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RICE UNIVERSITY

Atmospheric Carbonyl Compounds in Rural and Urban Texas: Formation, Methodology, and Statistical Modeling

by

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A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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ABSTRACT

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Atmospheric carbonyl compounds, specifically aldehydes and ketones, were measured in both rural and urban regions in Texas. The biogenic or rural study examined the extent of conversion from primary biogenic hydrocarbons to secondary carbonyls. The anthropogenic or urban studies investigated techniques for measuring carbonyl compounds; statistical modeling was applied in one such study to elucidate the primary and secondary contributions to formaldehyde formation.

From the biogenic study, the spatial variation of isoprene and its reaction products’ concentrations are strong functions of the immediate land cover. Spatial differences between sampling sites need to include NO\textsubscript{x} data to account for urban and rural influences. Finally, both ozone attributable to biogenic hydrocarbon oxidation and ozone formation potential are predicted to be insignificant under high VOC/NO\textsubscript{x} ratios typical of rural areas, but may be important under conditions where NO\textsubscript{x} levels are elevated.

From the anthropogenic studies, a daylong sampling period sufficiently captures persistent low-lying carbonyl levels, but overlooks small scale fluctuations. Furthermore, the low concentration precision limit of real-time sampling through a DFG sensor produces similar bias as time-integrated wet chemical quantification, and validates the use of the DFG system for urban atmospheric studies. Finally, two distinct statistical models attribute nearly two-thirds (ratio 1.75) of HCHO formation to secondary VOC reactions, and one-third to primary emissions.
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CHAPTER 1

INTRODUCTION

1.1. OVERVIEW

Atmospheric pollution leads to adverse effects on human health, plants and materials, and visibility (Leithe, 1971; Majumdar et al., 1991; Seinfeld and Pandis, 1998). Pollutants are found throughout the troposphere (lower atmosphere) and stratosphere (upper atmosphere, above ~10-15 km) as a result of both anthropogenic activity and emissions from natural sources. As atmospheric pollutants are transported without boundaries, it is important to determine pollutant concentrations not only in heavily populated urban centers but also in rural sites to isolate the importance of transport versus local emissions. The ultimate goal of such studies is to assess the importance of source emissions via accurate ambient measurement techniques to better understand how proposed air quality improvement plans might affect ambient air quality.

Pollutants fall into several classifications based on chemical composition, under the broader categories of gaseous and particulate pollutants. A list of gaseous air pollutants and examples of each is found in Table 1.1. These compounds are divided into primary and secondary categories; primary compounds are directly emitted from a source while secondary pollutants are formed from atmospheric chemical reactions of directly emitted species.

1.2. RESEARCH OBJECTIVES

The focus of this work is on the class of volatile organic compounds (VOCs) known as carbonyl compounds, specifically aldehydes (RCHO) and ketones (R₁COR₂), where the
defining characteristic is the C=O double bond. Concentrations of several carbonyls, including formaldehyde (HCHO), acetaldehyde (CH₃CHO), and methacrolein

<table>
<thead>
<tr>
<th>Class</th>
<th>Primary Pollutants</th>
<th>Secondary Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile organic compounds</td>
<td>H-C compounds</td>
<td>ketones, aldehydes, acids, organic aerosols</td>
</tr>
<tr>
<td>Sulfur-containing compounds</td>
<td>SO₂, H₂S</td>
<td>SO₃, H₂SO₄</td>
</tr>
<tr>
<td>Nitrogen-containing compounds</td>
<td>NO, NH₃</td>
<td>NO₂, HNO₃, (NH₄)₂SO₄(s)</td>
</tr>
<tr>
<td>Oxides of carbon</td>
<td>CO</td>
<td>--</td>
</tr>
<tr>
<td>Halogen compounds</td>
<td>HCl, HF</td>
<td>--</td>
</tr>
<tr>
<td>Photochemical oxidants</td>
<td>--</td>
<td>O₃, NO₂, H₂O₃, peroxycetyl nitrate</td>
</tr>
</tbody>
</table>

(CH₂C(CH₃)CHO), were measured in three rural sites and one urban site in Central Texas in a 1998 study. These compounds were simultaneously measured with the primary biogenic hydrocarbon isoprene (CH₂CHC(CH₃)CH₂). The objectives of the study were:

1. to examine the extent of conversion from primary biogenic hydrocarbons to secondary carbonyls and
2. to determine the ozone-forming potential of rural and urban regions.

This study is discussed in Chapters 3 and 4.

In addition to the study on rural carbonyls, additional sampling was completed to understand the importance of anthropogenic formation of atmospheric carbonyls (specifically formaldehyde) in Houston. The objectives of the various studies included:

3. continuing progress on a new quantification technique using chemical methods, particularly derivatization with a benzyl agent followed by mass spectrometric detection; this methods analysis is discussed in Chapter 5;
4. determining the accuracy and precision of traditional integrating sampling methods against a novel system for real-time formaldehyde quantification through an intercomparison study, discussed in Chapter 6; and

5. using statistical modeling to elucidate the primary and secondary contributions to formaldehyde formation, as well as establish a lead-lag relationship between formaldehyde and primary/secondary compounds (Chapter 7).

The results from the methods studies validated the need for real-time collection and provided a statistical basis from which to interpret pollutant data; the results are applicable not only at a given site but can be extrapolated to a larger region.

1.3. MOTIVATION

It is critical to study carbonyls, as these compounds are often the first stable intermediates in organic photooxidation mechanisms. The types and concentrations of carbonyls present in an airshed lend insight into atmospheric photochemistry, and can be used to quantify the extent of conversion of primary pollutants and photochemical oxidant production (Carlier et al., 1986; Vairavamurthy et al., 1992). This requires accurate and precise measurements not only of carbonyls, but also their precursor and product compounds. The concentration range of carbonyls is typically in the sub-ppbv (parts per billion volume) or low ppbv levels in clean air, to higher ppbv in polluted and/or urban atmospheres (Carlier et al., 1986; Martin et al., 1991; Lee et al., 1995). Thus, because low levels often exist in ambient conditions—especially in rural regions—determination of carbonyl compounds in the atmosphere poses challenging problems. Many measurement techniques for these compounds have been developed over the past four decades; however,
newly developed technology in near real-time measurements allows for advances to be made in studying regional atmospheric chemistry on a detailed level.

Field studies for both urban and rural settings provide ample opportunity to test different methods for measuring carbonyl compounds; while traditional wet chemistry methods prove to be reliable and relatively simple, the advantages of near real-time quantification enable concentration fluctuations to be regulated and the urban photochemistry of Houston to be more fully understood, especially with simultaneous measurements of precursor and product compounds. The traditional time-integrated carbonyl collection methods work well in the biogenic study; however, the advanced real-time collection in the anthropogenic studies validates the need for further improved quantification of carbonyls.
CHAPTER 2

LITERATURE REVIEW: CARBONYL COMPOUNDS, BIOGENIC EMISSIONS, AND SAMPLING TECHNIQUES

2.1. CARBONYL COMPOUNDS

Aldehydes and ketones have many sources, including vehicular exhaust, industrial emissions, and biogenic secondary formation. Several of the compounds are known or suspected toxins or carcinogens (National Research Council, 1981). The major chemical pathways involving carbonyls are seen in Figure 2.1. In this figure are critical sources and sinks of carbonyls. Reaction with the hydroxyl radical (OH•) leads to alkoxy radical formation, which further reacts to form other radical species. Likewise, straightforward pathways from alkanes and alkenes—including ozonolysis—lead to carbonyl formation. Thus, atmospheric carbonyls play a critical role in tropospheric chemical reactions, not only as the products of photochemical reactions, but also as the source of free radicals, organic aerosols, and eventually ozone and smog formation (Tanner et al., 1988; Grosjean et al., 1996), as shown in Section 2.1.1.

2.1.1. VOCs AND OZONE FORMATION

As stated above, VOCs—in particular the abundant smaller chain aldehydes and ketones—are important in shaping atmospheric chemical reactions. In particular, the propagation of highly reactive radical species leads to secondary and even tertiary reactions, whether forming other carbonyl compounds, carboxylic acids, or peroxyacetyl
Figure 2.1. The major chemical sinks and sources of atmospheric carbonyl compounds (Vairavamurthy et al., 1992).

nitrates (PANs), important oxidants which transport oxides of nitrogen (NOx). In atmospheres in which sufficient NOx concentrations exist, aldehydes and ketones are responsible for ozone formation.

Ozone (O3) exists in both the stratosphere and troposphere; stratospheric ozone protects the Earth's surface by absorbing the sun's ultraviolet radiation while tropospheric
ozone is commonly known for its role in smog formation. Ozone is a highly reactive oxidant naturally formed (and then destroyed) in the photostationary state relationship. Ultraviolet radiation dissociates NO$_2$ to yield NO and an oxygen radical, O($^3$P), which reacts rapidly with molecular oxygen in the atmosphere to form O$_3$. The ozone formed then reacts with the NO, destroying any ozone produced and replenishing NO$_2$. This following set of reactions and Figure 2.2 illustrate this relationship:

\[
\begin{align*}
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O}(^3\text{P}) \quad (2.1) \\
\text{O}(^3\text{P}) + \text{O}_2 & \rightarrow \text{O}_3 \quad (2.2) \\
\text{O}_3 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2 \quad (2.3)
\end{align*}
\]

In this system alone, there is no accumulation of ozone, since any ozone formed in (2.2) reacts away in (2.3). The cycle is disrupted, however, in the presence of VOCs because an oxygen atom is donated by VOC (alkoxy) radicals to convert NO to NO$_2$. The reaction of NO with VOCs is kinetically favored over NO-O$_3$ reaction in (2.3). Thus, NO$_2$ concentrations increase while NO concentrations simultaneously decrease, eventually resulting in a net accumulation of O$_3$.

Ozone is deemed a criteria pollutant and is of major concern because of its adverse effects on human health, crops, and forests (Plummer et al., 1996; TNRCC). The Environmental Protection Agency (EPA) established National Ambient Air Quality Standards (NAAQS) for attainment of ozone levels, yet after over 20 years of regulations, 100 urban areas in the United States still do not meet these levels. Houston and Los Angeles are annually the two metropolitan areas with the most days exceeding the NAAQS as well as the highest O$_3$ levels. In Houston, for instance, over 50 days in 1999 exceeded newly implemented 8-hour average NAAQS of 85 ppbv (TNRCC). Measurements of O$_3$
precursors such as acetone, formaldehyde, acetaldehyde, and propanal—and tests to develop the most accurate and efficient means of measuring these compounds—are therefore important in Houston for identifying: potential levels of $O_3$; sources and strength of emissions of the precursors; and possible effective means of control.

2.1.2. Anthropogenic Emissions

Carbonyl compounds are emitted directly from power plants and industrial emissions, automobile exhausts, and biomass burning (Berntsen et al., 1997; Piketh et al.,
1999), as well as from biogenic sources. Photooxidation of these primary hydrocarbons leads to \textit{in situ} formation of other hydrocarbons and chemicals, such as ozone, in the atmosphere.

Conventional fossil fuel power plants are an important source of air pollution, including an estimated 700,000 metric tons of VOC emissions in the United States in 1991 (Wark \textit{et al.}, 1998). In fact, total VOC emissions for 1991 in the US were approximately 17 million metric tons. One study in an industrialized region of Germany in 1992 indicated point source emissions were approximately 66 tons day$^{-1}$, and total VOC emissions for this area were almost 800 tons day$^{-1}$ (Schneider \textit{et al.}, 1996).

Vehicular exhaust constitutes another major primary source of urban emissions, where the VOC content is influenced by the fuel and engine type, technical condition of the vehicle, and vehicle speed (Haszpra and Szilagyi, 1996). Estimates in the United States (1991) for VOCs emitted from road vehicles are 3.8 million metric tons, and the total for all transportation vehicles is approximately 17 million tons (Wark \textit{et al.}, 1998). Furthermore, hydrocarbons emitted from motor vehicle exhaust are as high as 0.41 g mile$^{-1}$ for light-duty automobiles, and 0.9 g mile$^{-1}$ for light- and medium-duty trucks (Seinfeld and Pandis, 1998). Vehicular emissions comprise about 22\% of total emissions of VOCs; major metropolitan areas such as Los Angeles, New York City, and Houston are especially notorious for heavy daily volumes of traffic. Thus it is expected that aldehydes and ketones, as primary vehicular emissions, are likely to have relatively high concentrations in Houston.

\section*{2.2. Biogenic Emissions}

There is a high potential for ozone formation in rural areas downwind of cities given urban NO$_x$ transport and local carbonyl emissions in rural areas. Biogenic compounds
consist of VOCs emitted from vegetation, including trees, grasses, and plants. The
distribution of biogenic compounds depends on forest and plant composition for a region,
where oaks, poplars, and pines emit the highest concentrations of isoprene
(CH₂CHC(CH₃)CH₂). Concern with biogenic VOCs focuses on the formation,
concentrations, and reactivity of secondary atmospheric products (Altshuller, 1983).
Although interest in rural concentrations of aldehydes and ketones has risen over the past
two decades, there still exists a lack of emission and concentration measurements in remote
regions.

Isoprene emissions undergo diurnal and seasonal variations in rural areas and urban
sites surrounded by forests (Biesenthal et al., 1997). An increase in urbanization perpetuates
the problem of increased emissions, since urbanization leads to a relative increase in
temperature and a decrease in mean annual wind velocity, which decreases ‘ventilation’
within urban airsheds (Cardelino and Chameides, 1990). These patterns are a function of:
mixing within the mixed boundary layer; atmospheric depletion by OH•, O₃, and NO₃•
(Helmig et al., 1998); forest composition; and environmental climate factors (Geron et al.,
1997; Helmig et al., 1998). To study the spatial variations of isoprene and its reaction
products, and measure the potential for ozone formation, the Texas Isoprene Experiment
(TEXIE) was conducted in 1998 at one urban site and three surrounding rural sites
(Chapters 3 and 4).

2.2.1. Radical Formation and Atmospheric Chemistry

Biogenic hydrocarbon activity has far-reaching implications for atmospheric
chemistry. As stated above, the presence of (biogenic) VOCs leads to ozone formation by
disrupting the photostationary state relationship in a NOₓ-containing atmosphere. Reactions
of biogenic VOCs with OH• also can suppress OH• concentration and enhance the production of peroxy (HO₂• and RO₂•) radicals. Furthermore, photooxidation is potentially a major source of tropospheric CO (Kleindienst et al., 1998), which influences OH• concentrations (Fehsenfeld et al., 1992). Biogenic VOCs also lead to the generation of organic nitrates which can sequester NO₃ and allow its transport over great distances, while oxidation of certain biogenic hydrocarbons can lead to organic aerosols and contribute to haze in the atmosphere (Kamens et al., 1982).

The predominant OH• and NO₂• radicals and ozone initiate much of the biogenic chemistry. The dominant atmospheric depletion pathway of isoprene is with hydroxyl radical reaction (Helmig et al., 1998; Martin et al., 1991); reaction with ozone is also important, especially in urban settings dominated by heavy ozone concentrations. Considering typical concentrations for a relatively clean troposphere, the combined effects of OH radical reactions with isoprene and with O₃ lead to a lifetime of only a few hours. Isoprene and its products methacrolein and methyl vinyl ketone have much longer lifetimes with respect to NO₃ attack.

2.2.2. ISOPRENE REACTION PATHWAYS IN HIGH AND LOW CONCENTRATIONS OF NOₓ

Suggested isoprene reaction pathways follow (Lloyd et al., 1983; Fehsenfeld et al., 1992). In sunlit conditions, OH• radical attack on isoprene is the major pathway of reaction during the daylight hours. Ozone reaction with isoprene also occurs, however, the reaction is significantly slower than that of OH•-isoprene interaction. Figure 2.3a illustrates a simplified pathway under high NOₓ conditions. From the figure, OH• adds to one of isoprene's C=C double bonds, followed by fast reaction with molecular oxygen. The initially formed hydroxy-peroxy radical reacts with NO to yield a tertiary hydroxy-alkoxy radical that
decomposes into two fragments: methyl vinyl ketone \((\text{CH}_2\text{C}(=\text{O})\text{CH} =\text{CH}_2)\) and the \(\text{CH}_2\text{OH}^*\) radical, where \(\text{CH}_2\text{OH}^*\) reacts quickly to yield formaldehyde \((\text{HCHO})\) and \(\text{HO}_2^*\). An analogous pathway forms methacrolein \((\text{CH}_2 =\text{C(\text{CH}_3)}\text{C}(=\text{O})\text{CH}_2\text{OH})\), with \(\sim 48\%\) yield for both methacrolein and methyl vinyl ketone.

Although many similarities exist in the complicated pathways of isoprene reaction at both high and low levels of \(\text{NO}_x\), there are significant differences in initializing the reactions. A proposed pathway is illustrated in Figure 2.3b. When NO concentrations are close to zero, organic peroxy radicals react with other peroxy radicals, as these species have longer lifetimes. Peroxy-peroxy radical interaction can eventually produce alkoxy radicals, alcohols, aldehydes, or acids (Fehsenfeld, 1992).

2.2.3. 

**METHACROLEIN AND METHYL VINYL KETONE OXIDATION**

Methacrolein and methyl vinyl ketone, isoprene’s primary oxidation products, undergo further oxidation in the atmosphere. Studies have shown that the most likely mechanism of oxidation is through reaction with the \(\text{OH}^*\) radical with a resultant lifetime of about 10 hours; the photodecomposition of methacrolein and methyl vinyl ketone is considered unimportant since the \(\text{C} =\text{C}\) double bond and the carbonyl bond \((\text{C} =\text{O})\) lead to stabilization of the molecule from photolysis (Fehsenfeld *et al.*, 1992).

The reaction of these compounds with the \(\text{OH}^*\) radical can occur at either double bond (only terminal carbon attack is shown). Methyl vinyl ketone reaction eventually leads to the formation of the dicarbonyl methyl glyoxal \((\text{CH}_3\text{C}(=\text{O})\text{C}(=\text{O})\text{H})\) and formaldehyde, among other pathways. The \(\text{OH}^*\)-methacrolein reaction follows two pathways, including abstraction of the terminal hydrogen (which leads to PAN formation) and addition of \(\text{OH}^*\) to the \(\text{C} =\text{C}\) double bond. Hydroxyl-methacrolein reactions also yield methyl glyoxal.
Methyl glyoxal undergoes either photolysis or reaction with the OH radical to produce HO₂• radicals, peroxy radicals such as CH₃COO₂•, carbon monoxide (CO), and PAN. These are important atmospheric components; for example, radicals are highly reactive and often initiate most sets of reactions; CO is an important greenhouse gas; PAN serves as both a radical reservoir and means of transporting NOₓ over long distances.

2.2.4. BIgenic FORMALDEHYDE

Several steps in isoprene oxidation yield formaldehyde, which either reacts with OH• followed by addition of molecular oxygen or photodecomposes in sunlight. The hydroxyl reaction leads to a CO molecule and an HO₂• radical. Photolysis entails a molecular channel producing H₂ and CO, and a free radical channel forming HCO• and H• which react exclusively in the atmosphere to form HO₂• and CO. Rural versus urban formaldehyde concentrations are discussed in Chapter 4.

2.3. SAMPLING TECHNIQUES

Air pollution analyses provide a basis for the evaluation of damage to humans, plants, and materials which has already occurred or will potentially occur. Periodic or continuous air quality analysis for a given location or several air monitoring stations comprising a larger region are used to compile the composition of known foreign substances and determine unknown pollutants and pollution sources (Leithe, 1971). It is important to model the formation and reaction pathways that occur with these pollutants so that predictions can be made, for example, as to the likely formation of ozone, the transport of
Figure 2.3. a. Isoprene reaction pathways in high NO$_x$ conditions, typical of cities and urban airsheds. b. Isoprene reaction pathways in low NO$_x$ conditions, as in rural regions (Fehsenfeld et al., 1992).
pollutants to cleaner airsheds, and global effects such as warming and the cycling of elements. A primary goal of the present research is to validate the effectiveness of certain technical ambient atmospheric measurements, using both an intercomparison study at one location involving three analytical methods and correlating the spatial variation of measurements at different sites.

The ambient concentrations of carbonyl compounds in rural regions, though significant, are expected to be considerably lower than in urban settings because of the transport distance from anthropogenic primary emissions to outside areas. Measurement techniques with a lower limit of detection of carbonyls in the sub-ppbv range are therefore required for accurate quantitation in rural areas and in cities where aldehyde and ketone levels may drop to lower ppbv concentrations. Over the past forty years, several methods have been developed to detect low concentrations of carbonyls, and include colorimetric, chromatographic, and spectroscopic techniques (Vairavamurthy et al., 1992).

2.3.1. Colorimetric and Chromatographic Techniques

Many colorimetric techniques were developed for the detection of formaldehyde, the simplest and most abundant aldehyde, but were applicable to most smaller chain aldehydes as well. These methods, including chromatropic acid and fluorescence detection methods (Salas and Singh, 1986), for example, operate on the principle of functional group detection with spectroscopy. Colorimetric detection is now considered obsolete, however, as only total carbonyls present are typically measured as opposed to differentiating individual compounds. Thus, colorimetry lacks adequate sensitivity for ambient atmospheric sampling.

To separate individual species within a given sample, scientists in the 1970s began to develop chromatographic techniques coupled with derivatization to increase sensitivity and
selectivity, and thereby overcome the problems associated with colorimetry. An overview of several chromatographic methods for the determination of atmospheric carbonyl compounds is modified from Vairavamurthy et al. (1992) in Table 2.1. In the intercomparison project in the present study, two versions of chromatographic techniques from Table 2.1, dinitrophenylhydrazine derivatization and pentafluorobenzyl hydroxylamine hydrochloride oximes, were compared with a spectroscopic method, DFG.

2.3.2. DINITROPHENYLHYDRAZINE (DNPH) DERIVATIZATION

The "classic" method for atmospheric carbonyl measurement and analysis is through DNPH derivatization; this is the recommended method by air pollution control agencies in several countries (Grosjean and Grosjean, 1995). The technique allows nanogram amounts of carbonyls, in the derivatized 2,4-dinitrophenylhydrazone form, to be analyzed by HPLC and detected with ultraviolet spectroscopy.

Variations of the DNPH method have been developed over the last 20 years (Kochy and Fung, 1981), based on the well known reaction

\[ R_1R_2C=O + NH_2NHC_6H_3(NO_2)2 \rightarrow H_2O + R_1R_2C=NNHC_6H_3(NO_2)2 \]  

(2.4)

in which the carbonyl \((R_1R_2C=O)\) adds to the dinitrophenylhydrazine compound via nucleophilic addition, followed by 1,2-elimination of \(H_2O\) (Kochy and Fung, 1981). This reaction occurs in the presence of acid since DNPH is a weak nucleophile, requiring hydrochloric or phosphoric acid to complete the derivatization. Because the DNPH method is cost-effective and allows for low-level detection of carbonyls, numerous studies have been conducted to consider: the importance and accuracy of this method in both ambient and controlled smog-chamber studies; possible sources of interference; potentially high field
blank (control) levels; and improvements and variations of earlier developed DNPH methods.

**DNPH Sampling Methods**

DNPH sampling for atmospheric carbonyls entails collection of the pollutants onto a surface coated with a DNPH solution. Upon the surface, reaction (2.4) occurs, converting any carbonyls present to the hydrazone form, which is then extracted and quantified using liquid or gas chromatography. Several DNPH sampling techniques have been reported in the literature, including collection: by impingers coated with different solvents (Kuwata *et al.*, 1979; Fung and Grosjean, 1981; Johnson *et al.*, 1981); from tubes packed with DNPH-coated glass beads (Grosjean and Fung, 1982); and via chemical absorption onto glass filters impregnated with DNPH (Dalene *et al.*, 1992).

One of the most widely used techniques for carbonyl-DNPH sampling, however, employs a cartridge technique, where atmospheric carbonyls are brought into contact with either silica gel or C$_{18}$ silica gel cartridges coated with the DNPH reagent (Sirju and Shepson, 1995). This method is used in the Photochemical Assessment and Monitoring Stations (PAMS) program in heavily polluted (ozone) cities (Gilpin *et al.*, 1997). C$_{18}$ silica gel consists of a polymer of silicon and oxygen with surface C$_{18}$ groups; the surface groups in silica gel are hydroxyl moieties. Various advantages support the use of either cartridge type, however, C$_{18}$ cartridges were used in the present study, and a detailed description is given in Chapter 3. Potential ozone interference presents some possible concern with silica gel cartridge sampling (Kleindienst *et al.*, 1998; Gilpin *et al.*, 1997), whereas most researchers did not find a similar problem with C$_{18}$ cartridge sampling (Arnts and Tejada, 1989; Zhou and
Table 2.1. Overview of chromatographic techniques (Vairavamurthy et al., 1992).

<table>
<thead>
<tr>
<th>Analytical Technique</th>
<th>Sampling Procedure</th>
<th>Detection Limit</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas chromatography without derivatization</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC with flame ionization detection (FID)</td>
<td>solid sorbent sampling with Tenax GC and thermal desorption prior to analysis</td>
<td>&lt; 0.1 ppbv for a 3 L sample</td>
<td>poor selectivity; ozone interference is probably serious and has not been well-studied</td>
</tr>
<tr>
<td></td>
<td>sampling with bisulfite solution followed by stripping and preconcentration on Tenax GC</td>
<td>&lt; 0.1 ppbv for 2 h sampling at 33 L min⁻¹</td>
<td>reported for C₄ and C₅ aldehydes only; not useful for sampling ketones</td>
</tr>
<tr>
<td>GC with mass spectrometry</td>
<td>solid sorbent sampling with molecular sieve 13X</td>
<td>0.3 ppbv for a 1 L sample</td>
<td>used only for HCHO measurement; selective detection method</td>
</tr>
<tr>
<td>2-D gas chromatography</td>
<td>cryogenic collection followed by separation of water in a packed column and on-line recondensation of carbonyls</td>
<td>10 pptv for a 4 L sample</td>
<td>formaldehyde is not sensitively detected; effect of ozone has not been examined</td>
</tr>
<tr>
<td>Chemical derivatization coupled to gas chromatography</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As o-methyloxime and o-benzoxylximes; detector: NPD</td>
<td>impinger charged with reagent solution</td>
<td>40 ppbv for an 11 L sample</td>
<td>poor sensitivity as reported</td>
</tr>
<tr>
<td>As o-pentafluorobenzylxime derivatives; detector: ECD</td>
<td>acetonitrile/water (50:50) solution of pH 1.8 cooled to ice temperature</td>
<td>&lt; 0.1 ppbv for a 5 L sample</td>
<td>a useful derivatization method of sensitive determination of carbonyls by GC</td>
</tr>
<tr>
<td>Chemical derivatization coupled to liquid chromatography</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As 3-methyl-2-benzothiazolinone hydrazone (MBTH) derivatives; detector: uv-visible</td>
<td>used for atmospheric aqueous phase measurement (impingers may be used for gas-phase sampling)</td>
<td>&lt; 0.1 ≤ M for C₁-C₅ aldehydes</td>
<td>involves post-column derivatization; ketones cannot be derivatized</td>
</tr>
<tr>
<td>As azine derivatives with 2-diphenylacetyl-1,3-indandione-1-hydrazones; detector: fluorescence</td>
<td>impingers charged with reagent solution</td>
<td>&lt; 6 ppbv for a 20 L sample</td>
<td>used for contaminated air measurement of aldehydes; unsaturated aldehydes produce higher fluorescence yield than saturated compounds</td>
</tr>
<tr>
<td>As dazylhydrzones; detector: fluorescence</td>
<td>impingers: reagent-coated silica gel; microcartridges packed with reagent-impregnated porous-glass particles</td>
<td>analytical detection limit is &lt; 20 pptv for a 20 L sample; however high reagent blanks affect method detection limits seriously</td>
<td>reagent purification is a critical step; sampling and analytical protocols are not completely optimized in the reported methods:</td>
</tr>
<tr>
<td>As 2,4-dinitrophenylhydrazone derivatives; detector: uv-visible</td>
<td>a variety of methods using impingers, cartridges, or other</td>
<td>0.01-1 ppbv</td>
<td>sampling with DNPH-coated cartridges common; O₃ interference, high blanks are problematic</td>
</tr>
</tbody>
</table>

Mopper, 1990; Tanner et al., 1996), especially when sampling in polluted cities where high hydrazone levels are expected (Sirju and Shepson, 1995). Carbonyl collection on cartridges allows for easier handling and transportation than impinger methods (Dalene et al., 1992), but presents potential difficulty with coelution (Yu et al., 1995) and high blanks (Heikes et al., 1996; Tanner et al., 1996; Benning and Wahner, 1998).

### 2.3.3. Pentafluorobenzyl Hydroxylamine (PFBHA) Derivatization

To compensate for possible poor resolution and coelution using the DNPH method, a recently developed derivatization was introduced to detect atmospheric carbonyls. In the PFBHA procedure, the oxime form of the ketone or aldehyde is produced by taking advantage of carbonyls’ solubility in water and collecting (bubbling) a sample of air into a glass impinger. In this process, (α-2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA) hydrochloride reacts with carbonyls; the product oxime is extracted into a solvent and analyzed using gas chromatography followed by detection with mass spectrometry (GC/MS) (Yu et al., 1995). The advantages offered by the PFBHA method include high sensitivity and strong resolution for α-hydroxy carbonyls and dicarbonyls (such as glyoxal, a product of isoprene oxidation) and a means to identify unknown carbonyl compounds based on mass spectra.

Yu et al. (1995) tested PFBHA derivatization with laboratory standards and indoor/outdoor smog chamber experiments. There exists a lack of information in the literature as to the application of the PFBHA method for ambient sampling. In this study, the PFBHA method is used to analyze qualitatively the urban Houston atmosphere by identifying ketones and aldehydes at extremely low levels using mass spectra data.
2.3.4. Spectroscopic Techniques

Vairavamurthy et al. (1992) reviewed several in situ spectroscopic techniques, including: differential optical absorption spectroscopy (DOAS); Fourier transform infrared absorption (FTIR); laser-induced fluorescence spectroscopy (LIFS); and tunable diode laser absorption spectroscopy (TDLAS). TDLAS appears best suited of these techniques for atmospheric ambient measurements because of selectivity, sensitivity, and time resolution (Fried et al., 1991; Vairavamurthy et al., 1992), with trace gases measured in the sub-ppbv range (around 0.1 ppbv) (Fried et al., 1998). An improvement upon TDLAS for real time formaldehyde measurements has been accomplished with difference-frequency generation (DFG) in periodically poled LiNbO₃ (PPLN), which has high sensitivity and long term stability (Mine et al., 1997). This technique (DFG-PPLN) is used in this study in the intercomparison of formaldehyde collection.

Several intercomparison studies have been completed for the detection of formaldehyde (Trapp and de Serves, 1995; Heikes et al., 1996; Gilpin et al., 1997; Harder et al., 1997; Apel et al., 1998). These studies occurred in remote rural regions, and all but one used TDLAS sampling as one means of formaldehyde measurement. In fact, Gilpin et al. (1997) used the TDLAS system to confirm the absolute accuracy for all other ambient measurements. To date, there has not been a methods intercomparison study in a heavily polluted urban region such as Houston in which the DNPH, PFBHA, and DFG-PPLN methods are used simultaneously to measure formaldehyde. It is expected that this investigation will elucidate the differences, advantages, and disadvantages of the sampling methods involved.
SECTION 1
BIGENIC CARBONYL COMPOUNDS
CHAPTER 3

FIELD MEASUREMENTS OF ISOPRENE AND ITS REACTION PRODUCTS IN CENTRAL TEXAS*

3.1. INTRODUCTION

Biogenic hydrocarbons initiate many atmospheric reactions, including those leading to the production of tropospheric ozone, as described in Chapter 2. The total annual emissions of isoprene have been estimated at 17-20 TgC yr$^{-1}$ for the United States (Guenther et al., 1999); Wiedinmyer et al. (1999) found substantial isoprene emissions in the eastern half of Texas. Isoprene is highly reactive in the atmosphere, and thus its emissions and reaction products are expected to contribute significantly to the overall atmospheric chemistry and composition.

Chapters 3 and 4 detail the Texas Isoprene Experiment (TEXIE) (Wiedinmyer et al., 2000), a project designed to examine isoprene emissions in rural and urban areas and elucidate the extent of isoprene conversion to reaction products in the central portion of the eastern half of Texas (Central Texas). Surface layer concentrations of isoprene, formaldehyde, and methacrolein are reported in this chapter, along with an analysis of diurnal and spatial patterns of these compounds.

3.2. THE TEXAS ISOPRENE EXPERIMENT

3.2.1. FIELD LOCATIONS

TEXIE measurements were taken during August 11-21, 1998, in the regions of

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Central Texas shown in Figure 3.1. Four areas were selected for the study, based on pre-

determined local vegetation classification (Wiedinmyer et al., 1999). Figure 3.2 shows the
locations of the measurement sites and the local vegetation classifications. Samples were
taken at: Bastrop, TX (site 1, rural) on August 11-12; northern Austin, TX (site 2, urban),
August 15-16; Pedernales Falls State Park (site 3, rural), August 18-19; and Elgin, TX (site 4,
rural), August 21-22. As isoprene emissions are species-dependent, the selected sites
represented a variety of emitters. Pine and hardwood forests, relatively high isoprene
emitting species, dominate Bastrop; Pedernales contains low canopy vegetation of live oak
and ash juniper trees; and Elgin consists of post oak savannah and forest with croplands.
Figure 3.2. Locations of TEXIE samplings sites; regional vegetation types are shown.
3.2.2. Measurements

At each of the four sites (Bastrop, Austin, Pedernales, Elgin), four 3 m towers surrounded a central 3 m tower within a 20 km radius (Figure 3.2). Sampling equipment was placed at 3 m on each tower to reduce sample loss through excess tubing. Air samples were collected simultaneously at hourly intervals.

3.2.3. Isoprene Measurements

At each ground site, whole air samples were taken in 6 L electropolished, stainless steel canisters (Meriter, model X56l-4MCG). A critical orifice was attached to the inlet of each canister to ensure a constant flow rate over the one hour sampling period; inlets were calibrated every 3 to 4 days during the field study. Canister samples were analyzed daily with an ENTEK 7000 pre-concentrator, separated by a Hewlett Packard P5890 gas chromatograph with an HP-1 column and quantified with a flame ionization detector. One daily sample was also analyzed with a Hewlett-Packard Gas Chromatograph with a P5973 mass selective detector for quality assurance purposes. Seventy-six hydrocarbon species were identified during the analysis of the canisters, however, only isoprene concentrations are presented in this chapter.

3.2.4. Carbonyl Measurements

Formaldehyde and methacrolein were collected using 2,4-dinitrophenylhydrazine (DNPH) impregnated cartridges. Waters SepPak C_{18} cartridges were coated with a DNPH solution one to three days prior to their use in the field, according to the method of Trapp and de Serves (1995). A laminar flow hood with HEPA filter was used to minimize contamination when preparing the cartridges. Acetonitrile (5 mL) (Fisher, HPLC grade) was
flushed through each cartridge at 5 mL/min, followed by 2 mL DNPH solution. The DNPH solution was prepared with 25 mg twice recrystallized DNPH•HCl, 3 mL 5 M HCl, and 2 mL acetonitrile in a 20 mL capped vial which was sonicated for 10 min. A 0.600 mL aliquot of this solution was added to a volumetric flask which was filled to 100 mL with DI H₂O. A 2 mL aliquot of this solution was injected into the cartridges at 2 mL/min, and dried by a gentle stream of Ultra High Purity N₂ gas (TriGas Industrial Gases) for 10 min. All cartridges were stored at 10°C in individual 40 mL plastic capped vials prior to use in the field.

SKC Airchek Sampler pumps were used to collect air samples in the impregnated cartridges. The cartridges were wrapped in aluminum foil to minimize DNPH-light reactions within the cartridges. Nalgene tubing (30 cm) was attached to the pumps, and cartridges were placed at the end of the tubing to prevent sampling line losses. Samples were collected at a nominal flow rate of 1.2 Lpm. Pumps were calibrated with a Gilian Instrument Corporation primary flow calibrator before and after the experiment. One field blank was taken at each tower per day for most days by placing an impregnated cartridge at the top of the tower, with the cartridge wrapped in foil, during a sampling hour. The labeled cartridges were removed from the pumps and immediately placed in 40 mL plastic vials and stored in a cooler after each sampling period.

Cartridges were stored in the dark at 10°C until they were to be extracted and analyzed using liquid chromatography. To extract the samples, 2 mL acetonitrile was pushed through the cartridges at a rate of 2 mL/min into pre-weighed 6 mL capped septum vials. The vials were subsequently re-weighed and the exact extraction volume determined. Standards and samples were run through a Waters Nova-Pak C₈ guard column and Waters Nova-Pak C₈ 3.9 × 150 mm column with a 45/55 (v/v) Milli-Q water/acetonitrile eluent on
a Hewlett-Packard 1100 high performance liquid chromatograph (HPLC) equipped with a diode array detector. The following chromatographic parameters were used: injection volume, 10 µL; flow rate, 1.00 mL/min; column temperature, 36.0°C; and run time, 20 min, using a method adapted from Grosjean and Grosjean (1995).

Several analytical techniques were used to synthesize authentic 2,4-dinitrophenylhydrazone derivatives (Fung and Grosjean, 1981; Dalene et al., 1992; de Andrade and Tanner, 1992; Levin et al., 1996), which were used as calibration standards. Carbonyl-hydrazone crystalline standards used for calibrating instrument response were made with 100 mg twice-recrystallized DNPH•HCl, 10 mL pure ethanol, 0.5 mL 12 M HCl, and excess high-purity aldehyde, using the highest grade chemicals available. Carbonyl-hydrazone crystals were dissolved in acetonitrile and successively diluted to create a five- to seven-point standard calibration curve. Using the extraction volume, flow rate, and calibration curves for each carbonyl-hydrazone, the atmospheric concentration (ppbv) was determined for the samples.

Field blanks were collected throughout the two-week period and were variable as others have found when using the DNPH method (Sirju and Shepson, 1995; Tanner et al., 1996). The formaldehyde field blank levels were the most consistent among all blanks; however, because variability and high levels were found in other blank samples, the peak areas (in milli-Absorbance Units-seconds, mAUs) from all samples (including field blanks) were plotted for each compound, creating a sequence of high and low values, with the lower values mostly associated with blank samples. These lower values were taken as blank concentrations, while all other areas were considered concentrations greater than the blank levels. The average and standard deviation of the blank areas were calculated, where the standard deviation determined the lower limit of detection (LLD). The atmospheric
concentration for each compound was calculated after subtracting off the average blank value from the sample peak area. Average hourly and site concentrations were calculated using all values, where concentrations that were below the LLD were given the value of the LLD.

A total of 194 canister samples, 190 carbonyl cartridges and 29 cartridge blanks were collected during the experiment. An average of 20 canisters and 20 carbonyl cartridges were sampled daily. The measurements were taken during the midday hours, primarily between 1200 CDT and 1600 CDT, although on some days measurements were taken earlier in the day.

3.3. RESULTS

3.3.1. CONCENTRATION DATA

Isoprene concentrations ranged from 0 (LLD) to 10.2 ppbv in the rural atmospheres, and from 0 (LLD) to 6.0 ppbv in Austin. Rural ambient formaldehyde levels ranged from 0.4 ppbv (LLD) to 20.0 ppbv, while the observed range was smaller (0.4-3.4 ppbv) in Austin. Methacrolein levels did not show as much variation between rural and urban locales, where the rural observations ranged from 0.1 ppbv (LLD) to 3.7 ppbv and urban concentrations were between 0.2 and 5.7 ppbv.

The mean isoprene concentration at the three rural sites is consistent, at 2.4, 2.5, and 3.0 ppbv for Bastrop, Pedernales, and Elgin, respectively. The mean isoprene concentration at Austin is lower, at 1.2 ppbv. Mean values were calculated as an average of all the mean tower concentrations for all hours at each site. Mean concentrations of rural formaldehyde were 2.4 ppbv in Bastrop, 1.4 ppbv in Pedernales, and 1.0 ppbv in Elgin, while in Austin it was 1.2 ppbv. The mean methacrolein concentrations had the largest standard deviations; at
the rural sites, concentrations were 1.1, 0.4, and 0.3 ppbv for Bastrop, Pedernales, and Elgin, respectively, while in Austin, the mean methacrolein concentration was 0.8 ppbv.

Isoprene and methacrolein concentrations are expected to be proportional (Montzka et al., 1995) as methacrolein is a reaction product of isoprene; this proportionality, however, is limited because of transport and reaction of isoprene in the atmosphere. The average Austin methacrolein concentration is over double the averages measured at Pedernales Falls and Elgin, and approximately the same values as calculated for Bastrop. The ratio of methacrolein to isoprene should be greatest in Austin, since urban areas are expected to have a lower isoprene source strength and isoprene transported from surrounding rural regions undergoes chemical reactions during transport to yield higher methacrolein concentrations. As expected, the calculated methacrolein to isoprene ratio at Austin is 0.7, while at Bastrop, Pedernales, and Elgin the ratio is 0.5, 0.2, and 0.1, respectively.

The rural mean concentrations of formaldehyde in Central Texas are comparable to levels found in other rural regions (Table 3.1). Specifically, concentrations reported for rural Ontario, Canada and a rural region outside Nashville, TN were 1.3 and 0.9 ppbv respectively. The Austin concentrations of formaldehyde, however, are much lower than levels reported in other urban areas (5.3, 15.8 and 2.9 ppbv at Los Angeles, Long Island and Atlanta, respectively). This reflects possible lower urban source density in Austin compared to cities such as Los Angeles and New York City. The Central Texas rural methacrolein concentrations are of the same magnitude as those observed at other rural locations. In Alabama, the mean summer methacrolein concentration was reported as 0.5 ppbv, while in Japan, semi-rural concentrations were 0.8 ppbv.
3.3.2. Diurnal Variations

The temporal distribution of isoprene concentrations indicates that the isoprene concentrations observed were in fact from biogenic sources. The isoprene concentrations followed characteristic patterns throughout the day, as shown in Figure 3.3. This pattern is expected, as isoprene emissions are both light (PAR) and temperature dependent. Concentrations rise during the afternoon as temperature and PAR increase. The last hour shows a decrease in isoprene concentrations as a result of high temperature. At temperatures above 38°C, tree leaves will “shut down” and stop producing isoprene (Guenther et al., 1993).

Table 3.1. Reported carbonyl concentrations from various authors, including season, location and location type.

<table>
<thead>
<tr>
<th>source</th>
<th>acetaldheyde</th>
<th>formaldehyde</th>
<th>acetone</th>
<th>methacrolein</th>
<th>season</th>
<th>location</th>
<th>type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grosjean et al., 1996</td>
<td>4.0</td>
<td>5.3</td>
<td>1.6</td>
<td></td>
<td>early fall</td>
<td>Los Angeles, CA</td>
<td>urban</td>
</tr>
<tr>
<td>Apel et al., 1998</td>
<td>0.5</td>
<td>0.9</td>
<td>0.8</td>
<td></td>
<td>summer</td>
<td>outside Nashville, TN</td>
<td>rural</td>
</tr>
<tr>
<td>Tanner &amp; Meng, 1984</td>
<td>8.4</td>
<td>15.8</td>
<td></td>
<td></td>
<td>summer</td>
<td>Long Island, NY</td>
<td>semi-urban</td>
</tr>
<tr>
<td>Grosjean et al., 1993</td>
<td>3.0</td>
<td>2.9</td>
<td></td>
<td></td>
<td>summer</td>
<td>Atlanta, GA</td>
<td>urban</td>
</tr>
<tr>
<td>Shepson et al., 1991</td>
<td>1.4</td>
<td>1.3</td>
<td>1.0</td>
<td></td>
<td>summer</td>
<td>Ontario, CN</td>
<td>rural</td>
</tr>
<tr>
<td>Montzka et al., 1995</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td>summer</td>
<td>Alabama</td>
<td>rural</td>
</tr>
<tr>
<td>Yokouchi, 1994</td>
<td></td>
<td></td>
<td></td>
<td>0.8</td>
<td>summer</td>
<td>Japan through winter</td>
<td>semi-rural</td>
</tr>
</tbody>
</table>

Diurnal fluctuations of the carbonyls are shown in Figures 3.4 and 3.5.
Formaldehyde concentration increases with time at Bastrop; the levels are fairly constant except for a sharp peak at 1200-1300 CDT at Pedernales; and the concentration is roughly constant with a slight increase at 1400-1500 CDT at Elgin. Martin *et al.* (1991) observed formaldehyde levels that increased steadily from the morning until 1300-1400 EDT, after which time the levels decreased to that of the morning concentrations. At Pedernales and Elgin the methacrolein concentration is highest at 1000-1100 CDT, followed by low concentrations and then an increase again at 1500-1600 CDT. Martin *et al.* (1991) report similar fluctuations of methacrolein for rural Pennsylvania, with high levels at 1000-1100 EDT, followed by low levels, and then a steady increase after 1600 EDT. The carbonyl fluctuations indicate that these compounds are reaction products of isoprene, increasing with temperature and PAR. In general, formaldehyde levels in Central Texas were typically higher later in the day, while methacrolein concentrations were high in the morning and again in late afternoon.

![Graph](image)

**Figure 3.3.** Isoprene, temperature, and PAR measurements for Tower 1 on August 11, 1998.
Figure 3.4. Diurnal variability of formaldehyde concentration at the rural sites Bastrop, Pedernales, and Elgin.

Figure 3.5. Diurnal variability of methacrolein concentration at the rural sites Bastrop, Pedernales, and Elgin.
In Austin, formaldehyde concentrations remain approximately constant throughout the day, while methacrolein hourly concentrations are highest in the afternoon at 1500-1600 CDT (Figure 3.6). Average formaldehyde concentrations at Austin are between 0.4 ppbv and 1.4 ppbv, while some average concentrations at the rural sites were higher than 2.0 ppbv and even reached mean levels as high as 5.0 ppbv.

![Graph showing formaldehyde and methacrolein concentrations](image)

**Figure 3.6.** Formaldehyde and methacrolein diurnal variability in northern Austin (August 15-16).

### 3.3.3. Spatial Variation

**Rural versus Urban Concentrations**

The separation of cities from large rural sources of isoprene allows for mixing, dilution and reaction of isoprene during transport, resulting in typically lower levels of isoprene and higher concentrations of its oxidation products in urban areas (Montzka *et al.*, 1995). Urban atmospheres contain increased levels of hydroxyl radicals, ozone, and NOx that are available for reaction with isoprene, also leading to lower isoprene concentrations. Although Austin has a significant amount of vegetation for an urban area, the vegetation density in the urban area is much less than in rural areas. Thus, Austin is expected to contain much lower biogenic isoprene emissions than the rural areas outside of the city.
Figure 3.7 shows the ratio (formaldehyde + methacrolein) to isoprene at each site. This ratio in Austin is greater than that at Bastrop, and it is higher by a factor of approximately two and four than at Pedernales and Elgin, respectively. This ratio suggests that Bastrop is influenced by transport from urban areas, as predicted by its geographical location between the urban areas of Houston (to the Southeast), San Antonio (to the Southwest) and Austin (to the Northeast). Although Elgin is similarly located between these urban areas, the wind patterns on the sampling days in Elgin were from the Northeast where only rural sources exist. Sampling in Bastrop occurred on days in which winds were from the Southeast (downwind of Houston) and Southwest (downwind of San Antonio).

**Spatial Variations Between Towers**

Isoprene concentrations varied significantly from one tower to another. For example, the average isoprene concentrations measured for each tower at Bastrop (August 12) ranged from 0.8 to 4.7 ppbv. Figure 3.8 shows the isoprene concentrations of the ground level canister measurements taken at Bastrop (August 11 and 12) as an example. Standard deviations were often large and represent the variability of isoprene concentrations from different monitoring sites. This variation is primarily due to the placement of the monitor with respect to the immediate surrounding vegetation. Monitors located in close proximity to isoprene emitting trees (within 1-2 m) measure greater isoprene concentrations than monitors located in an area with many isoprene-emitting trees, but placed a long distance from them (over 20 m from trees).

Towers 1, 2, and 3 at Bastrop were sited within the Pine and Hardwood Forest classification. The isoprene concentrations for this region (Figure 3.8) follow similar trends for Towers 1 and 3, but Tower 2 reports much lower levels on an hourly basis. Towers 2
Figure 3.7. Ratio (formaldehyde + methacrolein) to isoprene at each site.

and 4 report similar isoprene concentrations, although they are located within different vegetation types. The variation in isoprene concentrations, regardless of the general

Figure 3.8. Isoprene concentrations (ppbv) observed at four 3 m tower sites on August 11 in Bastrop. Towers 1, 2 and 3 were located in Pine and Hardwoods Forests, while Tower 4 was located in an area designated as Post Oak Woods and Forests, bordered by croplands.
vegetation class in which the monitor is placed, is more dependent on the vegetation in the immediate vicinity of the monitor. Thus, a general description of an area's vegetation with a spatial resolution on the order of 1 km, as in Central Texas, is not specific enough to ensure an accurate prediction of a monitor reading from emissions modeling.

Carbonyl concentrations also vary between towers within a given site, as seen in Figures 3.9 and 3.10, and the (formaldehyde + methacrolein) to isoprene ratio is a good indication of proximity to isoprene sources, with lower ratios more representative of rural areas. At Bastrop, the ratio of (formaldehyde + methacrolein) to isoprene at Towers 1, 3, and 5 was similar to that of the towers at Pedernales and Elgin, ranging from 0.1 to 2.0. The ratio at Towers 2 and 4 at Bastrop, however, was higher at 2.7 and 5.1, respectively. Tower 4 results resemble urban ratios, and are probably influenced by industrial sources from a nearby military zone.

![Figure 3.9](image.png)

**Figure 3.9.** Spatial variation of formaldehyde concentrations among the tower locations at the four sites in Central Texas.
Figure 3.10. Spatial variation of methacrolein concentrations among the tower locations at the four sites in Central Texas.

At the Pedernales Falls site, the methacrolein to isoprene ratio ranges from 0.04 to 0.1 for all sites except Tower 1, where the ratio is 0.9. Tower 1 was placed in a large clearing, whereas all other towers were in closer proximity to wooded areas. In addition, the ratio at Tower 3 at Elgin (August 20 and 21) also shows a decreased influence of vegetation and is consistent with its location in a clearing, several hundred meters from wooded areas. This tower was also located along a major highway and was likely influenced by vehicular emissions, which might have led to an increase in the measured formaldehyde concentrations.

In Austin, the (formaldehyde + methacrolein) to isoprene ratios at three towers are even greater, as expected. These ratios are 1.5/0, 3.4, and 14 at Towers 1-3. The ratios at Towers 4 and 5, 2.1 and 0.4 respectively, are similar to those at the rural sites. The ratio at Tower 5 is atypical, resulting from an isoprene level that is over four times that of the other four towers. This tower was located in a suburban/rural area and away from urban sources, and thus is strongly influenced by the vegetation in the neighborhood.
CHAPTER 4

OZONE FORMATION POTENTIAL FROM ISOPRENE AND OTHER HYDROCARBONS

4.1. INTRODUCTION

The ozone forming potential of biogenic volatile organic compound (VOC) emissions in both rural and urban regions has been studied for several years (e.g., Altshuller, 1983; Lloyd et al., 1983; Liu et al., 1987; MacKenzie et al., 1991). Without significant levels of NOx (emitted mainly from combustion sources), biogenic VOC emissions alone will not lead to peak values of ozone. However, transport of biogenic VOC emissions from rural areas into urban centers or transport of combustion-generated NOx from urban centers to rural areas can lead to peak ozone levels. Evidence from biogenic emissions inventories (Wiedinmyer et al., 1999) suggests that rural biogenic VOC emission and transport into urban areas are particularly important in understanding ground-level ozone formation in Texas.

4.1.1. VOC-TO-NOx RATIO

Ozone (O3) is not emitted directly, but instead is formed through reactions involving the precursors VOCs and oxides of nitrogen (NOx) in the presence of sunlight. Hydroxyl radicals (OH•) initiate reactions between atmospheric gases, with both VOCs and NOx competing for reaction with the OH• radical (Seinfeld and Pandis, 1998). Because of this competition, the ratio of VOCs to NOx in large part governs O3 formation (Wolff and Korsog, 1992; Carter, 1995; Jiang et al., 1997). The ratio of the rate constant for the OH•-NO2 reaction is greater than that for the average OH•-VOC reaction by a factor of
approximately 5.5. Therefore, an atmosphere is typically considered NOx-limited when the VOC to NOx ratio is greater than about 5.5, while a VOC-limited environment has a ratio lower than 5.5. An increase in VOC concentration generally leads to an increase in O3 production; however, O3 levels can either increase or decrease with an increase in NOx concentration, depending on the prevailing VOC/NOx environment. The ozone yield from incremental increases in the VOC concentration varies widely between different organic structures as the hydroxyl radical reacts at different rates and yields different products, both of which affect O3 formation (Bergin et al., 1995; Yang et al., 1995).

4.1.2. Incremental Reactivity

To develop effective control strategies for O3 reduction, it is necessary to predict the effects of VOC and NOx emission reductions given the variable VOC components of the atmosphere (Cardelino and Chameides, 1990; Milford et al., 1994; Carter, 1995; Simpson, 1995). The effect of VOC emission reductions on O3 concentration is theoretically determined using the incremental reactivity (IR) characteristic to that VOC. Incremental reactivity is defined as the amount of O3 formed per quantity of VOC added to the VOC mixture of a given air parcel (Carter and Atkinson, 1987; Seinfeld and Bowman, 1994; Carter, 1995; Seinfeld and Pandis, 1998), or

\[
\text{IR}_i = \frac{\Delta O_3}{\Delta [\text{VOC}]} \quad (4.1)
\]

where \( \Delta O_3 \) is the maximum change of O3 (ppb) that occurs from the presence of organic species \( i \), and \( \Delta [\text{VOC}] \) is the incremental change in concentration (ppbC) of organic species \( i \). Although the impact and importance of biogenic VOCs on O3 formation has been an ongoing discussion and debate (e.g., Isaksen et al., 1978; Lloyd et al., 1983; Trainer et al., 1987;
Chameides et al., 1988; Logan, 1989; Bottenheim and Sirois, 1996), the implementation of an 8-hour average National Ambient Air Quality Standard (NAAQS) for O₃ provides motivation for investigating biogenic VOCs’ influence on O₃ concentrations in both rural and urban regions to assure compliance (Chameides et al., 1997; Holland et al., 1999).

4.1.3. OBJECTIVES

The overall objective in this chapter is to examine the extent of oxidation and ozone formation potential of rural and urban atmospheres as part of the Texas Isoprene Experiment (TEXIE) (Wiedinmyer et al., 2000). Specifically, the incremental reactivity of selected common VOCs is used to quantify both the O₃ attributable to photooxidation of measured VOCs and the O₃-forming potential in rural and urban atmospheres in Central Texas given actual atmospheric concentrations. The O₃ concentrations for the rural and urban sites in this study are calculated using both high and low VOC to NOₓ ratios, to indicate the relative importance of NOₓ levels on O₃ formation. Furthermore, the production of formaldehyde (HCHO) from the oxidation of isoprene is calculated and compared to measured HCHO levels for an urban and rural site, to gain additional insight into the oxidative capacity of these regions’ airsheds.

4.2. ANALYTICAL APPROACH

4.2.1. VOC/NOₓ MEASUREMENTS

The VOC/NOₓ ratio for each rural site was approximated using total VOC measurements (ppbC) from the stainless steel canisters and NOₓ measurements available from the Texas Natural Resources Conservation Commission (TNRCC) and a monitoring station run by the University of Texas (Allen et al., 1999). Although NOₓ measurements
were not taken at the sampling sites, wind directional data (Wiedinmyer et al., 2000) were combined with NO\textsubscript{x} concentrations measured at San Marcos, TX and Fayetteville, TX to estimate NO\textsubscript{x} levels at the TEXIE sites. San Marcos is located 72 miles southwest of Pedernales and 44 miles southeast of Bastrop; Fayetteville is located 46 miles southeast of Bastrop and 64 miles southeast of Elgin.

4.2.2. **Ozone Formation from Isoprene**

Isoprene is the biogenic compound emitted in the greatest quantities, has a relatively rapid rate of reaction with the hydroxyl radical, and thus is potentially important with respect to rural and urban O\textsubscript{3} formation. Numerous studies have independently reported isoprene's reaction products. Miyoshi et al. (1994) report a 22% yield of methacrolein as a primary reaction product of isoprene in both NO\textsubscript{x}-rich and NO\textsubscript{x}-free conditions. Tuazon and Atkinson (1990) report 21%, while Paulson et al. (1992) report a 25% yield, in close agreement with the value obtained by Miyoshi et al. (1994).

Using the measured methacrolein data at each tower at each site (Wiedinmyer et al., 2000) and a product formation yield of 0.22 from the photooxidation of isoprene, the concentration of reacted isoprene on a per-carbon basis was determined, termed Δisoprene (ppbC). Using calculated reacted isoprene values and isoprene's incremental reactivity, ΔO\textsubscript{3}—i.e., ozone produced from isoprene photooxidation—was calculated according to equation (3.1).

4.2.3. **ΔVOC\textsubscript{C} Calculations**

While over 70 compounds were measured during the sampling period and are used to quantify total VOC concentrations, a subset of 15 compounds was used to determine the
O₃ produced from photooxidation of VOCs and the O₃-forming capacity of the atmosphere (Table 4.1). The compounds listed in Table 4.1 were commonly quantified among the highest concentrations of VOCs and were selected to include a wide range of reaction rates with the hydroxyl radical and a variety of classes, including carbonyls, paraffins, olefins, and aromatics. This subset of compounds was used as a representative sample to approximate the actual atmospheric composition.

The value of ΔVOCᵢ, the concentration of reacted VOCᵢ, was calculated from

\[
\Delta \text{VOC}_i = \Delta \text{isoprene} \cdot \frac{k_{\text{VOC}_i}^{\text{OH}}}{k_{\text{isoprene}}^{\text{OH}}} \cdot \frac{[\text{VOC}_i]}{[\text{isoprene}]}
\]  

(4.2)

where \( k_{\text{VOC}_i}^{\text{OH}} \) and \( k_{\text{isoprene}}^{\text{OH}} \) are the rate constants listed in Table 4.1 for reaction of the hydroxyl radical and VOCᵢ, (Atkinson, 1990), and \([\text{VOC}_i]\) and \([\text{isoprene}]\) are the measured concentrations of VOCᵢ and isoprene (ppbC). If the isoprene measurement was below detection, usually with urban samples, the concentration was assigned a value of 1.7 ppbC, the lower limit of detection for isoprene. As with Δisoprene, the values of ΔVOCᵢ were used individually to calculate the O₃ formed by the addition of each VOC to the atmospheric mixture from equation (4.1).

4.2.4. CARBONYL INCREMENTAL REACTIVITY

Incremental reactivities for urban (VOC/NOₓ = 8.2) and rural (VOC/NOₓ = 20) scenarios are reported by Bowman and Seinfeld (1994) for fifteen classes of compounds. The values were determined using a chamber model simulation on the condensed SAPRC-90 chemical mechanism for 15 hour simulations (0600-2100) with the time-varying solar irradiation of June 21. General categories, such as carbonyls, were subdivided according to
hydroxyl-reaction rate constant and compound structure. Incremental reactivities (in ppb O₃ ppbC⁻¹) for urban and rural conditions are listed in Table 4.2. A MIX category is included in

Table 4.1. Compounds selected for use in O₃-forming studies and their kₒH reaction rate constants.

<table>
<thead>
<tr>
<th>Compound and Classification</th>
<th>Reaction Rate Constant b (kₒH VOC⁻¹) (10¹² cm³molec⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>isoprene (OLE3)</td>
<td>101.00</td>
</tr>
<tr>
<td>HCHO (HCHO)</td>
<td>9.77</td>
</tr>
<tr>
<td>butane (ALK1)</td>
<td>2.54</td>
</tr>
<tr>
<td>propane (ALK1)</td>
<td>1.15</td>
</tr>
<tr>
<td>hexane (ALK2)</td>
<td>5.61</td>
</tr>
<tr>
<td>toluene (ARO1)</td>
<td>5.96</td>
</tr>
<tr>
<td>o-ethyltoluene (ARO2)</td>
<td>12.30</td>
</tr>
<tr>
<td>m-ethyltoluene (ARO2)</td>
<td>19.20</td>
</tr>
<tr>
<td>p-ethyltoluene (ARO2)</td>
<td>12.10</td>
</tr>
<tr>
<td>n-propylbenzene (ARO2)</td>
<td>6.00</td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene (ARO2)</td>
<td>57.50</td>
</tr>
<tr>
<td>o-xylene (ARO2)</td>
<td>13.70</td>
</tr>
<tr>
<td>m-xylene (ARO2)</td>
<td>23.60</td>
</tr>
<tr>
<td>p-xylene (ARO2)</td>
<td>14.30</td>
</tr>
<tr>
<td>1-butene (OLE1)</td>
<td>31.40</td>
</tr>
</tbody>
</table>

aCompound classifications are those defined in Bowman and Seinfeld (1994) and used in incremental reactivity calculations (see also Table 4.2).

the table, incorporating a relative mixture of each compound class listed in Table 4.2. The incremental reactivity for MIX was calculated using the initial base case organic concentrations from Seinfeld and Bowman (1994), excluding CO and CH₄ concentrations. The MIX incremental reactivity was the sum of the weighted individual incremental reactivities (in ppb O₃ ppbC⁻¹) for the remaining classes (i.e., all categories excluding CO and CH₄).

Although incremental reactivity is based on the addition of a small amount of a compound to overall emissions, the calculated O₃ concentrations were extrapolated for higher compound concentrations. Thus the O₃ predicted is considered a theoretical upper
limit of formation and is greatly dependent upon VOC to NO\textsubscript{x} ratios, especially where limited NO\textsubscript{x} quantities result in limited O\textsubscript{3} produced, as in rural areas (Benjamin and Winer, 1998).

4.2.5. PROPAGATION OF ERROR

The error associated with ozone calculations was determined using the lower limit of detection (LLD) for methacrolein concentrations (0.10 ppbv) (Wiedinmyer et al., 1999). Reacted isoprene (\Delta isoprene) was calculated using the methacrolein lower limit, and subsequent calculations for individual compounds and for the mixture were also calculated.

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>Carbon Fraction (%)\textsuperscript{a}</th>
<th>VOC/NO\textsubscript{x} = 8.2</th>
<th>VOC/NO\textsubscript{x} = 20</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Carboxylics</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td>0.74</td>
<td>3.260</td>
<td>0.340</td>
</tr>
<tr>
<td>CCHO</td>
<td>0.43</td>
<td>1.210</td>
<td>0.078</td>
</tr>
<tr>
<td>RCHO</td>
<td>0.16</td>
<td>1.480</td>
<td>0.017</td>
</tr>
<tr>
<td>MEK</td>
<td>1.48</td>
<td>0.180</td>
<td>0.008</td>
</tr>
<tr>
<td><em>Alkanes</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALK1</td>
<td>32.07</td>
<td>0.070</td>
<td>0.037</td>
</tr>
<tr>
<td>ALK2</td>
<td>21.41</td>
<td>0.090</td>
<td>0.020</td>
</tr>
<tr>
<td><em>Aromatics</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ARO1</td>
<td>13.36</td>
<td>0.180</td>
<td>-0.110</td>
</tr>
<tr>
<td>ARO2</td>
<td>9.84</td>
<td>0.940</td>
<td>-0.040</td>
</tr>
<tr>
<td><em>Alkenes</em></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETHE1</td>
<td>6.80</td>
<td>0.660</td>
<td>0.170</td>
</tr>
<tr>
<td>OLE1</td>
<td>5.43</td>
<td>0.860</td>
<td>0.079</td>
</tr>
<tr>
<td>OLE2</td>
<td>2.62</td>
<td>1.050</td>
<td>0.047</td>
</tr>
<tr>
<td>OLE3</td>
<td>5.66</td>
<td>0.820</td>
<td>0.056</td>
</tr>
<tr>
<td>MIX\textsuperscript{b}</td>
<td>0.358</td>
<td>0.210</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Percent carbon fraction based on Bowman and Seinfeld's (1994) base case initial organic concentration, recalculated without CO and CH\textsubscript{4}

\textsuperscript{b}Incremental reactivity for the MIX (mixture of VOCs) is a weighted average of the VOCs using the percent carbon fraction.
by propagating these values. The average and one standard deviation of the ozone concentrations were calculated; the average and standard deviation reported in the results include only those values statistically different from values below the level of detection.

4.2.6. Predicted Formaldehyde Concentrations

The predicted concentration of formaldehyde was also calculated at each tower/hour for the three rural sites as a further measure of the extent of oxidative capacity of the atmosphere. Predicted HCHO concentrations were calculated from reacted isoprene, adjusted by a factor which accounts for the expected HCHO product. Thus,

\[ [\text{HCHO}]_{\text{predicted}} = \Delta \text{isoprene} \cdot f_{\text{HCHO}}, \]

where the quantity \( \Delta \text{isoprene} \) represents the concentration of reacted isoprene (ppbv) and \( f_{\text{HCHO}} \) is 0.63, the total fractional yield of HCHO from isoprene as reported by Carter and Atkinson (1996).

4.3. Results And Discussion

4.3.1. VOC/NO\textsubscript{x} Measurements

Total VOC concentrations (ppbC) were analyzed from the stainless steel canisters, where over 70 organic compounds were collected. At the rural sites, total VOCs ranged from 72 to 372 ppbC at Bastrop; 43 to 246 ppbC at Pedernales; and 50 to 217 ppbC at Elgin. A similar but slightly smaller range was found at Austin (39 to 182 ppbC). The mean concentrations of VOCs were similar for all four sites: 132, 120, 90, and 116 ppbC at Bastrop, Austin, Pedernales, and Elgin, respectively.
Meteorological data from Bastrop indicate that winds were from the Southeast and Southwest, respectively, on the two sampling days (August 11-12, 1998). Thus, data from Fayetteville (Allen et al., 1999) and the TNRCC San Marcos CAMS 62 site were used to estimate NO\textsubscript{x}. The NO\textsubscript{x} concentration average from San Marcos was 4.7 ppb NO\textsubscript{x}, and that from Fayetteville was 10.5 ppb NO\textsubscript{x}. CAMS 62 data were not available for the sampling date, and instead an average of NO\textsubscript{x} values from the following week was used as an estimate of NO\textsubscript{x} emissions measured at this site. The resulting average VOC/NO\textsubscript{x} ratio in Bastrop for August 11-12 is 19.2.

In Pedernales, measurements were taken on August 18-19, 1998. Meteorological data recorded in Pedernales indicate that winds were from the Southeast. Thus, San Marcos data were again required for reported NO\textsubscript{x} data, where the weekly NO\textsubscript{x} average concentration was 4.7 ppb, and the calculated VOC/NO\textsubscript{x} ratio is 19.1. In Elgin, meteorological data show that winds were coming from the North and North-Northeast; however, there were no monitoring stations from this direction. No urban centers or industrial NO\textsubscript{x} sources are upwind of Elgin under these meteorological conditions; thus, it is expected that actual NO\textsubscript{x} concentrations likely to be present on the sampling days in Elgin are much lower than even that at Bastrop/Fayetteville. Although the precise value for the ratio is unknown, the VOC/NO\textsubscript{x} ratio for Elgin was that assigned to the other rural sites, namely 20.

NO\textsubscript{x} data in Austin were not available on the sampling days. Summary data on the VOC/NO\textsubscript{x} ratio for various eastern United States cities were collected by Wolff and Korsog (1992), with median ratios ranging from 5.4 to 9.7 for urban centers such as Philadelphia, Cleveland, and Atlanta, and it is assumed that the ratio in Austin is similar only for purposes of predicting the potential for ozone formation. Bowman and Seinfeld (1994) found that
maximum incremental reactivity in simulations occurred at VOC/NO\textsubscript{x} ratios of 4 and 8.2. Thus, in the following discussion, the ozone formation potential was calculated at the maximum value (using incremental reactivity at VOC/NO\textsubscript{x} = 8.2, similar to that assumed to be in Austin) as well as a ‘rural’ value calculated when VOC/NO\textsubscript{x} = 20, representative of the VOC/NO\textsubscript{x} ratios found at Bastrop, Pedernales, and Elgin.

4.3.2. OZONE CONCENTRATIONS ATTRIBUTABLE TO PHOTOOXIDATION OF MEASURED VOCs

Reacted isoprene values (Δisoprene) were used to calculate ΔO\textsubscript{3} according to equation (4.1), and subsequently ΔVOC concentrations were calculated for all 15 compounds considered, according to equation (4.2). The sum of these individual compounds’ ΔVOC, or $\sum_{i=1}^{15} \Delta{\text{VOC}}_i$, was then used with the MIX value for the incremental reactivity (IR) to determine the ozone concentrations attributable to VOC photooxidation for the mixture of compounds. This calculation was made for each tower and each hour of sampling using both the MIX IR for urban (VOC/NO\textsubscript{x} = 8.2) and rural (VOC/NO\textsubscript{x} = 20) scenarios, and defined as urban,mix and rural,mix, respectively. The average ozone concentrations produced from VOC reaction at the four sampling sites is shown in Figure 4.1. The averages for each site were determined using only values above detection limits; error bars indicate one standard deviation from the mean (section entitled Propagation of Error).

As seen in Figure 4.1, ozone levels attributed to VOC reaction at the sites under typical rural VOC/NO\textsubscript{x} conditions (rural,mix) are much lower than if formed under a higher NO\textsubscript{x} setting. While the ozone concentration using a rural MIX IR is 0.6 ppbv at Pedernales
and Elgin and 0.8 ppbv at Bastrop and Austin, the range and values of ozone concentrations using urban incremental reactivity data are much greater, from 8.7 ppbv at Pedernales to 20.0 ppbv at Bastrop.

4.3.3. Spatial Variation

The various concentrations of ozone that are attributable to VOC photooxidation at the urban and rural sites are indicative of the spatial differences between these sites. One objective of the TEXIE study was to measure simultaneously primary and secondary biogenic emissions to lend further insight into the oxidizing capacity of the atmosphere. From Wiedinmyer et al. (2000), the overall ratio of methacrolein to isoprene at Pedernales and Elgin is 0.2 and 0.1, while this ratio at Bastrop and Austin is 0.5 and 0.7, respectively.

![Bar chart showing ozone concentrations at different sites](image)

**Figure 4.1.** Average ozone concentrations (ppbv) attributable to photooxidation of VOCs at the TEXIE sampling sites using the incremental reactivity of a mixture of components in the atmosphere. All averages comprise those values calculated when methacrolein levels were above the lower limit of detection. Error bars represent one standard deviation.

The atmosphere measured in Pedernales and Elgin shows less oxidation than that of Bastrop and Austin, indicated by the higher measured concentrations of the primary component isoprene and reduced levels of the secondary product, methacrolein. The highest methacrolein to isoprene ratio is in Austin, as higher NOx levels are typical of urban
centers, leading to atmospheric oxidation. Despite the higher ratio of methacrolein to isoprene in Austin, the highest ozone concentration, from VOC reaction, was found in Bastrop. Average measured isoprene concentrations in Bastrop were double the concentrations measured in Austin (2.4 vs. 1.2 ppbv), and methacrolein concentrations were also higher in Bastrop (1.1 vs. 0.8 ppbv). The high methacrolein levels are an indication of the oxidizing capacity of Bastrop, which can be characterized as a rural area surrounded by industrial NOx sources, while lower measured isoprene concentrations in Austin lead to lower measured methacrolein concentrations (and subsequent lower measured ozone formation).

4.3.4. Diurnal Patterns

The concentration of O3 ascribed to photooxidation of VOCs during each hour, given incremental reactivities for both rural and urban VOC/NOx ratios, was averaged for the three rural sites (Bastrop, Pedernales, and Elgin). From Figure 4.2, the hourly average of the three sites follows the diurnal pattern most commonly associated with isoprene emissions. Isoprene emissions increase with light and temperature (Fehsenfeld et al., 1992; Yokouchi, 1994; references therein), leading to higher overall isoprene emissions in the afternoon in the course of a day, and in the summertime in the course of a year. It thus follows that levels of methacrolein, a product of isoprene, also increase as temperature and sunlight increase throughout the day. The difference in O3 formation between rural- and urban-associated incremental reactivities is again quite large, where the rural conditions indicate only 0.4-1.6 ppb O3, while the urban conditions indicate 7.3 to 27.4 ppb O3. While the low persistent levels of O3 from natural sources and under ‘rural NOx’ conditions are of concern to air quality, the potential for O3 to form from NOx transport is significant
in the afternoon, given urban morning rush-hour vehicular emissions (Wolff and Korsog, 1992) and sufficient compound lifetime to allow transport to occur. Further, rural area non-attainment for O₃ NAAQS is considered to become more likely as the requirements for attainment become more stringent and the potential to form O₃ from urban sources persists in rural sectors (Chameides et al., 1997).

4.3.5. OZONE FORMATION POTENTIAL FROM ISOPRENE MEASUREMENTS

Ozone formation potentials vary widely between different VOCs, as seen in the range of values of incremental reactivity (Table 4.2). Although some compounds have a high IR, such as formaldehyde, the overall contribution to O₃ formation can be small because of low ambient concentrations. In rural atmospheres, isoprene is the most prevalent biogenic compound, and in the present study, calculations for the MIX incremental reactivity and hence for O₃ formation included only about 6% isoprene (OLE3 in Table 4.2), derived from the base case scenario presented by Bowman and Seinfeld (1994). At Bastrop,
Pedernales, and Elgin, however, the mean average isoprene percentage of VOCs measured was 10, 17, and 12%, respectively.

Because of this underestimation of isoprene in calculating the MIX incremental reactivity and the importance of isoprene in rural atmospheres, potential O$_3$ formation was calculated for the four sites as a result of isoprene concentrations alone, where actual measured isoprene concentrations were used in equation (4.1). Thus, the calculated O$_3$-forming potential is independent of methacrolein concentrations. Ozone predictions based solely on isoprene considerations were made for incremental reactivities of urban (VOC/NO$_x$ = 8.2) and rural (VOC/NO$_x$ = 20) conditions, termed urban,iso and rural,iso, respectively (Figure 4.3). The O$_3$-formation potential—comparing urban,iso O$_3$ concentrations—is highest at the three rural sites and lowest in Austin. The O$_3$ formation calculations are a direct product of the measured isoprene concentrations, hence the formation of ozone is expected to be highest nearer the source strength of isoprene emissions and concentrations, namely in rural locations. This potential does not necessarily imply that these rural areas have a higher oxidative capacity than Austin; rather, the predicted concentrations are an indication of isoprene-induced O$_3$ formation when NO$_x$ is transported to these rural areas. When VOC/NO$_x$ is 20, the potential for O$_3$ formation is small (at around 1 ppbv), but is considered a persistent concentration, regardless of urban NO$_x$ input.

Predicted O$_3$ concentrations, along with the O$_3$ concentrations that are derived from VOC reaction as illustrated in Figure 4.1, indicate that in rural regions, the potential exists for relatively high concentrations—along the order of 10 to 20 ppbv—given biogenic input into the atmosphere. In addition, the predicted concentrations should be considered an underestimation of actual O$_3$ levels, as only isoprene was used as the basis for formation
potential. Thus, even without an influx of NOx from urban sources, the rural,iso ozone levels would be even higher than 1 ppbv in any of the regions studied.

![Graph showing ppb O3 levels at different sites](image)

**Figure 4.3.** Average potential ozone formation (ppbv) at the TExIE sampling sites where calculations were made from the incremental reactivity of isoprene and measured isoprene concentrations only. Error bars represent one standard deviation.

### 4.3.6. Predicted Formaldehyde Concentrations

Formaldehyde (HCHO) in rural areas is dominated by secondary formation from isoprene photooxidation because of a relative lack of anthropogenic emissions. Urban centers such as Austin, however, are expected to contain HCHO from both primary and secondary sources. Predicted HCHO concentrations from the photooxidation of isoprene were calculated using equation (4.3) to compare with ambient measured HCHO concentrations.

Calculations to predict HCHO were made to compare urban and rural differences in the TExIE study; because the average methacrolein concentration in Bastrop was significantly higher than that in the other rural sites (1.1 ppbv in Bastrop vs. 0.4 and 0.3 ppbv in Pedernales and Elgin, respectively) (Wiedinmyer et al., 2000), the predictions were made for Bastrop and Austin, the urban site. The mean predicted HCHO concentration in
Bastrop is 3.1 ppbv, while the mean measured concentration is 2.4 ppbv. This difference implies that there are no (or few) primary sources of HCHO in Bastrop, and that HCHO formed from photooxidation of isoprene reacts more rapidly than methacrolein (as the measured HCHO is less than predicted).

In Austin, it is expected that primary sources exist in addition to the secondary formation of HCHO, and thus the observed levels of HCHO should be higher than predicted based on biogenic formation. The mean measured concentration of HCHO in Austin is 1.3 ppbv, while the mean predicted HCHO concentration, however, is 2.1 ppbv. Although this result is contrary to expectation, it should be noted that sampling in Austin occurred during a weekend, where significant reductions in vehicular emissions and hence anthropogenic sources of HCHO are expected. Furthermore, observed concentrations are in fact higher than predicted levels at four of the five towers: with the exception of Tower 2 in a wooded neighborhood, the mean measured HCHO concentration is 1.4 ppbv and the predicted concentration is 0.8 ppbv. Anomalous methacrolein concentrations were recorded at Tower 2 (an average of 2.7 ppbv), thus skewing the predicted HCHO concentrations in Austin.

4.3.7. Uncertainties in Calculations

Potential sources of error exist in making the calculations, given various assumptions needed to complete the analysis. For example, there is uncertainty in the accuracy of incremental reactivities of organic compounds in polluted atmospheres, including errors in product yield and rate constants (Yang et al., 1995). Furthermore, the composition of the air that is used to calculate the MIX IR is based on a scenario which is not necessarily representative of most atmospheres. The percent of each compound from each class may be
somewhat under- or overestimated, especially for extreme atmospheric conditions such as completely rural versus heavily polluted regions. Though there is strong agreement as to the product yield in various smog chamber studies, the product yield of methacrolein from isoprene in actual ambient conditions is expected to be quite variable based on several factors, including the prevailing VOC/NO\textsubscript{x} ratio, mean mixing height, and meteorological conditions. A further consideration is the titration of ozone with NO\textsubscript{x}, which tends to occur in urban centers, leading to over-predictions of ozone formation in urban areas. Though subject to these uncertainties, potential ozone calculations are useful for determining ozone concentrations at least qualitatively, which are especially useful for policy-making and reduced emissions strategies.

4.3.8. Discussion

Altshuller (1983) reports the lifetime of atmospheric isoprene in the presence of O\textsubscript{3} and OH\textsuperscript{*} radicals as varying from 1.3 to 34.0 hours, depending on the respective concentrations of O\textsubscript{3} and OH\textsuperscript{*}. Thus, the influx of biogenic VOCs from nearby rural to urban centers is likely given the lifetime of isoprene. Isaksen et al. (1978) also concluded that O\textsubscript{3} production from the release of urban NO\textsubscript{x} reaches a maximum level far outside the urban point source of release, and remains high for several hours. Trainer et al. (1987) concluded that, in the presence of significant isoprene emissions, a reduction in anthropogenic hydrocarbons will most likely not reduce high rural O\textsubscript{3} levels; however, NO\textsubscript{x} reductions will decrease O\textsubscript{3} levels. Thus, given the importance of potentially high O\textsubscript{3} levels at rural areas under urban VOC/NO\textsubscript{x} conditions, it is evident that to effect control of O\textsubscript{3} produced primarily from biogenics, a reduction in urban NO\textsubscript{x} emissions is required, as rural sources entering urban centers or NO\textsubscript{x} emissions entering rural regions potentially cause
large increases in total O₃ formation. Further, there remains a concern for meeting NAAQS requirements in rural regions because of the persistent low levels of O₃ that exist from biogenic emissions coupled with the potential for peak O₃ episodes.
SECTION 2
ANTHROPOGENIC CARBONYL COMPOUNDS
CHAPTER 5

AMBIENT SAMPLING AND CARBONYL IDENTIFICATION USING PFBHA DERIVATIZATION AND GC/MS

5.1. INTRODUCTION

5.1.1. BACKGROUND

Aldehydes and ketones exist in the atmosphere in relatively high concentrations, typically on the order of sub-parts per billion volume (ppbv) in rural regions up to 10 - 20 ppbv in many urban settings for the most prevalent carbonyls (Carlier et al., 1986). Both anthropogenic and biogenic emissions contribute to elevated levels of these carbonyl compounds. In large metropolitan areas such as Houston, the emissions from such sources as vehicular exhaust and power plants predominate the relatively lower biogenic emissions. Mixing of anthropogenic and biogenic compounds in surrounding and downwind areas produces elevated concentrations which potentially lead to high ozone (O₃) formation and smog production as well as associated health risks.

In 1999, Houston recorded the highest number of days of United States cities in which O₃ levels exceeded national standards. Furthermore, carbonyl emissions alone account for many health concerns, potentially leading to increased allergies, eye irritation, and respiratory difficulties (Johnson et al., 1981). Most aldehydes and ketones are also known or suspected toxins or carcinogens at high levels of exposure (National Research Council, 1981). In the presence of high concentrations of oxides of nitrogen (NOₓ), many carbonyl reactions yield radicals, carbon monoxide (CO), or peroxyacetyl nitrate (PAN) (Fehsenfeld et al., 1992; Grosjean et al., 1996b).
5.1.2. Motivation

Quantification of carbonyl compounds serves as an important predictor for measuring O₃ levels as well as setting standards for emissions based on health issues. In addition to the concerns of higher level carbonyl emissions, measurements are also required at very low levels, even as low as several hundred parts per trillion volume (pptv). Although many carbonyl compounds can persist in the pptv range, they are typically not monitored by regulatory agencies because of the individual small relative contribution to the overall carbonyl atmospheric composition or because of difficulty in detecting and quantifying these compounds. The sum of these smaller contributions, especially if unregulated, can further increase O₃ formation and health risks. Most sampling techniques overlook aldehydes and ketones in this range because of predominance of other compound concentrations, chromatographic coelution, or instrument detection limits (Lewis et al., 2000).

5.1.3. PFBHA Study Objectives

Over the last several decades, many techniques have been used for carbonyl collection and quantification, including colorimetric, chromatographic, and spectroscopic detection (Kuwata et al., 1979; Salas and Singh, 1986; Vairavamurthy et al., 1992; Grosjean and Grosjean, 1995). In this chapter, a gas chromatographic derivatization method with spectrometric detection is used to identify low-lying levels of ambient atmospheric carbonyls. Aldehydes or ketones are derivatized by o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) to form the corresponding oxime. The PFBHA method was originally developed for carbonyl isolation for biological purposes (Koshy et al., 1975; Fitzpatrick et al., 1977), but was later adapted for use in
analyzing water contamination (Glaze et al., 1989) and atmospheric carbonyl collection (Yu et al., 1995).

The PFHBA collection method maintains several advantages over 2,4-dinitrophenylhydrazine (DNPH) cartridge collection, as PFHBA collection uses increased sensitivity and selectivity with mass spectrometric (MS) detection to determine and identify low concentration levels. The MS in electron ionization (EI) mode detected carboxyls on the order of several hundred pptv, as opposed to several hundred ppbv with DNPH collection (Tanner and Meng, 1984; Trapp and de Serves, 1995). Identification of unknown carboxyls via mass spectrum analysis becomes possible with this method.

Although Yu et al. (1995) tested the PFHBA method with a controlled input smog chamber and TFE bag collection, limited reports to date employ this method with ambient measurements. Friedfeld et al. (2000) previously tested the method on formaldehyde collection by simultaneous comparison with an optical sensor, resulting in a -1.2 ppbv bias and 1.5 ppbv gross error. Although reported levels of carboxyls are time-integrated averages using PFHBA collection, compared to near real-time data from the optical sensor collection, the PFHBA method offers the advantage of potentially collecting a wide spectrum of compounds at very low levels, rather than isolating one compound.

In this chapter, the study objectives included quantifying carboxyl compounds over a one-week period using the PFHBA/EI method, and identifying less commonly measured carboxyls using standard fingerprints such as retention time (RT) and mass structure.
5.2. MATERIALS AND METHODS

5.2.1. PREPARATION OF STANDARD COMPOUNDS

Standard derivatives were prepared for representative atmospheric carbonyl compounds (Table 5.1). These model compounds serve as a basis for identifying sample peaks using mass spectra patterns and RT. To formulate each standard, the oxime form of each model ketone or aldehyde was synthesized. Specifically, 10 mg/L aqueous solutions of each pure (>99%) compound were prepared and stored in amber glass vials. A 5 mL aliquot of this aqueous solution was added to another aqueous solution containing the derivatizing agent, comprised of 5 mg/mL PFBHA to ensure complete derivatization. One drop of 12 M HCl was added to lower the pH to about 1 to 2 to catalyze the overnight reaction. In the final step, 2 drops 12 M HCl were added to the solution immediately preceding the addition of 1 mL hexane. The pH of the solution was lowered to prevent excess PFBHA from entering the GC column to minimize deterioration (Yu et al., 1995). The hexane extract was removed from solution with an efficiency >99%; all extracts and subsequent dilutions in hexane were stored at -5°C.

5.2.2. MODEL CARBONYL RESULTS

The model compounds in Table 5.1 represent common pollutants in the atmosphere, divided into four classes to aid in identifying unknown carbonyls: (1) monofunctional aldehydes, compounds with a terminal HC=O moiety; (2) monofunctional ketones, compounds with one C=O bond; (3) hydroxy carbonyl compounds, carbonyls with an OH functional group; and (4) dicarbonyls, characterized by two C=O bonds.

**TABLE NOTATION.** In the table, MW denotes carbonyl molecular weight; M represents oxime molecular weight; and retention time (RT) is in minutes. In the acid-
catalyzed derivatization reaction, the carbonyl carbon forms a bond with the amine group of the PFBHA (C₆F₅CH₂ONH₂) while releasing H₂O. Both M and related mass fragments common to most of the model compounds aid in identifying or fingerprinting a carbonyl. The mass fragment in the highest abundance is also given, and facilitates carbonyl identification. While the presence of a carbonyl is confirmed in the mass spectra by both the \( m/z \) 181 (C₆F₅CH₂⁻) and 195 (C₆F₅CH₂O⁻) peaks, the mass fragment at \( m/z \) 181 is typically greater than the next highest peak by one order of magnitude. Thus, all mass fragment abundances listed in Table 5.1 are relative to the \( m/z \) 195 peak abundance.

**Spectrometric Patterns.** Other patterns are useful in identifying unknown carbonyls; two peaks signify compounds that are asymmetric about the carbonyl carbon, while symmetric compounds produce only one chromatographic peak. \( M^* \) designates mass fragments for dicarbonyl compounds only, where \( M^* \) represents the oxime molecular weight (M) with the additional loss of 2 H⁻ atoms. In addition, \( m/z \) M – 17 identifies most ketones and dicarbonyls, and several straight chain aldehydes, where M – 17 indicates the loss of H₂O from the MH⁻ ion. The M – 30 mass peak corresponds to the loss of two methyl groups (CH₃), typical of lower monofunctional aldehydes, monofunctional ketones, and hydroxy carbonyls. The presence of a mass fragment at M – 181 and M – 211 (corresponding to a loss of C₆F₅CH₃⁻ and C₆F₅CH₂ON⁻) confirmed most oxime MWs (hydroxy carbonyls were an exception). Finally, PFBHA does *not* derivatize any carbonyl group bonded to another oxygen atom, including carboxylic acids and ethers such as methyl methacrylate and vinyl acetate.
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<th>Compound</th>
<th>RT (min)</th>
<th>Formula</th>
<th>MW</th>
<th>M</th>
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<th>M-181</th>
<th>M-211</th>
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Table 5.1. [previous page] Model compounds used for the identification of unknown carbonyl atmospheric compounds. Compounds are divided into four classes: monofunctional carbonyls and ketones, hydroxy carbonyls, and dicarbonyls. MW, molecular weight of the carbonyl; M, molecular weight of the PFBHA-carbonyl oxime; M*, M – 2 typical of the dicarbonyls.

5.2.3. SAMPLING AND ANALYZING PROCEDURES

For ambient sampling, an SKC AirChek sampler pump at a nominal 2.0 L min\(^{-1}\) flow rate collected air into a 30 mL vacuum-sealed glass impinger containing 20 mL deionized water. The impinger was connected to the pump via 52 cm Tygon tubing (5/16” i.d., 1/8” wall); the external end of the impinger was attached to 5 m TFE Teflon tubing to 3 m height outside a sampling trailer. After each 24 h sample, 5 mL of the deionized water was collected in 8 mL vials and immediately added to 0.5 mL PFBHA solution with 1 drop 12 M HCl. The solution was treated exactly as the model standards, with hexane extraction following overnight reaction.

A Hewlett Packard (HP) 6890 Series Gas Chromatograph (GC) coupled with 5973 Mass Selective (MS) Detector was used to analyze all standards and samples, employing an HP-5MS column (cross-linked 5% PH ME siloxane; dimensions 30 m × 0.25 mm × 0.25 μm). The following temperature program eluted all oximes between 6 and 35 min: 60°C constant for 1 min; 5°C/min up to 200°C; 4°C/min up to 225°C; held constant at 225°C for 5 min. All injections were 1 μL volume with a preprogrammed 2 min solvent delay.

5.2.4. SITE

The Texas Natural Resource Conservation Commission (TNRCC) operates several sites in the Houston area for monitoring pollutants. The TNRCC Continuous Air Monitoring Station (CAMS) site at Deer Park is situated south of the Houston Ship Channel
entrance into the City of Houston, and west of the Ship Channel head. Deer Park is an industrialized city situated between Houston and the Gulf of Mexico (Figure 5.1). One-day (24 hour) time-integrated samples were taken from June 14 to June 20, 2000. During the sampling period, temperature and relative humidity varied from 23-33°C and 48-98% RH.

5.3. RESULTS AND DISCUSSION

5.3.1. MODEL CARBONYL COMPOUND IDENTIFICATION

The 24-hour time-integrated samples from each day of the study produced similar chromatograms both in the number and elution of peaks. While all seven samples were used for qualitative carbonyl identification, only four samples (0614, 0618, 0619, and 0620) were sufficiently recovered for compound quantification. The chromatogram from June 14 (sample 0614) is representative of the number and elution times of carbonyls detected from each day of sampling (Figure 5.2), thus only this chromatogram is used for descriptive purposes.

FORMALDEHYDE, ACETONE, ACETALDEHYDE. These compounds are typical components of both urban and rural atmospheres (Tanner et al., 1988; Zhang et al., 2000), resulting from primary and secondary anthropogenic and biogenic sources (Vupputuri, 1988; Moussiopoulos, 1990; Lee et al., 1995; Benning and Wahner, 1998). Given standard RTs, the formaldehyde, acetaldehyde, and acetone peaks are respectively labeled A, B1 and B2, and C in Figure 5.2. In Table 5.2, the compounds are identified (or suggested, for those unable to be identified); Table 5.3 includes the concentrations and several ratios of carbonyls observed.
Equivalent atmospheric concentrations for: formaldehyde, acetaldehyde, and acetone ranged from 2.4 to 7.7 ppbv; 0.37 to 0.43 ppbv; and 0.5 to 1.1 ppbv, respectively, throughout the weeklong campaign. The average ratio of acetaldehyde to formaldehyde ranged from 5% to 15%, considerably lower than that generally reported in other studies. Salas and Singh (1986) reported simultaneous acetaldehyde and formaldehyde measurements at various US cities, with ratios ranging from 8% (Pittsburgh) to 60% (Southern California). Grosjean et al. (1996) measured significantly higher acetaldehyde than formaldehyde concentrations, with ratios from 60% to 100%; Tanner et al. (1988) also found a 60% ratio.
Though the data presented in this study represent a limited sampling base, the low ratio suggests that strong biogenic inputs may exist,

![Graph](image)

**Figure 5.2.** Entire chromatogram for sample 0614, on June 14, 2000. Each run lasted 40 minutes; the peaks are labeled as in Table 5.2. All seven day-long samples were qualitatively identical; hence, the compounds detected are representative of each sampling day. X-axis: elution time; Y-axis: mass abundance.

where isoprene oxidation leads to high formaldehyde levels but does not yield acetaldehyde (Tanner and Meng, 1984; Fehsenfeld et al., 1992)—more likely, however, strong primary sources of formaldehyde exist in the Deer Park area from industrial emissions, in addition to numerous secondary anthropogenic origins of formaldehyde.

**Other VOCs.** Based on retention time alone, peaks D1 and D2 in Figure 5.2 represented methyl ethyl ketone (MEK), a four-carbon ketone that is found in both rural and urban atmospheres. In industrialized regions, MEK is emitted as a by-product in solvent and insecticide production, among other uses. The mass spectrum confirmed the MEK peaks based on a fragment at $m/\chi 250$ ($M - 17$); this $m/\chi$ fragment has the highest
Table 5.2. Atmospheric carbonyl compound identification for sample 0614 (June 14, 2000) at Deer Park, TX.

<table>
<thead>
<tr>
<th>Peak Name</th>
<th>Retention Time</th>
<th>Compound</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>6.1</td>
<td>formaldehyde</td>
<td>standard match</td>
</tr>
<tr>
<td>B1</td>
<td>8.4</td>
<td>acetaldehyde</td>
<td>standard match</td>
</tr>
<tr>
<td>B2</td>
<td>8.6</td>
<td>acetaldehyde</td>
<td>standard match</td>
</tr>
<tr>
<td>C</td>
<td>10.1</td>
<td>acetone</td>
<td>standard match</td>
</tr>
<tr>
<td>D1</td>
<td>12.1</td>
<td>methyl ethyl ketone</td>
<td>m/z 250; see text</td>
</tr>
<tr>
<td>D2</td>
<td>12.2</td>
<td>methyl ethyl ketone</td>
<td></td>
</tr>
<tr>
<td>E1</td>
<td>15.2</td>
<td>pentanal</td>
<td>see text</td>
</tr>
<tr>
<td>E2</td>
<td>15.4</td>
<td>pentanal</td>
<td>see text</td>
</tr>
<tr>
<td>F1</td>
<td>15.6</td>
<td>3-hexanone</td>
<td>identified as match</td>
</tr>
<tr>
<td>F2</td>
<td>15.7</td>
<td>3-hexanone</td>
<td></td>
</tr>
<tr>
<td>G1</td>
<td>16.0</td>
<td>2-hexanone</td>
<td>identified as match</td>
</tr>
<tr>
<td>G2</td>
<td>16.3</td>
<td>2-hexanone</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>18.0</td>
<td></td>
<td>m/z 276; MW 98?</td>
</tr>
<tr>
<td>I1</td>
<td>18.6</td>
<td></td>
<td>MW 98?</td>
</tr>
<tr>
<td>I2</td>
<td>18.7</td>
<td></td>
<td>MW 98?</td>
</tr>
<tr>
<td>J</td>
<td>20.7</td>
<td></td>
<td>MW 196?</td>
</tr>
<tr>
<td>K1</td>
<td>22.0</td>
<td></td>
<td>dicarbonyl?; MW 72?</td>
</tr>
<tr>
<td>K2</td>
<td>22.4</td>
<td></td>
<td>dicarbonyl?; MW 72?</td>
</tr>
<tr>
<td>L1</td>
<td>27.8</td>
<td>glyoxal</td>
<td>standard match</td>
</tr>
<tr>
<td>L2</td>
<td>28.1</td>
<td>glyoxal</td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>28.2</td>
<td>methyl glyoxal</td>
<td>standard match</td>
</tr>
<tr>
<td>M2</td>
<td>28.8</td>
<td>methyl glyoxal</td>
<td></td>
</tr>
</tbody>
</table>

abundance, resulting from the loss of H₂O from the MH⁺ compound. Only m/z 250 appeared in D1, however, additional mass fragments (M and M – 181) in D2 confirmed MEK identification. The overall MEK concentration is relatively low, producing a correspondingly weak signal.

The peaks at 27 and 28 min matched with standard carbonyl chromatograms, namely peaks L1 and L2 were formed from glyoxal, and M1 and M2 from methyl glyoxal, compounds commonly found as secondary products of isoprene emissions or via aromatic hydrocarbon oxidation in urban environments (Plum et al., 1992). These dicarbonyl compounds can be readily identified by mass fragments equal to M + 165 and M + 195,
Table 5.3. Atmospheric concentrations (ppbv) for sampling from Deer Park, TX.

<table>
<thead>
<tr>
<th>Sample</th>
<th>form</th>
<th>ace</th>
<th>act</th>
<th>gly</th>
<th>mgly</th>
<th>2hex</th>
<th>3hex</th>
<th>mek</th>
<th>ace/form</th>
<th>$^{a+a+b}$ tot c</th>
</tr>
</thead>
<tbody>
<tr>
<td>0614</td>
<td>3.4</td>
<td>0.4</td>
<td>0.5</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.7</td>
<td>0.2</td>
<td>0.12</td>
<td>0.61</td>
</tr>
<tr>
<td>0618</td>
<td>7.7</td>
<td>0.4</td>
<td>1.1</td>
<td>0.8</td>
<td>0.7</td>
<td>0.2</td>
<td>0.3</td>
<td>0.1</td>
<td>0.05</td>
<td>0.81</td>
</tr>
<tr>
<td>0619</td>
<td>2.4</td>
<td>0.4</td>
<td>0.7</td>
<td>dnd*</td>
<td>dnd</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.15</td>
<td>0.76</td>
</tr>
<tr>
<td>0620</td>
<td>4.9</td>
<td>0.4</td>
<td>1.0</td>
<td>dnd</td>
<td>dnd</td>
<td>0.7</td>
<td>0.3</td>
<td>0.2</td>
<td>0.09</td>
<td>0.80</td>
</tr>
</tbody>
</table>

*form = formaldehyde
ace = acetaldehyde
act = acetone
gly = glyoxal
mgly = methylglyoxal
2hex = 2-hexanone
3hex = 3-hexanone
mek = methyl ethyl ketone
*dnd = did not detect

peaks that arise from the additional derivatization that occurs on the second C=O bond. Glyoxal concentrations were slightly higher than methyl glyoxal concentrations, however, glyoxal concentrations were at the limits of detection for two of the four samples (Table 5.3). Though small sampling sizes can prove unreliable, the ratio formaldehyde to glyoxal ratio ranges from ~4 to ~9 and the formaldehyde to methyl glyoxal ratio ranges from 6 to 11. According to Lee et al. (1992), isoprene oxidation reaction alone yields a formaldehyde to methyl glyoxal ratio of 7. As at Deer Park, Lee (1992) reported similar glyoxal and methyl glyoxal concentrations, and attributed the similar concentrations to an additional source of glyoxal, since the biogenic reaction should produce a factor of three more methyl glyoxal than glyoxal.

**Mass Peak Extraction.** The entire extracted chromatogram at mass 181 for sample 0614 is given in Figure 5.3. The $m/z$ 181 mass fragment positively indicates the presence of the PFBHA derivative ($181 = C_6F_5CH_2^+$, the PFBHA base). Most carbonyl compounds—with the typical exception of formaldehyde, acetaldehyde, and acetone—were collected at low concentrations; the ion extraction thus provides a qualitative array of volatile
organic compounds (VOCs) that comprise urban pollution and for which no regular monitoring exists.

![Ion chromatogram extraction for the Deer Park 24-hour sample 0614 (June 14). The ion extraction at m/z 181 yields all peaks containing that mass fragment, evidence of successful PFBHA derivatization. X-axis: elution time; Y-axis: mass abundance.](image)

**Figure 5.3.** Ion chromatogram extraction for the Deer Park 24-hour sample 0614 (June 14). The ion extraction at m/z 181 yields all peaks containing that mass fragment, evidence of successful PFBHA derivatization. X-axis: elution time; Y-axis: mass abundance.

### 5.3.2. **UNKNOWN CARBONYL COMPOUND IDENTIFICATION**

The mass spectra for peaks E1 and E2 at retention times 15.2 and 15.4 min indicate only mass fragmentation at m/z 181, indicating PFBHA presence without evidence of the carbonyl; following concentrating the sample five-fold, there was still no fragmentation to enable identification. Based on model carbonyl RTs, it is tentatively suggested that peaks E1 and E2 indicate the presence of pentanal, a 5-carbon straight chain aldehyde. The isomers 3-methyl-2-pentanone and 4-methyl-2-pentanone were also considered when investigating the unknown peaks, based on RT (these compounds were not further considered because overlap with only one peak was found for either standard).

Peaks F1 and F2, at RT 15.6 and 15.7 min, yield nearly identical mass spectra; and thus derive from the same asymmetric compound. Strong mass fragment abundances occur
at \( m/z \) 250, 267, 278, and 295. While no model carbonyl standard eluted at said RTs, the fragmentation suggested the oxime MW at 100. Only asymmetrical aldehydes and ketones (with MW 100) were considered; 3-hexanone \((\text{CH}_3\text{CH}_2\text{C(O)}(\text{CH}_3)_2\text{CH}_3)\) matched both RT and mass spectral pattern for both peaks F1 and F2. The oxime of another \( C_6 \) ketone, 2-hexanone \((\text{CH}_3\text{C(O)}(\text{CH}_2)_3\text{CH}_3)\), was synthesized to match potentially the F peaks; however, 2-hexanone produced peaks G1 and G2, based on both RT and mass spectra match.

### 5.3.3. Unmatched Chromatographic Peaks

Peaks H through K in Figure 5.2 did not correspond to model carbonyl standards, requiring fingerprint techniques for identification. Using the mass spectra and RT as a basis from which to develop new oxime standards, several new compounds were tested but did not match the chromatograms of the Deer Park samples. Because the atmospheric concentrations of these compounds was low, the corresponding masses of the derivatived oximes were also low and provided little information on mass breakdown. For example, peak H yielded only a mass fragment \( m/z \) 276, corresponding to MW 81, for which there exists no carbonyl match. It was hypothesized that \( m/z \) 276 might correspond to \( M - 17 \), leading to MW 98. Similarly, peaks I1 and I2 were tentatively identified as having an oxime molecular weight (M) of 293 (thus, MW 98). There was no match, however, for any MW 98 oximes with these retention times, as methyl isobutenyl ketone (MW 98) and cyclohexanone (MW 98) eluted at RT 16.3/17.0 and 19.3 min. The cyclic compound 1,3-cyclopentanedicione was considered based on MW, but the dicarbonyl eluted much later than 18.7 min.

Peak J (20.7 min) also did not produce a strong enough signal to allow for definitive identification after concentrating the sample five-fold. In the mass spectrum, two small peaks appeared at \( m/z \) 361 and 391. From the spectrum, it was hypothesized that M equals
391 with a corresponding carbonyl MW of 196; however, few aldehydes or ketones have MW 196. One possible ketone, C_{12}H_{20}O_{2} is also an ether where the ether oxygen atom is attached to the carbonyl carbon, and thus undetectable by the PFBHA method. It was considered that the compound which produced the peak at RT 21 min was a dicarbonyl, but this is infeasible because the MW would be lower than the smallest possible dicarbonyl compound. Based on this information, it is probable then that the peak is an artifact of column deterioration, of the detection method, or of the derivatization process itself.

The final two peaks, at 22.0 (K1) and 22.4 min (K2), appear to be from an asymmetric compound in higher ambient abundance, providing more mass fragmentation than the previous peaks, including strong signals at m/z 253 and 267. A compound eluting at 22 min which is assumed to have a MW of only 72 would most likely be a dicarbonyl, such as methyl glyoxal (MW 72), which elutes at approximately 28 min. Another dicarbonyl with MW 72 which might elute at this time is propanedioic acid, a three-carbon dialdehyde. This compound, however, is not commercially available to use in creating an authentic standard for testing.

**Biogenic Compound Testing.** As Deer Park is situated nearby industrial sources including the Houston Ship Channel, anthropogenic compounds were the principal carbonyls tested as potential sources of peaks in the recovered samples. The region, however, is also likely to be characterized by biogenic carbonyls in the atmosphere, given the transport of winds from the greater region, including Galveston Bay and the Gulf of Mexico, as well as from local treed sources. While isoprene and monoterpenes dominate biogenic emissions in the atmosphere, several new compounds—in fact, several hundred organic species (Hewitt, 1999)—comprise carbonyl inventories. In several recent biogenic emissions studies (Fruekilde et al., 1998, and references therein), 6-methyl-5-hepten-2-one (6MHO) was
found in all samples. Similar observations have been made of the leaf aldehyde \textit{trans}-2-hexenal (Atkinson \textit{et al.}, 1995; Grosjean \textit{et al.}, 1996a). Oxime derivatives were created for these two important biogenic carbonyl compounds. The \textit{trans}-2-hexenal oxime eluted at 19.1 min with a characteristic peak at $m/z$ 250; the 6MHO oxime similarly did not match with the unknown peaks delineated in Table 5.2. Instead, the 6MHO peaks appeared at 20.2 and 20.6 minutes. The elution time—20.6 min—nearly matches that of an unknown, \textit{i.e.} 20.7 minutes. The assumed MW of the unknown, however, is 196, while the 6MHO MW is 112. Several revealing mass fragments of 6MHO appeared: $m/z$ 221, 236, 253, 278, and 320; as reported by other authors, relatively little is known of the compound to date.
CHAPTER 6

FIELD COMPARISON OF A NOVEL OPTICAL SENSOR FOR FORMALDEHYDE QUANTIFICATION*

6.1. INTRODUCTION

Accurate measurements of formaldehyde (HCHO) concentrations are important for a complete understanding of the basic chemistry that occurs in the atmosphere. Formaldehyde, directly emitted from primary sources and formed by the atmospheric oxidation of anthropogenic and biogenic hydrocarbon emissions, and is readily photolyzed in the atmosphere leading to radical formation and elevated ground-level ozone concentrations (National Research Council, 1991).

Typical concentrations of HCHO range from sub-ppbv (parts per billion volume) levels in remote and rural areas to higher levels (up to 10-20 ppbv) in urban atmospheres (Carlier et al., 1986; Lee et al., 1995). Chemical derivatization methods have long been used for HCHO detection. However, these techniques are limited by the required time integration of sample collection, which does not describe the rapid fluctuations in HCHO concentrations. The scale of these fluctuations is important as HCHO is an intermediate in the photooxidation of hydrocarbons that undergoes rapid photolysis to produce HOx radicals (Fried et al., 1998). Despite the advantages of HCHO derivatization such as simplicity and relatively low cost, spectroscopic techniques provide a reliable and reproducible means of time-resolved collection of atmospheric HCHO concentrations (Vairavamurthy et al., 1992; Fried et al., 1998).

Several comparison studies have monitored HCHO formation and degradation (Trapp and de Serves, 1995; Gilpin et al., 1997; Apel et al., 1998). These studies compared spectroscopic techniques, such as tunable diode laser absorption spectroscopy (TDLAS), Fourier transform infrared spectroscopy (FTIR), and differential optical absorption spectroscopy (DOAS), to wet chemical techniques (both near-real time and time-integrating) usually based on derivatization with 2,4-dinitrophenylhydrazine (DNPH) (Tanner, et al., 1996). However, advances in nonlinear optical materials have allowed a novel optical sensor, based on difference frequency generation (DFG), to be developed for high quality HCHO concentration measurements that does not require cryogenic cooling. Building upon previous efforts (Minc et al., 1997; Lancaster et al., 1998; Richter et al., 1998, Lancaster et al., 1999), the DFG based sensor can now provide real-time detection of atmospheric HCHO with a minimum detectable sensitivity of approximately 0.5 ppbV (Lancaster et al., 2000). The wavelength selectivity of the DFG method results in less susceptibility to interference from water vapor.

In this paper, we report on results from an in situ comparison between two derivatization methods, DNPH and o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA), and a DFG-based gas sensor for the collection of atmospheric HCHO. This represents the first field comparison of a DFG sensor which promises reliable and robust HCHO quantification using a real-time, autonomous diode laser based sensor (Lancaster et al., 2000), with well established wet chemical trace gas detection techniques. The results of this comparison show the DFG precision to be roughly equal to the bias between simultaneous DFG and time-integrating wet chemical HCHO measurements, validating the use of a DFG sensor for quantitative measurements of HCHO in urban areas.
6.2 EXPERIMENTAL SECTION

6.2.1. SITE

The comparison study occurred from November 29 to December 6, 1999 on a rooftop at an elevation of 20 meters on the Rice University campus. During sampling, temperature and humidity varied from 5-25°C and 65-95% RH and included a period of precipitation. The campus is situated in central Houston, where vehicular and industrial emissions of HCHO mix with biogenic hydrocarbons emitted from local parks and treed neighborhoods so that both primary and secondary sources of HCHO might be important. The rooftop location allowed free airflow in all directions so air sampled represented the nearby region rather than localized sources.

6.2.2. DERIVATIZATION METHODS

DNPH and PFBHA. In the DNPH method, Waters SepPak C\textsubscript{18} cartridges were coated with a DNPH solution consisting of twice-recrystallized pure DNPH and the highest grade 5 M HCl and acetonitrile. Air was sampled at a rate of 1 liter min\textsuperscript{-1} for typically a period of 3 to 4 hours using SKC Airchek Sampler pumps which were calibrated both before and after the experiment. For each sample, a field blank was also taken simultaneously at the site. The cartridges were extracted with acetonitrile, and the resultant HCHO hydrazones were analyzed with liquid chromatography (LC) followed by UV detection using a Hewlett Packard 1100 LC (Fung and Grosjean, 1981). The HPLC instrument response was calibrated using commercially available standards.

For the PFBHA method, air (1 L min\textsuperscript{-1}) is pulled into a glass impinger containing deionized water (15 mL). Upon sampling completion, an acidic solution of PFBHA is added, and the resultant oxime is extracted into hexane and subsequently analyzed with gas
chromatography/mass spectrometry using a Hewlett Packard 5973 Mass Sensitive Detector (Yu et al., 1995).

**Diode Laser-based Method.** For highly selective optical quantification of HCHO, a fundamental ro-vibrational absorption line near 2831.64 cm\(^{-1}\) (3.5315 μm) free from potential interfering background gases (H\(_2\)O, CH\(_4\)) was monitored using a mid-infrared DFG based spectroscopic source. Since the DFG system requires only Peltier cooling, no consumables such as liquid nitrogen are needed. This offers the potential for long term remote gas monitoring and control using a modem connection.

A schematic of the DFG sensor configuration is shown in Figure 6.1. The two diode seed lasers are a fiber-coupled single frequency 2 mW, 1561 nm DFB diode laser and a 50 mW, 1083 nm DBR diode laser. An Er\(^{3+}\) doped fiber amplifier increases the 1561 nm seed power to 30 mW to saturate the gain in the 0.6 W Er/Yb fiber amplifier while the 1083 nm diode directly seeds 1.6 W Yb amplifier (Goldberg et al., 1999). To combine the two DFG pump channels into a single fiber, a wavelength division multiplexer (WDM) is used and the two pump beams are imaged by a 1 cm focal-length achromatic lens into the 19 mm long periodically poled lithium niobate (PPLN) crystal with grating periods ranging from 29.7 to 30.5 μm. A 5 cm focal length CaF\(_2\) lens then collects the tunable, narrow-band (<60 MHz) radiation generated in the PPLN crystal. While up to 0.7 mW of mid-infrared DFG power has been generated previously, this work used 0.1 mW (Lancaster et al., 1999), sufficient power for a balanced detection scheme. The collimated DFG beam is then divided into two beams by a ZnSe wedge. The primary beam is directed through an astigmatic Herriot multipass absorption cell, configured for a path length of 100 m to a low noise HgCdTe (MCT) detector. The remaining reference beam is incident onto a second MCT detector. Such a dual beam absorption technique leads to a significant reduction
of optical noise due to interference effects by the various optical components in the beam path, which is eliminated by ratioing the signals from both MCT detectors. The MCT detectors were operated in a photoconductive mode and DC coupled to preamplifiers with 3-db bandwidth of 200 kHz. The data from the spectroscopic measurements were acquired simultaneously by the use of two analog-digital data acquisition cards and interfaced to a laptop computer. Spectral lines were acquired by direct current modulation of the 1561 nm pump diode laser (triangular waveform modulation at 0.1 to 1 kHz). Although determination of absolute concentrations is an inherent feature of direct absorption spectroscopy, the DFG sensor calibration was confirmed prior to HCHO concentration measurements in ambient air. For this purpose a certified mixture of HCHO (760 ppbv) in N₂ from Scott Speciality Gases was used. Lower concentrations down to 20 ppbV with accuracy of 10% were produced using N₂ dilution by mean of a dual mass flow controller based gas mixing system. Measured HCHO concentrations were in good agreement with the mixed calibration gas composition.
6.2.3. DFG Measurements

The DFG sensor acquired continuous on-line concentration data for 52-second sampling periods. The optimum HCHO sampling pressure is a compromise between absorption sensitivity (best at high pressure) and line selectivity (best at low pressure). As the sampling pressure is reduced, the detection sensitivity does not decrease below the value at atmospheric pressure until a point at which Lorentzian and Doppler linewidths are equal (which typically occurs between 10 and 50 torr). This is the pressure regime at which this HCHO sensor was operated (i.e., 40 torr). In this pressure range the lineshape can be described as a convolution of Lorentzian and Doppler lineshapes known as a Voigt profile.

The particular molecular transition of interest occurs at 2831.6417 cm\(^{-1}\). This line is free from interference of other transitions as mentioned above and shows a weak satellite transition at 2831.6987 cm\(^{-1}\) (Fried et al., 1998). This smaller peak provides additional information that can be used to improve precision and accuracy of HCHO concentration measurements. Since the distance between the peaks as well as their locations are given by the HITRAN spectroscopic data base, the frequency per point in the algorithm can be calculated. The line intensity of both peaks as well as their ratio, and Voigt linewidth of 1.436\cdot10^{-2} \text{ cm}^{-1} \text{ (FWHM)}, are also known from HITRAN.

A representative HCHO concentration measurement of ambient air obtained with the 100 m long multipass cell at a total pressure of 40 torr is shown in Figure 6.2. An average of 5000 spectra were acquired in a time interval of 140 s for each concentration measurement. The DFG based sensor employs real time data analysis based on Labview software and no further computer processing is required. A dual-Voigt profile is fitted using a nonlinear least squares technique known as the Levenberg-Marquardt algorithm.
Figure 6.2. Spectrum of atmospheric HCHO at 2831.6417 cm\(^{-1}\) (3.53 \(\mu\)m) in a multipass cell with an effective optical path length of 100 m at P=40 Torr. This measurement was taken over 5000 averages at a 100 Hz scan rate.

and is overlaid on the experimentally obtained spectrum indicating a concentration value of 4.3 ppbV HCHO. The residual between the data and the Voigt line fit displays a standard deviation of \(\pm 1.1 \times 10^{-5}\), corresponding to a concentration of 0.4 ppbV, a precision limit of the current instrument.

6.3. **RESULTS AND DISCUSSION**

The HCHO concentration data are plotted in Figure 6.3 using a 9-point rolling average for the DFG measurements. The data are divided into three time segments, depicted by vertical lines in the figure. There was no precipitation in the first and third segments; in the second segment, 25.8 cm rain fell during 36 hours. Furthermore, the divisions also coincide with three sets of DNPH-impregnated cartridges, which were freshly prepared at the beginning of each 2-day segment to minimize potential contamination through excessive storage.
The horizontal bars of Figures 6.3a and 6.3b represent the time-integrated average HCHO concentrations measured using the DNPH and PFBHA methods, respectively. The DNPH results were calculated by subtracting the overall average blank concentration from each sample concentration, as determined from HPLC-detector peak area. HCHO levels quantified from field blanks were, on average, approximately 30% of HCHO quantified from collected samples. This average field blank level is equivalent to an atmospheric HCHO concentration of 1.2 ppbV. The variability of the field blanks is significant with a standard deviation equivalent to an atmospheric HCHO concentration of 0.9 ppbv, and is a limit to the sensitivity of the DNPH method. This is a common shortcoming of the DNPH method (Sirju and Shepson, 1995). Error bars for the DNPH and PFBHA measurements are given in the figure for the estimated precision of the measurements and were determined separately by parallel sampling for three-hour periods for both derivatization methods.

The bias and gross error between the DNPH measurements and the DFG measurements and the PFBHA and DFG measurements were calculated. Bias is defined as the mean residual concentration ($C_{\text{DNPH}} - C_{\text{DFG}}$ or $C_{\text{PFBHA}} - C_{\text{DFG}}$) based on a comparison of all individual observations, while absolute gross error is the mean absolute value of the residual concentrations. A cut-off value of 0.1 ppbv was used, where measurements below 0.1 ppbv were excluded from the calculation. The bias and gross error between HCHO concentrations from DNPH and DFG methods were -1.7 ppbv and 2.6 ppbv, resulting in a normalized bias and normalized gross error of -24% and 49%, respectively. For the comparison of the PFBHA and DFG methods, bias and gross error were -1.2 ppbv and 1.5 ppbv; normalized bias and gross error were -23% and 30%.
Figure 6.3. Comparison of atmospheric HCHO concentration measurements for a 9 day period from November 29 to December 7, 1999 by three independent trace gas detection techniques in Houston, TX. Several brief gaps in the DFG based measurements are apparent. These occurred as a result of unscheduled power interruptions and scheduled sensor performance verification.

Time-resolved data measurements indicate the daily fluctuations in HCHO concentration in Houston. Though the time-integrated methods indicate general trends over a relatively long period of time (3 to 4 hours) compared to per minute measurements from
DFG spectroscopy, the often sudden shifts in HCHO levels are not apparent with time integration. For example, the last three reported HCHO concentrations in segment 1 (Figure 3b, PFBHA vs. DFG) are 3.3, 4.9, and 4.2 ppbv, respectively. The per minute DFG measurements, however, reveal over six peaks and valleys during the same sampling time, with concentrations ranging from around 0.5 ppbv to almost 14.0 ppbv. Similar observations exist for all time segments and with both derivatization methods compared to DFG measurements. Monitoring HCHO fluctuations, along with simultaneous time-resolved measurements of parameters such as ozone and oxides of nitrogen, is key to understanding the complexity of atmospheric reactions and for predicting atmospheric chemistry.
CHAPTER 7

STATISTICAL ANALYSIS OF PRIMARY AND SECONDARY ATMOSPHERIC FORMALDEHYDE*

7.1. INTRODUCTION

Volatile organic compounds (VOCs) and oxides of nitrogen (NOx) react in the presence of sunlight to yield ozone (O3), one of six criteria pollutants regulated under the Clean Air Act. Elevated concentrations of tropospheric O3, the primary component in photochemical smog, are commonly measured in urban centers and across regional airsheds, impacting human health and causing damage to materials and buildings in addition to creating crop losses, forest damage, and potential climatic effects (Moussiopoulos, 1990; Berntsen et al., 1997; Seinfeld and Pandis, 1998). Continuous exposure to substantial levels of O3 irritates the eyes and lungs at low persistent levels, and causes respiratory illness at higher concentrations (Johnson et al., 1981; World Health Organization, 1992; Pryor, 1998). For those regions in violation of the federal O3 standard, oxidant control strategies for attainment purposes require an understanding of O3 formation precursors, including VOCs. In particular, it is important to differentiate and establish a relationship between primary and secondary precursors of VOCs to direct government policy for source identification, regulation, and control of these emissions.

Primary atmospheric pollutants include direct emissions from stationary point sources and area sources. Formaldehyde (HCHO) is a highly reactive VOC found in high urban and rural concentrations; primary HCHO sources include vehicular exhaust and fugitive industrial emissions (Altshuller, 1993). Secondary pollutants form in the atmosphere
from the reaction between or breakdown of primary compounds. Primary sources and secondary formation must both be included in calculating VOC loadings in the troposphere for purposes of predicting concentrations of O₃ or other species. Differentiating between primary and secondary sources of HCHO is, however, important for regulatory and control purposes.

In this study, primary and secondary contributions to HCHO concentrations are estimated through statistical methods of analysis of simultaneous real-time measurements of HCHO, carbon monoxide (CO), and O₃. Significant previous research has focused on HCHO, as the photolysis of HCHO during daylight hours produces atmospheric radicals that drive photochemical smog formation (National Research Council, 1991). A component of this research (Altshuller, 1993; Possanzini et al., 1996; Kawamura et al., 2000) has investigated the production of HCHO from both primary and secondary sources by comparing estimates of HCHO from vehicular emissions with estimates of HCHO from alkene and alkane atmospheric reactions. The advantage of the current study is that by using simultaneous real-time measurements and rigorous statistical analysis in determining these relative contributions, the statistical accuracy of the estimations can be quantified.

Carbon monoxide is a stable colorless and odorless gas emitted during materials combustion, with an atmospheric lifetime of two to four months. Anthropogenic primary emissions constitute virtually all atmospheric CO in Houston, TX. In Houston, mobile sources contributed approximately 90% of the CO, and stationary point sources contributed 8% (Houston-Galveston Area Council, 1999). For the purposes of this study, statistical analogy to CO measurements represents the primary contribution to HCHO formation.

Ozone exists solely as a secondary compound, formed and destroyed in the atmosphere via a cyclical series of reactions involving NO$_x$ and sunlight. When this cycle remains uninterrupted, O$_3$ does not accumulate. However, the presence of competing atmospheric VOCs, including HCHO, disrupts O$_3$ depletion and simultaneously facilitates O$_3$ formation. For this study, statistical analogy to O$_3$ represents the secondary formation of HCHO.

Formaldehyde concentrations are governed by both primary emissions and secondary formation. The simplest, most reactive, and most abundant atmospheric carbonyl, HCHO levels typically range from about 10 to 20 ppbv in most urban settings (Carlier et al., 1986). During a recent sampling campaign (Rehle et al., 2001), HCHO concentrations in Houston reached almost 45 ppbv in a heavily industrialized section, presumably near a primary HCHO emission source. Primary sources of HCHO include vehicles that use oxygenated fuels (Grosjean et al., 1993) and stationary sources (Grosjean and Swanson, 1983). Alkane and alkene reaction with the hydroxyl radical (OH) accounts for secondary anthropogenic HCHO in urban atmospheres, and isoprene interactions account for a large percentage of biogenic secondary HCHO (Altshuller, 1993; Harder et al., 1997).

The objectives of the study were to determine the relative contribution of primary emissions and secondary formation to the atmospheric HCHO concentrations, based on the statistical relationship between HCHO, CO and O$_3$. The temporal relationship between these pollutants was sought to determine the relative staging of pollutant concentrations. While this work was conducted in Houston, the results can generally be extrapolated given certain limitations, including (1) likely contributors to both primary and secondary HCHO formation will only be generally approximated by CO and O$_3$ concentrations; (2) source
contributions vary in importance, which cannot be elucidated when using only one primary and only one secondary compound in the analogy (Duarte-Davidson et al., 1997); and (3) atmospheric lifetimes ($\tau$) of aldehydes are on the order of hours, where loss occurs mostly via reaction with OH radicals and photolysis (Tanner et al., 1988).

7.2. METHODS

7.2.1. SAMPLING SITE

Over thirty Continuous Air Monitoring Stations (CAMS) are operated by the Texas Natural Resource Conservation Commission (TNRCC), the City of Houston, and the Houston Regional Monitoring Corporation throughout Houston and the surrounding counties. These sites collect hourly concentrations of gaseous pollutants such as ozone, carbon monoxide, oxides of nitrogen, and meteorological variables. The compound data in the present study were continuously collected between June 14 to June 21, 2000 at Deer Park CAMS 35 (operated by the TNRCC) located south of the heavily industrial Houston Ship Channel, and northwest of Galveston Bay and the Gulf of Mexico.

During the one-week sampling period, temperature and relative humidity ranged from 23 – 33°C and 48 – 98% RH. The period included several hours of precipitation, from midday June 15 to mid-morning June 16, during which HCHO data were not recorded. All instrumentation was kept inside the CAMS trailer, with tubing leading to the rooftop for ambient air collection. Sampling from the 4 m rooftop allowed free airflow in all directions. The collection instruments were maintained at 26°C in an air-conditioned monitoring station.
7.2.2. Data Acquisition

Though TNRCC-operated instruments at Deer Park record O$_3$ and CO concentrations every 5 min, the data are reported publicly as hourly averages, reflecting federal standards such as NAAQS. To understand more clearly the regional atmospheric chemistry, however, requires accurate measurements at shorter intervals to account adequately for rapid fluctuations in atmospheric concentrations (Fried et al., 1998). Traditionally, HCHO concentrations were measured hourly or daily (Salas and Singh, 1986; Possanzini et al., 1996; Gilpin et al., 1997) due to a lack of technology for accurate real-time collection and analysis, in addition to relative simplicity with time-integrated methods. The present study employed a relatively new spectroscopic technique based on difference frequency generation (DFG), designed to measure HCHO on a real-time basis with a sensitivity of ~0.5 ppbv (Lancaster et al., 2000). In a recent study, the DFG sensor was shown to be a robust and accurate method for HCHO quantification (Friedfeld et al., 2000). The configuration and theory behind the DFG sensor is presented by Rehle et al. (2001).

Data were collected at 5 minute intervals from June 14, 2000 (1400 CDT) to June 21, 2000 (1100 CDT) with several periods of data missing for instrument recalibration and maintenance. Examination of the data demonstrated a few observations missing at random until an 11 hour rainstorm (June 15 and 16, 2000) and disruption of DFG collection, followed by a reasonably contiguous period for the remainder of the week with some further random missing data. Due to a large data pool following the 11 hour disruption of HCHO collection, we focused analysis on this latter period; overall, nearly 5900 measurements were collected simultaneously for the three compounds of concern. To treat missing data from either instrument re-calibration or maintenance of the DFG monitor, a univariate auto-regression (AR) model was fit to each series separately, where the sample mean value was
assigned to all missing data points. The missing observations were imputed by simulating random values based on the sampling distribution of the estimator, at that point in time. The new imputed observations do not incorporate cross-correlative structure, as only univariate models were considered; thus, resulting estimates of possible interactions between pollutants are conservative.

7.2.3. Diagnostic Statistics

All statistical analysis was performed with the software package S-Plus © (www.insightful.com, 2000). Time series analyses are generally used to understand the stochastic mechanism that gives rise to an observed series or to predict future values based on series history (Box et al., 1994). The time series data collected at Deer Park allow for statistical investigation of primary and secondary inputs to atmospheric chemical reactions. Modeling the time series using the chosen methodologies, however, requires a transformation of each series to correct for the skewness of the data. Quantile plots were thus developed to assess the symmetry and tail behavior of various data transformations of the series, including comparing the original data with natural log, square root, and negative inverse transformations of the three series.

To remove the autocorrelation within each series so that we can identify lagged correlations between series, a fitted autoregressive equation was determined for each series, and the residuals (error terms) from each equation obtained. Only cross-correlation effects between series therefore remained. Both the autocorrelation function (ACF) and the partial autocorrelation function (PACF) were evaluated using the residuals of the model fit to the square-root transformed data to attribute both the cumulative and individual influence of primary and secondary compounds on HCHO (through analogy with CO and O₃.
measurements). Recall, only data following the rainstorm on June 15 and June 16 were included in the analyses; any few remaining missing values were accounted for as previously described.

The ACF represents the sample correlation between sets of ordered data pairs; the sample correlation was computed for HCHO at time t (\(HCHO_t\)) and CO at time \(t - 1, t - 2, \ldots, t - 25\), as well as \(O_3\) at the same lagged values. Recall in this study the time unit is 5 minutes, thus \(CO_{t,25}\) and \(O_{3,t,25}\) indicate concentrations measured approximately 2 hours prior to \(HCHO_t\). By definition, the ACF indicates the cumulative effect of all lag periods on the present concentration. The PACF, on the other hand, measures the correlation between the present concentration and the concentration at one lag only.

### 7.2.4. Statistical Modeling

The complexity of the data—\(~5900\) simultaneous measurements—requires rigorous statistical analyses to discern a lag-lead relationship and primary vs. secondary HCHO precursor contributions. Two linear regression models were applied to the HCHO, CO, and \(O_3\) series. The first model uses a basic linear regression of HCHO at time \(t\), with explanatory variables \(CO_{t-1}\), \(O_{3,t-1}\), and \(HCHO_{t-1}\), that is, at 1 lag unit of time as per the equation

\[
HCHO_t = \beta_0 + \beta_1 CO_{t-1} + \beta_2 O_{3,t-1} + \beta_3 HCHO_{t-1} + \varepsilon_t \tag{7.1}
\]

where the coefficients \(\beta_1\) and \(\beta_2\) approximate the true nature of the contribution of primary and secondary lag concentrations on HCHO as measured by a linear relationship and \(\varepsilon_t\) is the error term that is assumed to be independent with constant variance and mean zero. This simple linear regression model provides a preliminary assessment of the relationship between HCHO and the primary and secondary variables (CO and \(O_3\)).
Improving on the previous model, we consider a regression model relating lagged values of CO and O₃ to HCHO but also accounting for the serial correlation in the error process. More specifically, the second model considered is

$$HCHO_t = \beta_0 + \beta_1 C_{O_t} + \beta_2 O_{O_t} + z_t$$

(7.2)

where $j$ and $k$ equal lag (0, 1, 2, ...) and $j$ may or may not equal $k$. The error process $z_t$ is assumed to follow an autoregressive process of order $p$; the order of the process is estimated from the observed series. In this analysis, the constant term, $\beta_0$, is estimated as the sample mean of the HCHO series. The Cochran-Orcutt method (Box et al., 1994) was used iteratively to obtain estimates of the remaining regression coefficients and the parameters of the autoregressive error process.

7.3. RESULTS AND DISCUSSION

7.3.1. DIAGNOSTIC STATISTICS RESULTS

TIME SERIES ANALYSIS. Separate time series plots were created for all three compounds of interest (Figure 7.1a). The x-axis is marked by 1200 CDT on each sampling day, while the y-axis represents atmospheric concentration in ppbv (HCHO and O₃) or ppmv (CO); each graph is scaled individually to emphasize diurnal patterns. For CO, the overall average, minimum, and maximum concentrations are 0.37, 0.28, and 0.62 ppmv. The CO concentrations follow a relatively cyclical pattern, with an average daily maximum of 0.51 ppmv occurring at around 0600 CDT during the weekdays (and at 2000 CDT on the weekend, June 17 and 18); the mean daily minimum was 0.30 ppmv, with varied times throughout the week.
Figure 7.1. (a) Time series plots of CO, HCHO, and O₃ measured at Deer Park. The x-axis is time, marked at 1200 CDT. The y-axes are the concentration: in ppmv for CO and ppbv for HCHO and O₃. (b) Overlay of O₃ and HCHO time series plots.

The O₃ concentrations fluctuate in a less distinct diurnal cycle highlighted by extreme values, with a weekly minimum of 0.4 ppbv and maximum of 77.3 ppbv. The average O₃ concentration was 18.4 ppbv, and the average daily maximum was 38.0 ppbv, and the
highest levels occurred between 1000 and 1300 CDT almost daily. From the figure, there is a noticeable spike on June 18 at 1300 CDT, where the concentration reached 77 ppbv. The missing data for HCHO during the rainstorm on June 15 to June 16 are shown as a straight line simply for graphical purposes and do not reflect interpolated values. Formaldehyde concentrations ranged from 0.2 to 19.6 ppbv, with a weeklong average of 4.9 ppbv. Typical diurnal fluctuations remained limited between 1.2 and 9.5 ppbv, the daily minimum and maximum averages. As with O₃, a concentration spike up to ~20 ppbv occurred in early afternoon on June 18. The smaller and more rapid fluctuations of HCHO highlight the importance of real-time measurements in studying regional atmospheric chemistry.

Figure 7.1b contains an overlay plot of HCHO and O₃, as these compound concentrations follow a more irregular pattern than CO levels. The regular CO pattern presumably arises from the primary nature of CO sources, devoid of external interferences such as wind patterns, meteorology, temperature, and other compound concentrations and reaction conditions. The CO cycle changes during the weekend, reflecting different industrial production and vehicular usage. Secondary compounds are all subject to similar external influences; the June 18 spike for both secondary compounds indicates the presence of such an influence (Figure 7.1b). While similar cyclical patterns exist throughout the week, the small range of HCHO concentration fluctuations requires statistical considerations for further analysis.

**Quantile Plots.** Figure 7.2 contains quantile plots of the non-transformed data along with the natural log, square root, and negative inverse transformations. Each row represents a time series (HCHO, O₃, and CO, respectively) and each column represents a transformation (original data (x), ln (x), \(\sqrt{x}\), and \(x^{-1}\), respectively). The x-axis indicates the percentile of a value in the series centered about 0 and the y-axis represents each value.
Visually, the most well-behaved data occur with the square root function. While all transformations appeared generally symmetric with the CO data, the log and negative inverse functions lose symmetry about the median for HCHO and O₃ values. The square root transformation is not perfectly normal for all three data sets, but appears the most symmetric transformation nonetheless.

**Figure 7.2.** Quantile plots of original and transformed data series for HCHO (top row), O₃ (center), and CO (bottom). The transformations include: original data, natural log, square-root, and negative inverse. The x-axis indicates the percentile of a value in the series centered about the median (0); the y-axis represents the transformed value. The square-root transformation is considered to be the most symmetric.

**ACF and PACF.** The ACF and PACF were plotted against time (in lag units of 5 min) for CO and O₃ correlated with HCHO. The ACF as a function of lagged time for both CO and O₃ correlated with HCHO indicates an overall strongly positive relationship. Similarly overall positive partial autocorrelations are observed as well. Although the ACF and PACF values are small, they are highly significant in general.
7.3.2. **Statistical Modeling Results**

Table 7.1 contains a summary of the results and the statistical significance of the fitted simple linear regression for equation (7.1). The p-value (denoted by $\Pr(>|t|)$) indicates that there is approximately zero probability (truncating at four significant digits) that with any of the estimates of the coefficients, the true nature of the relationship between the gases for the equation considered is 0. Each coefficient can therefore be considered not only statistically significant, but in fact a good estimate of the true (theoretical) value. The p-value of the F-statistic is 0, further demonstrating that there exists a non-zero relationship between the response and explanatory variables. Considering solely primary and secondary contributions in this model, 64% of HCHO, concentrations can be attributed to $O_{3 \gamma}$ (coefficient $\beta_2$, 0.2247) and 36% to $CO_{\gamma}$ (coefficient $\beta_1$, 0.1287), or a ratio of 1.75. It is prudent for us to note some obvious limitations of this modeling strategy, given that CO and $O_3$ concentrations would not fully represent accurately and completely the primary and secondary compounds. Many other reactive compounds exist and contribute to the complexity of the atmospheric composition and chemistry.

**Table 7.1.** Regression coefficients and related statistics from a simple linear regression model for Deer Park data, June 2000. The term $\Pr(>|t|)$ indicates that the coefficients on the regressors are acceptable at the 95% confidence interval. The ratio of coefficients (contribution of $2^\circ$ to $1^\circ$) is 1.75.

| Compound | Coefficient | Standard Error | t-value | $\Pr(>|t|)$ |
|----------|-------------|----------------|---------|-------------|
| CO       | 0.1287      | 0.0250         | 5.1454  | 0.0000      |
| $O_3$    | 0.2247      | 0.0261         | 8.6016  | 0.0000      |
| HCHO     | 0.3277      | 0.0251         | 13.0691 | 0.0000      |

Table 7.2 contains summary results for the fitted model of equation 7.2. To determine the lag periods for which CO and $O_3$ most significantly lead to the formation of HCHO, the contributions to a multiple regression model for varying lags in the presence of one another were compared. The most significant lags in the regression, when compared
with other lags, include lag 1 (5 min) for CO and lag 0—that is, simultaneous concentrations—for O₃. These lag periods (0 and 1) emphasize that hourly or daily time-integrated measurements do not accurately represent the true nature of the atmospheric chemistry of a region; a significant simultaneous secondary concentration (HCHO and O₃) highlights the need for historical data with statistical analyses to predict peak O₃ concentrations.

As described above, missing values were replaced with random imputed values; thus, the iterative process was simulated ten times each for CO₁₀ and O₃₉, the most significant lag periods. The mean coefficient for both compounds is listed in Table 7.2; the mean p-value suggests that the results are significant for CO at 94.5% confidence and O₃ at 99.9% confidence. The auto-correlated error-processes model produced an identical result to the basic linear regression model, with a ratio of β₃(O₃) to β₁(CO) of 1.75.

Table 7.2. Mean values from ten simulations of the auto-correlated error processes model. The Pr(> |t|) terms indicate that the CO coefficient is acceptable at the 95% confidence interval, and the O₃ coefficient is acceptable at the 99% confidence interval. The ratio of coefficients (contribution of 2° to 1°) is 1.75.

| Compound | Coefficient | Pr(> |t|) |
|----------|-------------|-------|
| CO       | 0.0850      | 0.0546|
| O₃       | 0.1491      | 0.0010|

As described in the time series analysis above, a noticeable spike in concentration occurred for both HCHO and for O₃; the remaining data appeared to follow repetitive diurnal cycles. In Figure 7.3 a plot of the residuals vs. each of the predictors was created to assess the effect of outliers, such as that on June 18, on the fitted auto-correlated error processes model. Although there are a few moderate outliers, they do not overly influence the fitted models.
Figure 7.3. Plots of the residuals vs. predictors for both CO and O₃ indicate that outliers, such as the spike in concentration of O₃ and HCHO on June 18, do not affect the results of the auto-correlated error processes model, and thus the model is considered valid in assessing the 1ˢᵗ and 2ⁿᵈ contributions to HCHO production.

**IMPLICATIONS.** Both modeling strategies attribute nearly two-thirds (ratio 1.75) of HCHO formation to secondary VOC reactions, and only one-third to primary emissions. Earlier studies have been conducted similarly investigating the contribution of primary and secondary precursors to HCHO formation. As previously stated, these studies often relied on estimates of vehicular exhaust and assumptions of reactant concentrations and reactant constants.

Possanzini et al. (⁹) measured HCHO and CO at 1-hour time-averaged intervals and obtained vehicular emissions from a previous source. Using average O₃ and OH reaction concentrations for estimating secondary reactions with alkenes, the group found between 44
and 49% of the HCHO formation could be attributed to secondary formation. Others used similar procedures, but obtained results closer to those in this study, where secondary emission precursors predominate HCHO formation. Altshuller (1993), for example, investigated aldehyde formation from primary and secondary sources during night and early morning hours; the investigation entailed an emissions inventory estimate from 1980s vehicles and typical diurnal concentrations and rate constants for alkenes, NO₃, and O₃. The mean result for that investigation led to ~78% HCHO attributable to secondary reactions and 22% to primary emissions for 0600 to 0900 h. A high ratio of secondary/primary compounds was also calculated by Kawamura et al. (2000). Kawamura et al. used historic 1980s Los Angeles data for both vehicular exhaust and compound concentrations and concluded that secondary photochemical reaction contributed approximately 87% to aldehyde production during daylight hours.

The present study incorporates simultaneous measurements of primary and secondary compounds at relatively short intervals over a statistically significant time period and therefore provides the most accurate assessment of HCHO formation. These studies are all complicated by the fact that measured HCHO concentrations need to account for both formation and destruction, that is, net production. Altshuller (1993) emphasizes only HCHO production, but states also that HCHO reaction with O₃ is extremely slow; thus, the short (5 min) time intervals do not need to account for that reaction. Formaldehyde reaction with OH does serve as an important mechanism of HCHO destruction; however, this reaction is considered implicitly in the regression models, since any estimate of the destruction (e.g., rate constant k_{OH-HCHO} and OH concentration) would be subtracted equally from each HCHO concentration in the data series prior to statistical modeling, and
subsequently not affect the resultant coefficients $\beta_1$ and $\beta_2$. Kawamura et al. (2000) simply accounted for net production by assuming a conservative change of $2/3$ in concentration.

The assumptions used in this study are important in interpreting the results. Many sources emit primary HCHO, and many reactions and precursors contribute to secondary HCHO production. Thus, the analogy using only CO and O$_3$ concentrations serves only as an approximation; nonetheless, the results of this study can be extrapolated to other urban areas with similar O$_3$ problems more readily than can the results from previous studies, as both real-time and simultaneous measurements greatly decrease the gross assumptions made by others. Because the models showed that nearly two-thirds of HCHO production is attributable to secondary reactions in the atmosphere, legislative efforts to reduce primary emissions of higher aldehydes and ketones—those compounds that break down in the atmosphere to form HCHO—will more effectively contain HCHO production, and ultimately O$_3$ production as well. A future shift in gasoline composition to methanol or natural gas could result in higher primary emissions of HCHO and thus create a likewise shift in the secondary/primary contribution of HCHO. Obviously, decreasing primary emissions of HCHO along with a simultaneous decrease in emissions of higher carbonyl compounds as part of an implementation plan would most effectively reduce O$_3$ concentrations.
CHAPTER 8

CONCLUSIONS AND FUTURE RESEARCH

8.1. SUMMARY OF CONCLUSIONS

The projects presented in the previous chapters provide insight into the formation, reaction, and behavior of atmospheric carbonyl compounds in both rural and urban Texas. The project TEXIE was designed specifically to measure isoprene emissions from various forested areas around Austin; simultaneous measurements of isoprene carbonyl products enabled a view of diurnal and spatial variations. The spatial differences were viewed not only between rural sites consisting of different vegetation, but also between rural and urban locales and even differences within one site itself. The project also created an opportunity to study incremental reactivity of O₃ and VOC/NOₓ ratios in an ambient setting.

The polluted urban atmosphere of Houston provided a backdrop for studying methods to improve carbonyl collection and analyze formation and destruction of a particular carbonyl, namely formaldehyde. The PFBHA derivatization method proved a more powerful tool in identification than the more common DNPH method, however, limits exist with either method. The DFG system produced near real-time data for formaldehyde measurements; its use in an ambient weeklong study, combined with data from other measurements, made possible a detailed data set for statistical modeling. In particular, several conclusions can be drawn from the previous chapters:

- biogenic studies

- the spatial variation of isoprene and its reaction products’ concentrations in the surface layer are strong functions of the immediate land cover surrounding the sampling sites

- spatial differences between sampling sites need to include NOₓ data to account for urban and rural influences, as rural sites influenced by urban emissions can resemble urban sites
both ozone attributable to biogenic hydrocarbon oxidation and ozone formation potential are predicted to be insignificant under high VOC/NO\textsubscript{x} ratios typical of rural areas, but may be important under conditions where NO\textsubscript{x} levels are elevated

- predicted formaldehyde concentrations compared to actual measured concentrations indicate the oxidizing capacity of a region

*anthropogenic*

- with the PFBHA method, chemical ionization (CI) coupled with electron ionization (EI) would serve best in identifying any unknown carbonyls, as EI mode serves well only in confirming masses while potentially omitting important identifying details

- the 24 hour sampling period is deemed sufficient for capturing carbonyl compounds that exist in persistent low-lying levels, but does not capture important information such as concentration fluctuations on a small time scale

- the 1 – 2 ppbv precision limit of the DFG is similar to the bias calculated between DFG measurements and time-integrating wet chemical quantifications and validates the use of the DFG system for HCHO measurements in urban environments

- both the linear multivariate auto-regression model and the auto-correlated error processes models attribute nearly two-thirds (ratio 1.75) of HCHO formation to secondary VOC reactions, and only one-third to primary emissions

### 8.2. Future Research

Further research opportunities for studying air quality exist throughout the State of Texas. Outside of Houston, other major cities within the state share similar ozone non-attainment problems, specifically Dallas and El Paso. The growing population density of these cities as well as Fort Worth and San Antonio brings further air quality problems, as a result of increased vehicular emissions and increased industrial productivity. These problems, as evidenced by the biogenic studies, not only affect the immediate urban region and surrounding suburban regions, but also have consequences in rural areas located hundreds of miles away.
Thus, similar studies in these other ozone-polluted cities would provide a large database from which to determine chemical formation and pathways—namely, the importance of primary and secondary carbonyl sources can be estimated. In addition to similar studies in other urban regions, several other opportunities exist for study. For example, the class of compounds known as carboxylic acids has been little studied, but like carbonyl compounds, can influence ozone formation and concentrations, especially when considering the many acids at low levels that are often overlooked. Furthermore, computer modeling, using meteorological data such as wind direction and wind speed, coupled with a detailed database of carbonyl compounds, would provide the predictive capabilities required for directing governmental policy as it relates to VOC and/or NOx reductions. Finally, the statistical modeling worked extremely well with the real-time measurements. To continue this work, the predictions of HCHO—e.g., HCHO_{n+1} and HCHO_{n-1}—should be calculated based on previous concentrations of CO and O3. This would potentially elucidate any interactions between HCHO and O3 that existed. The study should certainly be validated at both rural and urban locations, in addition to varying times throughout the year to control for any ozone effects.
CHAPTER 9

LITERATURE CITED


TNRCC (Texas Natural Resource Conservation Commission), *www.tnrcc.state.tx.us*


