIMS) in that source, and the strength of the correlation indicates whether the compound was consistently highly enhanced. The emission profiles for gasoline vapor, gasoline exhaust, and diesel exhaust are in Table 6.4. I report the enhancements relative to toluene (ppb VOC/ppb toluene), which was significantly enhanced in each source and is also commonly reported in the literature.

Figure 6.3 Correlations between CH$_4$, CO, CO$_2$, N$_2$O and the PMF vehicle emission factors. Within each row, highlighted (bold, larger) points are when the PMF factor is elevated and no other PMF factor is present.
Table 6.4 Emission factors of VOCs from the gasoline exhaust, gasoline vapor, and diesel exhaust sources. The \( R^2 \) gives the correlation coefficient between VOCs and the PMF time series profile of each emission source, restricted to plumes from that source.

Figure 6.4a compares the NO\(^+\) CIMS on-road mixing ratio enhancement profiles to several vehicle emission profiles from the literature which include both evaporative and tailpipe emissions. The literature profiles include measurements in the Caldecott tunnel (Gentner et al., 2012; Gentner et al., 2013; Kirchstetter et al., 1999; Ban-Weiss et al., 2008; Kean et al., 2001), Gubrist tunnel (Legreid et al., 2007), Brisbane tunnel (Smit et al., 2017), and laboratory (May et al., 2014; Schauer et al., 2002; Yamada et al., 2015). As a whole, the literature profiles are similar to the gasoline exhaust and vapor profiles, and quantitatively can be reconstructed using a linear combination of the gasoline vapor and gasoline exhaust factors (Figure 6.4b).
Figure 6.4 VOC emission source profiles comparison to literature.
(a) Comparison of NO+ CIMS on-road gasoline vapor, gasoline exhaust, and diesel exhaust profiles (calibrated to ppb) with profiles from literature. NO+ CIMS profiles are shaded by VOC species correlation coefficient ($R^2$) with factor time trace; e.g. isopropanol is occasionally enhanced in the diesel time-series but overall does not correlate well with other diesel exhaust VOCs. (b) Literature profiles compared to linear combination of gasoline exhaust and gasoline vapor profiles.
3.4 Variability within sources

It is both important and interesting to know if there is variability within a source profile. Analysis of this variability can provide information about the precision of the PMF source identification, and whether several relatively similar, but ultimately different sources may have been grouped together.

To determine VOC compositional variability within the gasoline vapor and gasoline exhaust profiles, I used the “mask” described in Section 3.3 to select a large number of isolated plumes from each source. Seventy-nine gasoline exhaust plumes and forty-three gasoline vapor plumes were identified. Diesel exhaust plumes were much rarer, and were not encountered frequently enough to apply a similar analysis. This shortcoming is discussed further in Section 3.6, “Assessment of pilot study”. For each plume, the VOC compositional profile was determined, using the 183 VOC product ions that were used for the PMF analysis, and an additional six product ions. In a compositional profile, each VOC is described by the fraction of total signal it accounts for within a plume. The variability of the compositional profile between plumes can then be described by the variability of each VOC fraction.

This method of analysis is analogous to the “bootstrapping” often used in assessment of PMF results (Reff et al., 2007). In a bootstrapping assessment, the full data set is broken down into smaller sequential time periods. PMF is re-applied to each smaller time period, and the resulting factor profiles and time series are compared to the overall solution. If the factors from the smaller time periods differ significantly from the corresponding factor in the overall solution, this could indicate that the overall PMF solution is not particularly robust, or that the factor in the overall solution includes several different sources. For the statistical assessment described here, rather than selecting shorter time periods, individual plumes (= individual vehicles) are selected. This method is better suited to the characteristics of this data set: some periods of time contain no VOC enhancement, which would create a nonsensical bootstrapping result; additionally, variability within a plume is determined only by instrument precision, while variability between plumes could indicate real source variability.
An example of how variability is quantified is shown in Figure 6.5. In the gasoline exhaust factor resulting from the PMF analysis, ethanol (m/z 45.034 C_2H_5O^+) accounts for about 10% of the total ion signal. When many plumes are compared, it can be seen that ethanol generally comprises between 6% and 15% of total ion signal. The distribution of these fractions is normally distributed, is centered on 10%, and has a standard deviation of 0.014. The standard deviation of 0.014 is a measure of the precision of ethanol within this factor profile. Table 4 includes the standard deviation of each of the 31 calibrated VOCs for both the gasoline exhaust and gasoline vapor profiles. In Table 6.4, the standard deviations have been converted to a calibrated ratio to toluene, to indicate the uncertainty of the ratio. A few VOCs in the “gasoline vapor” profile, such as 1,3-butadiene, have very large standard deviations. These compounds are very poorly correlated with plumes of gasoline vapor and have a large degree of scatter even within a plume.

Figure 6.5. Variability of ethanol within the gasoline exhaust PMF profile.
(a) The gasoline exhaust profile resulting from PMF analysis. Each ion mass is described by the fraction of total signal it accounts for within that factor. The ethanol product ion, m/z 45.034 C_2H_5O^+, accounts for just under 10% of total signal. The colors in the mass spectrum indicate the chemical structure of the VOC and are the same as in Figure 6.2. (b) The ethanol fraction of signal within a plume was determined for 79 gas exhaust plumes. On average, ethanol accounts for just under 10% of the total signal, but ranges from 6% to 15% of the signal. The red line shows a Gaussian best-fit to this distribution. The standard deviation is reported as a measure of precision. (c) m/z 45.034 C_2H_5O^+ vs. total ion signal in all exhaust plumes, showing a high degree of consistency between plumes.
The composition of the gasoline exhaust factor is very consistent with respect to ethanol, C6-C10 aromatics, C6-C8 cycloalkanes, and C4-C9 alkanes (these groups comprise the majority of the signal in this factor). The composition of the gasoline vapor profile is consistent with respect to ethanol and C4-C9 alkanes, but the aromatics appear to have a bi-modal distribution: potentially, there are two highly similar sources that differ only in aromatics composition contributing to the gasoline vapor profile (Figure 6.6).

Figure 6.6. Variability of aromatics within the gasoline vapor source. Top row: histograms of the distribution of aromatics composition in different plumes. Bottom row: relationship between aromatics signal and total signal in various gasoline vapor plumes. Each color is a different plume.

3.5 Relative contributions to ambient air of emission sources

With this PMF analysis the relative contributions of different emission sources to the total on-road emissions of a particular VOC or class of VOCs can be determined. For example, it can be calculated how much of total ethanol emissions come from evaporation compared to exhaust.
Figure 6.7 shows the relative source contributions to ethanol, iso-pentane, cycloalkanes, and aromatics. The cycloalkane and aromatics categories are further subdivided into the contributions from different species in those categories. For example, the area in the pie chart marked “C7” in the “gasoline exhaust” fraction of the cycloalkanes shows that methycyclohexane and dimethylocyclopentane (C7 cycloalkanes) comprise about 1/3 of the cycloalkanes emitted by gasoline exhaust. It can be seen that larger cycloalkanes (C8 and C9 cycloalkanes) are more important in the emissions from diesel.

![Pie chart](image)

**Figure 6.7. Relative contributions of different emission sources to ethanol, cycloalkanes, and aromatics.**

About half of ethanol is emitted by gasoline exhaust, and one-third by gasoline vapor. The majority of aldehyde and ketone emissions come from gasoline exhaust (~50%), but a notable fraction (~20%) also comes from diesel exhaust. Aromatics are dominated by emissions from gasoline exhaust. Small alkanes, such as iso-pentane, however, have a significant contribution (~20-50%) from gasoline vapor. Cycloalkanes include contributions from diesel exhaust, gasoline exhaust, and gasoline vapor. Gasoline exhaust contributes about 50% of cycloalkanes regardless of molecular size, but gasoline vapor contributes a larger
fraction of small cycloalkanes (30% of methylcyclopentane) and less of large cycloalkanes (1% for C9 cycloalkanes). The opposite is true of diesel exhaust, which contributes about 50% of C9 cycloalkanes but less than 10% of methylcyclopentane. Alkene masses are relatively evenly split between gasoline exhaust and gasoline vapor.

Using the mixing-ratio enhancement profiles discussed in section 3.3, I also compared the NO$^+$ CIMS on-road profiles to emission ratios measured in ambient air in Los Angeles, CA during the 2010 CalNex campaign (Borbon et al., 2013). The emission ratios in the CalNex profile already account for the effects of chemistry. This comparison can help quantify the relative contribution of vehicle sources to different VOCs. The comparison also provides a second way to estimate how much of vehicular emissions comes from gasoline vapor vs. gasoline exhaust.

The CalNex emission ratio profile was reconstructed using a linear combination of the gasoline exhaust and gasoline vapor profiles (Figure 6.8, next page). The linear combination was determined by a best fit of:

$$\text{CalNexProfile} = a \times \text{GasVaporProfile} + b \times \text{GasExhaustProfile}$$

with “a” and “b” chosen to minimize the error between the reconstructed profile and the CalNex profile using least squares. We did not include the isopropanol and diesel exhaust profiles. Without identifying the isopropanol factor source, we cannot be sure that this source was also present in LA during the CalNex campaign. Additionally, it is dominated by one compound (isopropanol), so the addition to the best fit would just account for the isopropanol in the CalNex profile and not add much other information. The diesel profile was much smaller than the gasoline exhaust and vapor sources in our roadside measurements; also, adding it to the best fit does not significantly improve the results. We also excluded ethanol, isopropanol, and acetone from the best fit. These three compounds are clearly outliers and have suspected sources from solvents. The CalNex ethanol emission ratio is also so large that including it pulls the best fit results away from the other compounds, making the analysis of other compounds less certain.
The linear combination of a gasoline exhaust + b gasoline vapor is able to account for aromatics, alkanes, alkenes, and some carbonyls in the CalNex profile ($R^2 = 0.86$, excluding ethanol, isopropanol, and acetone). Isopropanol, hexanals, benzaldehyde, acetone, and MEK are greatly underpredicted by the vehicle-exhaust best fit, and have other sources, likely solvent use. The larger cyclic alkanes are overpredicted, possibly because only a few isomers were included in the CalNex profile. The best fit also
suggests the relative contributions of gasoline exhaust and vapor to total emissions of each VOC. Aromatics are emitted mainly by gasoline exhaust (80% by mol), while small alkanes and ethanol include a larger fraction from gasoline vapor (71% and 65%, respectively). This is qualitatively consistent with the calculation of relative contributions to emissions of different VOC species in the on-road measurements in the first part of this section, in that aromatics are dominated by gasoline exhaust while ethanol and small alkanes have substantial contribution from gasoline vapor.

3.6 Assessment of pilot study: recommendation for future work

I have demonstrated application of NO$^+$ CIMS to on-road measurement of individual vehicle emissions. Application of PMF to NO$^+$ CIMS data can be used to identify important classes of emissions, and can provide emission profiles of important VOCs. Future experiments need to include additional instrumentation, such as a NO$\textsubscript{x}$ monitor with high time resolution, which would be helpful for source identification and providing information useful to inventory assessments and modeling.

Too few vehicles were sampled during the roadside measurement to robustly identify sub-categories based on their VOC emission profiles. This is especially true of the diesel vehicle category. A longer sampling period, and possibly sampling during different seasons, is highly desirable. Laboratory samples of exhaust from more types of vehicles, under different engine load, might also help to interpret the highway in-situ sampling. I especially recommend sampling of a larger (non-passenger) diesel vehicle.

Because of light, variable wind speeds, plumes of vehicle exhaust measured by the UV/IR cross-road beam system were not always measured with the NOAA mobile laboratory chemical instrumentation. The time of interception of the plume also occurred at different times for the two sets of instrumentation. Therefore, we were not able to combine the two data sets well during such a limited measurement period. Measurements need to be done during days with consistent high wind speed in an appropriate direction. This would allow the combination of the two data sets. Once combined, the VOC measurements can be related to the large dataset collected by Bishop and Stedman (2008) in order to use the statistical information about vehicle type, age, and high emitters.
4. Conclusions

On-road vehicle emissions from individual cars were measured using NO⁺ ToF-CIMS. PMF was used to separate and identify emission sources. Four major sources were identified: gasoline exhaust, gasoline vapor, diesel exhaust, and an unidentified source of isopropanol. The comparison between the PMF vehicle emission profiles and profiles from literature and laboratory samples confirms the source identifications.

I was able to determine the relative contributions of different emission sources to a number of VOCs. I found a surprisingly high contribution of evaporated gasoline relative to gasoline exhaust for many important compounds, especially ethanol and small alkanes. For example, gasoline vapor contributed half of isopentane emissions and a third of ethanol emissions. Aromatics were dominated by gasoline exhaust. Diesel exhaust was small compared to gasoline exhaust, but accounted for a third of cycloalkane emissions. Similar results were found by comparing the gasoline vapor and gasoline exhaust profiles to measurements of emission factors of ambient air in Los Angeles (CalNex measurement). This comparison also emphasized that many oxygenates clearly have non-vehicle sources.

Despite a relatively short data collection time (~4 hours), this experiment resulted in a scientifically interesting data set. NO⁺ ToF-CIMS is ideal for in-situ, fast measurement of vehicle-related VOCs. The instrument has time resolution fast enough to capture individual plumes, and high enough sensitivity to produce detailed emission profiles. The ability of NO⁺ CIMS to detect alkanes, cyclic alkanes, and long-chain alkanes was essential to distinguishing and characterizing different emission sources. Minor changes to the experimental setup, and longer measurement, would provide more robust and detailed results. This application is highly promising and could contribute significantly to our understanding of vehicle emissions.
Chapter 7. Summary and Conclusions

Use of fossil fuels, and their atmospheric impacts on global, regional, and local scales, is one of the defining issues of modern environmental chemistry. There has been tremendous success in improving local and regional air quality through tighter controls on vehicle emissions. At the same time, developments in the production phase of the life cycle of fossil fuels have sparked new concerns about air quality. Volatile organic compounds have a central role in these air quality issues. Detailed and reliable measurements of these species can help us to understand emissions and oxidation chemistry, and are crucial to making informed policy decisions.

In this thesis I have described the development and application of mass spectrometric tools to measure VOCs associated with fossil fuels. During the course of this work, we have made significant advances in our ability to measure VOCs, including the development of the H$_3$O$^+$ ToF-CIMS instrument, which provides measurement of many more species, and the development of NO$^+$ reagent ion capability, which enables measurement of species that are not easily measureable with PTR-MS. The applications of CIMS tools have focused on VOC emissions and chemistry in oil and gas-producing regions, which have experienced a recent increase in production and associated air quality issues. I have additionally described a pilot study using NO$^+$ CIMS to study vehicle emissions.

Chapter 1 described the deployment of a quadrupole PTR-MS instrument during the Uintah Basin Winter Ozone Study in 2013. This atmospheric chemistry situation was interesting because enhanced carbonyl photolysis chemistry led to very high winter ozone concentrations (Edwards et al., 2014). I used a simple box model relying on VOC ratios to investigate the photochemical aging of the aromatic compounds measured by PTR-qMS. Despite its simplicity, the box model provided very reasonable values for the emission rate of primary compounds, the composition of primary emissions, and the concentration of ambient OH. This method could be a useful tool to understand VOC chemistry in other situations where inversions trap pollution in an enclosed basin. The analysis of the oxygenated and photochemically produced compounds measured by PTR-qMS was less straightforward. The ability of a similar box model
to reproduce the behavior of acetone, formic acid, and other secondary oxygenates was not especially satisfying. It was also clear that methanol and formaldehyde had behavior quite different from that of other small oxygenates – possibly indicating a large primary source of these compounds.

Finally, I used a full suite of gas phase, snowpack, and aerosol measurements to try to reveal the existence of unquantified secondary species, and constrain their concentration. Unquantified secondary species certainly existed – their product ions were detected with a PTR-ToF-MS. Constraining these species is an important aspect of VOC measurement. We would like to know if our instrumentation captured a significant portion of reactive carbon, and whether we understand the mechanisms by which photochemical species are formed. I investigated these species through carbon mass balance, and investigated the rate of oxidation of primary compounds. My assessment of the carbon mass balance is that without much better constraints on physical loss mechanisms, it is not a good approach to closing the carbon budget. Analysis of the rates of primary species oxidation and secondary species formation suggested that unquantified species were forming at a significant rate. In retrospect, this method probably includes too many simplifying assumptions to be usefully quantitative. Concurrently with the work described in Chapter 2, Yuan et al. (2015) investigated the formation of formic acid during the UBWOS 2013 campaign using a very highly detailed chemical model. Even with the inclusion of a number of new gas-phase reaction pathways, air-snow exchange processes, and aerosol reactions, the detailed chemical model was able to explain less than half the formation of formic acid.

Clearly, our understanding of VOC oxidation chemistry in oil and gas-producing regions is incomplete. One of the ways we can help resolve this problem is through improved measurement of VOCs. The deployment of the PTR-ToF instrument at the Uintah Basin site demonstrated the advances possible with this type of instrument (Warneke et al., 2015). We developed a custom-built PTR-ToF instrument (the NOAA H$_3$O$^+$ ToF-CIMS) based on the Aerodyne CIMS. This instrument is designed to be deployable on a mobile platform, and had significantly higher sensitivity than instruments commercially available at the time (such as the PTR-ToF instrument deployed in Utah). We extensively characterized the sensitivity,
performance, and behavior of this instrument, including the effects of the RF-only segmented quadrupole ion guides and the response to changing ambient humidity (Chapter 3). The rate of PTR-MS development has been rapid. At the time of writing this thesis, new instruments have been developed that have even higher sensitivity (Sulzer et al., 2014) and higher mass resolving power (ToFWERK, 2017). The characterization described in this chapter (and published in Yuan et al. (2016a)) will be useful to operators of these instruments, as well as PTR-ToF.

The new H$_3$O$^+$ ToF-CIMS was deployed on the NOAA WP-3D aircraft during the SONGNEX 2015 campaign, which surveyed a number of oil and gas producing regions across the United States. In Chapter 4, I described the VOCs and other species measured with the H$_3$O$^+$ ToF-CIMS. Some species, such as aromatics, methanol, and small carbonyls, have been frequently measured with PTR-qMS, but the H$_3$O$^+$ ToF-CIMS allowed the measurement of these species with much higher spatial resolution. I provide a comparison of these species between nine oil and natural gas producing regions. Aromatics concentrations were highly variable, and the statistics of their mixing ratios within basins indicates the importance of large point sources as well as smaller distributed sources. Average aromatics concentrations were frequently as high as those measured downwind of large urban areas. Methanol was universally the most abundant VOC measured by the H$_3$O$^+$ ToF-CIMS. The overall highest mixing ratios of VOCs were encountered in the Permian Basin, a large oil and natural gas field that covers a large part of West Texas and East New Mexico. Despite being the largest oil field in the United States, and the field with the highest production, the atmospheric chemistry of this region has not been thoroughly investigated and very few VOC measurements exist. We detected many species not usually measured by PTR-qMS, including cycloalkane oxidation products, cyclic nitrogen-containing organics, and high concentrations of hydrogen sulfide.

Much more analysis will done with the measurements taken during SONGNEX, and the work described in this chapter is necessary groundwork for the use of the H$_3$O$^+$ ToF-CIMS data. In addition to the overview of SONGNEX measurements, this work provides a guide to interpreting PTR-ToF measurements in oil and gas producing regions.
Some species important to the VOC chemistry of fossil fuels are not easily measurable by PTR-MS. These species include alkanes, cyclic alkanes, and alcohols; additionally, PTR-MS cannot provide separate measurement of isomers such as ketones and aldehydes. Some previous work had been done investigating the use of NO$^+$ ionization chemistry to overcome these difficulties (Inomata et al., 2013b; Wyche et al., 2005) and developing PTR-MS instruments capable of switching to NO$^+$ ion chemistry (Jordan et al., 2009a), but this technique had not been used extensively in the field. I modified the PTR-qMS and H$_3$O$^+$ ToF-CIMS instruments to use NO$^+$ ionization chemistry (Chapter 5). Using a combination of laboratory and ambient sampling with GC-CIMS and parallel GC-MS and NO$^+$ ToF-CIMS, I assessed the sensitivity and specificity of a large number of NO$^+$ VOC product ions. NO$^+$ CIMS can provide fast, sensitive, and chemically specific measurements of ethanol and a number of small branched alkanes, cyclic alkanes, aldehyde and ketone isomers, and long-chain alkanes.

These are exactly the kinds of VOCs expected from vehicle exhaust. In a collaboration with researchers from the University of Denver, we ran a pilot study using the NO$^+$ ToF-CIMS deployed in a mobile laboratory to sample emissions from highway vehicles in a real-world situation. The fast time response of the NO$^+$ ToF-CIMS allowed us to measure individual plumes from separate vehicles. Application of positive matrix factorization clearly identified several important classes of emissions and their VOC composition. This study will be continued in the near future to collect more data on a wider range of vehicles, and to tie the NO$^+$ ToF-CIMS measurements to vehicle characteristics.

The work described in this thesis has applications beyond measurement of VOCs associated with fossil fuels. In Fall of 2016, we used the H$_3$O$^+$ ToF-CIMS, NO$^+$ ToF-CIMS, and GC-CIMS instruments and techniques described in this thesis to characterize biomass burning emissions at the Forest Service Fire Sciences Laboratory in Missoula, Montana. These new techniques provided far more chemical information than has been previously available. In the future, I expect these techniques will greatly improve our understanding of VOCs in the atmosphere.
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Appendix 1. Supplemental information for Chapter 3: Development of H$_3$O$^+$ ToF-CIMS instrument

Figure A3.1. H$_3$O$^+$ ToF-CIMS inlet diagram.

Figure A3.2. MCP voltage setting over several years. Time periods of various instrument development projects and field missions are marked on the graph. Crystal ball prediction: someone else will have to change the MCP in November.
Figure A3.3. Behavior of primary ions (left) and VOC ions (right) as a function of BSQ RF amplitude. The selected setting of 350V is shown by the gray dashed line.

Figure A3.4. Standard deviation vs. signal for VOC calibrations. The cps signals are not-duty cycle corrected.
Figure A3.5. Comparison of VOC sensitivity in the original instrument (with SSQ) and modified instrument (without SSQ).
Non-duty-cycle-corrected cps are shown. The 10 compounds measured with the 10-component transfer standard are highlighted in red. These species have been calibrated many times with both the original and modified instruments, and the standard deviations (typically 10%) are shown with the error bars.
Appendix 2. Supplemental information for Chapter 4: Observations of VOC emissions and chemical products over US oil- and gas-producing regions using high-resolution H$_3$O$^+$ CIMS (PTR-ToF-MS)

A4.1. Peak fitting errors: data quality assessment

At the resolution of the H$_3$O$^+$ ToF CIMS instrument (~4000 m/dm), peaks at the same nominal mass frequently overlap. To separate the contribution from overlapping peaks at the same nominal mass, the Tofware peak fitting software (Aerodyne Resarch Inc./Tofwerk AG) iteratively fits a set of pseudo-gaussian high-resolution peaks to the sum signal across that nominal mass. The number of peaks at a given nominal mass, the peak shape, and the exact m/z of each peak center are user-defined. However, problems can occur in circumstances where a peak is much smaller than its neighbor, or where the m/z separation between peaks is unusually small. Under these circumstances, the returned peak-fit intensity can be highly inaccurate. The magnitude of the error depends on the relative size, closeness in m/z space, mass calibration precision and accuracy, and peak shape of the overlapping peak, and so it can change over time. These nonrandom errors can create false variability in a particular ion mass. This peak fitting issue is well known for both CISM and AMS instruments but has not yet been completely addressed (Müller et al., 2011; Cubison and Jimenez, 2015; Stark et al., 2015; Corbin et al., 2015b).

Although there is not yet a quantitative method to determine the extent and magnitude of peak overlap errors in every situation, Tofware provides qualitative assessment tools that rely on the dependence of peak-fitting error on mass calibration precision (Timonen et al., 2016). Several studies have suggested that mass calibration precision and accuracy are strong controls on peak fitting error (Corbin et al., 2015b; Cubison and Jimenez, 2015). When applied to a particular high-resolution peak, the tool re-calculates the fitted peak intensity for a range of expected error in the mass calibration (±10 ppm). Peaks that are strongly affected by peak overlap error will have highly variable fitted peak intensity. All high-resolution peaks reported in this work are not strongly affected by peak fit error, i.e., the fitted peak intensity is independent of mass calibration uncertainty.
A4.2. Limit of detection calculation

The measured instrument signal (ion counts) is the product of the measurement time $t$, the sensitivity $C_f$, and the concentration $[X]$:

$$S = C_f[X]t$$

Instrument noise is related to the square root of the signal:

$$N = \sqrt{S} = \sqrt{C_f[X]t}$$

The signal to noise ratio is therefore:

$$\frac{S}{N} = \sqrt{\frac{C_f[X]t}{C_f[X]t}} = \sqrt{C_f[X]t}$$

We define the “limit of detection” as the concentration $[X]$ at which the signal to noise ratio $(S/N)$ equals 3:

$$\frac{S}{N} = 3 = \sqrt{C_f[X]_{LOD}t}$$

By solving for $[X]_{LOD}$, it can be seen that the limit of detection is inversely proportional to the measurement time:

$$[X]_{LOD} = \frac{9}{C_ft}$$

This is different from noise, which decreases as the square root of the measurement time.

For several reasons, the measurement limit of detection is actually somewhat higher than the calculations above would suggest. First, there is some background count rate $B$, and the VOC signal is determined from the difference between the ambient signal and the background signal. Second, because of additional error from high-resolution peak fitting, the noise is somewhat higher than the square root of the signal. To account for this additional error, a linear scaling factor $\alpha$ is included in the calculation of noise.

With the inclusion of the background $B$ and scaling factor $\alpha$, the signal to noise calculation is (Bertram et al., 2011):
The detection limit \( |X| \) can then be solved for using the quadratic equation. Detection limits given in this work were calculated using raw counts-per-second, without reagent ion normalization or a ToF duty-cycle correction applied.

### A4.3. Photochemical aging analysis

The relative ratios of different VOCs can be used to establish relative photochemical aging. Using PTRMS measurements of C6-C10 aromatic species, this method has been applied to photochemical aging of VOCs in urban areas (de Gouw et al., 2005; Warneke et al., 2007) and in an oil and gas producing region (Koss et al., 2015). Benzene (C6 aromatic), has the slowest reaction rate with OH; as the cumulative OH exposure of an air mass increases, the ratios of other aromatics to benzene should decrease. The ratio of an aromatic VOC to benzene at time \( t \) can be written as:

\[
\left( \frac{VOC}{\text{Benzene}} \right)_t = \left( \frac{VOC}{\text{Benzene}} \right)_0 \times e^{(k_{\text{benzene}} - k_{\text{VOC}}) \int_0^t [OH] dt}
\]

Where \( \left( \frac{VOC}{\text{Benzene}} \right)_0 \) is the ratio of the aromatic to benzene at time \( t=0 \), \( k_{\text{benzene}} \) and \( k_{\text{VOC}} \) are the rate constants of benzene and the aromatic with OH, and \( \int_0^t [OH] dt \) is the integrated OH exposure. If the ratio at time \( t \), the emission ratio, and the OH rate constants are known, the integrated OH exposure can be calculated.

I restricted this analysis to the three plume transects in the southwest portion of the flight survey. These three plumes have similar VOC composition, are located close to one another, and can be reasonably assumed to be the same air mass. The flight was from south to north, so the northmost transect was latest in the day. The ratios of C7-C10 aromatics decrease from south to north (Figure SI 1).

I calculated integrated OH exposure in each of the three transects using toluene, C8 aromatics, C9 aromatics, and C10 aromatics. OH rate constants for C8, C9, and C10 aromatics were taken from Koss et al. (2015). OH rate constants for benzene and toluene were taken from Atkinson and Arey (2003). The average of the highest 5% points in the southmost transect was used as the ratio at time \( t=0 \). We note that
in this analysis, time $t=0$ is not necessarily the time of emission. We set time $t=0$ to be the age of the least aged air mass. The exact emission ratio is not relevant to the analysis of pyrrole presented in the manuscript, since we are mainly interested in the relative rate of aging.

The calculated OH exposures from C7-C10 aromatics were averaged to give the final OH exposure used in the analysis. The separately calculated OH exposures were within 40% of the mean. The OH rate constant for pyrroline was calculated using an exponential best fit to the pyrroline:benzene ratio as a function of the integrated OH exposure.

Figure SI 1. Aromatics and photochemical aging in the southwest section of the flight survey. (a) concentration of toluene. (b) ratio of toluene to benzene. (c) integrated OH exposure. In the highlighted (colored) section of the flight track, the markers are sized and colored by the integrated OH exposure.
A sensitivity analysis for the calculated pyrroline OH rate constant is given below:

<table>
<thead>
<tr>
<th></th>
<th>OH rate constant, cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>Emission ratio pyrroline:benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original calculation</td>
<td>$1.72 \pm 0.14 \times 10^{-11}$</td>
<td>$0.126 \pm 0.006$</td>
</tr>
<tr>
<td>Using maximum OHdt calculated from all aromatics</td>
<td>$1.39 \pm 0.11 \times 10^{-11}$</td>
<td>$0.142 \pm 0.008$</td>
</tr>
<tr>
<td>Using minimum OHdt calculated from all aromatics</td>
<td>$1.78 \pm 0.17 \times 10^{-11}$</td>
<td>$0.096 \pm 0.004$</td>
</tr>
<tr>
<td>Actual concentration 2x lower</td>
<td>$1.72 \pm 0.14 \times 10^{-11}$</td>
<td>$0.252 \pm 0.012$</td>
</tr>
<tr>
<td>Actual concentration 2x higher</td>
<td>$1.72 \pm 0.14 \times 10^{-11}$</td>
<td>$0.063 \pm 0.003$</td>
</tr>
</tbody>
</table>
Figure A4.2. Data selection based on flight altitude for each flight.
Figure A4.3. Distribution of acetaldehyde, acetone, MEK, and acetic acid during each flight.
Figure A4.4 PTR-ToF-MS measurement of m/z 137 C<sub>10</sub>H<sub>16</sub>H<sup>+</sup> and m/z 81 C<sub>6</sub>H<sub>9</sub>* during the UBWOS 2013 campaign in the Uintah oil and gas field, Utah.

The right two panels show the ion ratios to benzene, which indicate whether they belong to primary or photochemically produced species. We note that frequently, m/z 137 C<sub>10</sub>H<sub>16</sub>H<sup>+</sup> is interpreted as monoterpenes, and m/z 81 C<sub>6</sub>H<sub>9</sub>* as a monoterpene fragment (e.g. Kim et al. (2010)). In both Utah (UBWOS 2013) and the Permian (SONGNEX 2015) these two masses are uncorrelated, and m/z 81 has much higher intensity than m/z 137.
Figure A4.5 Potential diamondoid ion masses in SONGNEX measurement (top), headspace of West Texas Crude (middle), compared to reported distribution of diamondoids (bottom) (Stout and Douglas, 2004). Diamondoid masses are the bold sticks in the mass spectra. The three distributions are somewhat different. This could be because: (1) the $\text{C}_{10}\text{H}_{16}^+$ detected during SONGNEX is not a diamondoid; (2) inlet effects reduced the measured amount of higher molecular weight species; (3) distribution of diamondoids in other fuels can differ from that presented by Stout and Douglas (2004); (4) The higher molecular weight species have a shorter atmospheric lifetime.
Figure A4.6 Comparison of $\text{H}_3\text{O}^+$ ToF-CIMS masses m/z 77 $\text{C}_2\text{H}_4\text{O}_3\text{H}^+$, m/z 91 $\text{C}_3\text{H}_6\text{O}_3\text{H}^+$, and m/z 46 $\text{NO}_2^+$ to various reactive nitrogen species during the April 23 SONGNEX flight. Ten-second average data is shown for clarity. For the comparison to small alkyl nitrates, the $\text{H}_3\text{O}^+$ ToF-CIMS data has been averaged to the iWAS sampling times. Small differences exist between the CaRDS and Chemiluminescence measurements; these were averaged where both were available. The choice of $\text{NO}_x$ and $\text{NO}_y$ data source does not affect my conclusions.
Figure A4.7 $\text{H}_3\text{O}^+$ ToF CIMS m/z 46 NO$_2^+$ tracer measurements compared to PAN. The high m/z 46 during the 4-21 Bakken flight was within an aged biomass burning plume (identified by enhanced acetonitrile).

Figure A4.8 Further comparison of $\text{H}_3\text{O}^+$ ToF-CIMS masses to NO$_z$ species. (a) $\text{H}_3\text{O}^+$ ToF-CIMS m/z 46 compared to NO$_z$ from all flights, colored by the fraction of NO$_z$ accounted for by PAN. (b) $\text{H}_3\text{O}^+$ ToF-CIMS m/z 77 compared to PAN from all flights, colored by relative humidity proxy m/z 37 $\text{H}_5\text{O}_2^+$:m/z 19 $\text{H}_3\text{O}^+$. 
Figure A4.9 Comparison of the distribution of unsaturated nitrogen species C_xH_{2x+1}NH^+ between (a) oil- and gas-related VOCs measured during the April 23 Permian flight, and (b) a biomass burning plume encountered during the April 21 Bakken flight. The series is m/z 28 HCNH^+, m/z 42 C_2H_3NH^+, m/z 56 C_3H_5NH^+, m/z 70 C_4H_7NH^+, etc. The values shown are the average signal enhancement (ncps enhancement) in the boundary layer during the Permian flight, and the average signal enhancement (ncps enhancement) in the biomass burning plume compared to immediately before the plume during the Bakken flight.

A4.4. Comparison of nitrate reactivity to literature

The estimated average pyrroline nitrate reactivity is $15 \times 10^{-3} \text{s}^{-1}$ (assuming the same nitrate reaction constant as pyrrole).

For comparison, Stutz et al. (2010) measured nocturnal nitrate loss rates in Houston, TX in an area influenced by emissions from the petrochemical industry. Total nitrate loss frequency was typically around 20 to $60 \times 10^{-3} \text{s}^{-1}$ during the middle of the night. VOC nitrate reactivity ranged from 0 to $50 \times 10^{-3} \text{s}^{-1}$ and was typically the dominant loss mechanism. Indirect loss via $\text{N}_2\text{O}_5$ uptake to aerosol was the second most important pathway and ranged from 0 to $40 \times 10^{-3} \text{s}^{-1}$.

Crowley et al. (2011) measured nocturnal nitrate loss frequency in polluted air in Spain. Total nitrate loss frequency was on the order of $5 \times 10^{-3} \text{s}^{-1}$ to $50 \times 10^{-3} \text{s}^{-1}$. Loss of $\text{NO}_3$ to VOCs, and loss via $\text{N}_2\text{O}_5$ uptake to aerosol were both important loss mechanisms, each on the order of $5 \times 10^{-3} \text{s}^{-1}$.

Conversely, (Tsai et al., 2014) found that loss via $\text{N}_2\text{O}_5$ uptake to aerosol accounted for nearly all of the typically $50 \times 10^{-3} \text{s}^{-1}$ $\text{NO}_3$ loss in the Los Angeles metropolitan area.
Appendix 3: Supplemental information for Chapter 5: Evaluation of NO$^+$ reagent ion chemistry for on-line measurements of atmospheric volatile organic compounds

Figure A5.1. Ion source and drift tube schematic.
Figure A5.2. Ion guide voltage settings.
The top panel shows the absolute voltage setting (from ground); the middle panel highlights the changes in voltage potential between H$_2$O$^+$ and NO$^+$ settings, and the bottom panel is a cartoon of the ion guide section taken from the CI-API manual (Aerodyne Inc./Tofwerk AG). The horizontal (axial) distances are not to scale.
Figure A5.3. (a) Background and ambient measurements taken during urban air sampling with the NO$^+$ ToF-CIMS. (b) Example multiple-point calibrations of the NO$^+$ ToF-CIMS showing sensitivity linear with concentration.
Figure A5.4. Comparison of product ion distributions between NO\(^+\) CIMS and H\(_3\)O\(^+\) CIMS. The complete product ion distribution of \(n\)-propylbenzene is shown as an example of a compound with a complex mass spectrum resulting from H\(_3\)O\(^+\) chemistry, and a simple mass spectrum resulting from NO\(^+\) chemistry.
Table A5.1. VOCs sampled in series GC-ToFCIMS laboratory experiments.

<table>
<thead>
<tr>
<th>VOC name</th>
<th>Formula</th>
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<td><strong>alkanes</strong></td>
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<tr>
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Figure A5.5. Product ion distributions of selected aliphatic hydrocarbons, at a relative humidity of 20%.

Figure A5.6. Example chromatograms and relative sensitivity calculation of ethanol for Table 5.2.
Figure A5.7. Humidity dependence of primary ions and VOCs.
(a) Impurity ions and water clusters. (b) Carbonyls. (c) Aromatics. (d) Acetonitrile. Acetonitrile is detected with poor sensitivity using NO$^+$; the NO$^+$ and H$_3$O$^+$ products are approximately equal in magnitude.
Figure A5.8. Speciated contributions to various NO$^+$ CIMS masses, in urban air. Values on Y-axes are the fractional contribution of each VOC to total signal. Includes m/z 41 - m/z 78.
Figure A5.8, continued. Includes m/z 82-m/z 111.
Figure A5.8, continued. Includes m/z 113-m/z 144.

Figure A5.9. Example isobaric interferences for heptanone measured with H$_3$O$^+$ CIMS, at m/z 115 C$_7$H$_{14}$OH$^+$, and with NO$^+$ CIMS, at m/z 144 C$_7$H$_{14}$ONO$^+$. Although the resolution m/dm is better at m/z 144, there are more possible isobaric interferences and the average distance to neighboring peaks is smaller. The m/z range of each window is 10 FWHM. H$_3$O$^+$ ToF-CIMS mass spectrum courtesy of M. Coggon, collected in Boulder, CO in Dec. 2015.
Appendix 4. Supplemental information for Chapter 6: Direct measurement of on-road VOC emissions from vehicles using NO⁺ ToF-CIMS

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Figure A6.1. Seed effect on Q/Q_{exp}.
Figure A6.2. FPEAK effect on Q/Q\text{exp}.

Figure A6.3. Correlations between different factors as a function of FPEAK.
Figure A6.4. Effect of number of factors on $Q/Q_{\text{exp}}$.

Figure A6.5. Effect of number of factors selected on factor “splitting”.
A6.1 Literature VOC profiles: conversion to m/z space

Gentner et al. (2013) provide highly chemically speciated profiles of gasoline and diesel exhaust, derived from on-road measurements of vehicle exhaust in the Caldecott tunnel, California, in 2010; and of gasoline and diesel exhaust, derived from laboratory measurement of fuel composition. These profiles are the most chemically detailed we were able to discover in a literature search. The Gentner et al. profiles are provided in terms of relative mass concentrations. To compare more directly to measurements taken by NO⁺ ToF-CIMS, we converted the literature profiles to molar concentration, then applied sensitivity factors and product ion patterns determined in Koss et al. (2016). Where product ions, fragmentation and sensitivity were not known, we estimated using VOCs of similar size and functional group. The resulting profiles are likely “skewed” somewhat due to uncertainty in fragmentation pattern and sensitivity factor, so comparison to these literature profiles should be only qualitative. The “diesel exhaust” profile from Gentner et al. shown in Figure 2 is an average of the on-road and laboratory profiles of diesel exhaust; the two published diesel profiles differ significantly.