# Signatures of terminal alkene oxidation in airborne formaldehyde measurements during TexAQS 2000

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[1]  Airborne formaldehyde ($CH_2O$) measurements were made by tunable diode laser absorption spectroscopy (TDLAS) at high time resolution (1 and 10 s) and precision ($\pm400$ and $\pm120$ parts per trillion by volume (pptv) ($2\sigma$), respectively) during the Texas Air Quality Study (TexAQS) 2000. Measurement accuracy was corroborated by in-flight calibrations and zeros and by overflight comparison with a ground-based differential optical absorption spectroscopy (DOAS) system. Throughout the campaign, the highest levels of $CH_2O$ precursors and volatile organic compound (VOC) reactivity were measured in petrochemical plumes. Correspondingly, $CH_2O$ and ozone production was greatly enhanced in petrochemical plumes compared with plumes dominated by power plant and mobile source emissions. The photochemistry of several isolated petrochemical facility plumes was accurately modeled using three nonmethane hydrocarbons (NMHCs) (ethene ($C_2H_4$), propene ($C_3H_6$) (both anthropogenic), and isoprene ($C_5H_8$) (biogenic)) and was in accord with standard hydroxyl radical (OH)-initiated chemistry. Measurement-inferred facility emissions of ethene and propene were far larger than reported by inventories. Substantial direct $CH_2O$ emissions were not detected from petrochemical facilities. The rapid production of $CH_2O$ and ozone observed in a highly polluted plume (30+ parts per billion by volume (ppbv) $CH_2O$ and 200+ ppbv ozone) originating over Houston was well replicated by a model employing only two NMHCs, ethene and propene.    *INDEX TERMS:* 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* formaldehyde, tropospheric oxidation, urban pollution, alkene oxidation, petrochemical facility emissions

## 1.  Introduction

[2]  Gas-phase formaldehyde ($CH_2O$) is a ubiquitous component of the troposphere and is typically the most abundant carbonyl compound found in the boundary layer atmosphere. $CH_2O$ is largely produced in situ, as an intermediate in the oxidation of a large array of volatile organic compounds (VOCs). However, only a small number of VOCs are both abundant and efficient $CH_2O$ producers. In the polluted boundary layer the terminal alkenes are generally the most important $CH_2O$ precursors, particularly isoprene ($C_5H_8$), ethene ($C_2H_4$), and propene ($C_3H_6$) [*Dodge*, 1990; *Lee et al.*, 1998b; *Goldan et al.*, 2000]. In many cases, the important $CH_2O$ precursors also contribute substantially to total hydrocarbon hydroxyl radical (OH) reactivity ($\Sigma[k_xOH * [VOC_x]$), and thereby total VOC reactivity. Here $k_x$ is the bimolecular rate constant for reaction of OH with each VOC. Due to the heterogeneous spatial distribution of $CH_2O$ precursors, and the relatively short lifetime of $CH_2O$ (2–4 hours in the sunlit troposphere), continental boundary layer $CH_2O$ concentrations span nearly 2 orders of magnitude [*Grosjean*, 1991; *Fried et al*, 1997; *Lee et al.*, 1998b], providing a sensitive indicator of recent VOC oxidation.

[3]  $CH_2O$ is also emitted directly into the atmosphere by incomplete fossil fuel combustion [*Sigsby et al.*, 1987; *Altshuller*, 1993; *Anderson et al.*, 1996], biomass burning

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[Lee et al., 1998a; Yokelson et al., 1999], industrial processes, and vegetative emissions [Carlier et al., 1986]. However, primary CH$_2$O emissions are typically small relative to photochemical production. Using ambient measurements, Li et al. [1994] have estimated that the amount of CH$_2$O directly emitted from eastern North America is 16 times less than that produced by the oxidation of emitted anthropogenic and biogenic VOCs.

[4]  Since VOC oxidation also drives tropospheric ozone production in the polluted boundary layer [Haagen-Smit, 1952; Chameides et al., 1992; Sillman, 1999], CH$_2$O measurements are useful to deconvolving sources of ozone pollution, an issue central to urban and regional air quality. For instance, CH$_2$O measurements made during the 1995 Southern Oxidants Study (SOS 95), based in Nashville, TN, were used to corroborate the contribution of biogenic isoprene to regional ozone production [Lee et al., 1998b]; and satellite measurements of CH$_2$O have been used to evaluate biogenic isoprene emissions over North America [Chance et al., 2000; Palmer et al., 2001]. To similar ends, the present study utilizes high time resolution airborne CH$_2$O measurements collected during the Texas Air Quality Study (TexAQS) 2000 to examine the role of various hydrocarbons in the photochemistry of the Houston, Texas area.

[5]  During the 1990s, ozone levels in exceedance of National Ambient Air Quality Standards (NAAQS) were regularly reported for the greater Houston, TX metropolitan area. On average, only Los Angeles reported more intense episodes of ozone pollution during this period [Lin et al., 2001]. Over 4 million people live in the greater Houston metropolitan area [U.S. Census Bureau, 2000], resulting in large mobile source emissions of VOCs and NO$_x$ [TNRCC, 1996]. One of the largest electric utility power plants in the nation, the W.A. Parish facility, is located just outside of Houston (see Figure 1) (D. K. Nicks et al., Fossil-fueled power plants as a source of atmospheric carbon monoxide, submitted to Atmospheric Environment, 2002). In addition, a large fraction of the U.S. olefin production capacity is found in the Houston–Galveston–Brazoria area, with an especially high density located along the Ship Channel inside Houston city limits (see Figure 1). Biogenic emissions are also a source of VOCs in and around Houston, although detailed vegetation surveys [Wiedinmyer et al., 2001] indicate that these emissions should be substantially less than in areas such as Tennessee [Geron et al., 1994; Goldan et al., 2000].

[6]  The TexAQS 2000 mission was conducted to elucidate the role of such emissions, along with meteorology, in Houston's intense photochemical pollution [Kleinman et al., 2002]. The study was conducted from mid-August to mid-September 2000 and involved the combined efforts of the Texas Natural Resource Conservation Commission (TNRCC), the National Oceanic and Atmospheric Administration (NOAA), the National Center for Atmospheric Research (NCAR), Brookhaven National Laboratories (BNL), the University of Texas, Baylor University, and many other laboratories and universities. Multiple well-instrumented aircraft and ground sites were employed.

[7]  The present study addresses four primary questions utilizing airborne CH$_2$O observations collected during TexAQS 2000: (1) What were the major sources of CH$_2$O (and
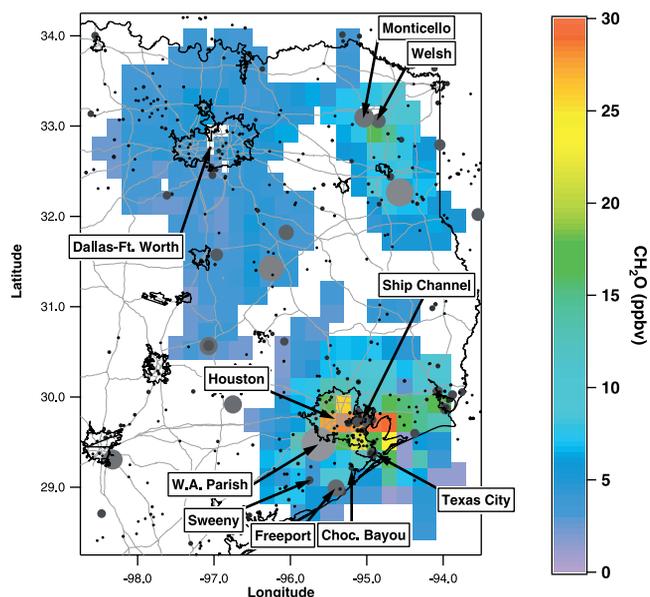


**Figure 1.**  Regional distribution of CH$_2$O maximums measured below 1000 m flight altitude for 0.2° latitude by 0.2° longitude grid cells. The solid circles show the location of NO$_x$ emitters and are sized according to reported NO$_x$ emissions. Labels are provided for cities (Houston and Dallas–Fort Worth), utility power plants (W.A. Parish, Monticello, and Welsh), isolated petrochemical facilities (Sweeny, Freeport, and Chocolate Bayou), and areas of concentrated petrochemical production (Ship Channel and Texas City) discussed in the text.

CH$_2$O precursors) in the Houston atmosphere? (2) Can the fast CH$_2$O measurements reported here be used to accurately extrapolate intermittent, lower resolution CH$_2$O precursor measurements made on the same aircraft? (3) To what extent did the important CH$_2$O precursors contribute to rapid ozone production in the Houston area? and (4) Were emission inventories accurate with respect to the important CH$_2$O precursors?

## 2.    Experimental
### 2.1.    Airborne Sampling

[8]  The measurements considered here were made from the NCAR L-188C Electra aircraft. CH$_2$O measurements were made by the NCAR tunable diode laser absorption spectrometer (TDLAS). Supporting measurements included 1 Hz ozone, CO [Holloway et al., 2000], CO$_2$, NO, NO$_2$, NO$_y$ [Ryerson et al., 2000], HNO$_3$ [Huey et al., 1998; Neuman et al., 2002], SO$_2$, size-resolved aerosol number [Brock et al., 2000], and spectrally resolved actinic flux. Peroxyacyl nitrate compounds were measured once every 3.5 min by gas chromatography (GC) (F. Flocke et al., The behavior of PANs and the budget of total reactive nitrogen (NO$_y$) during the TOPSE campaign, manuscript in preparation, 2002). Acetaldehyde was measured by proton transfer mass spectrometry (PTRMS) [Lindinger et al., 1998]. Thirty-nine whole air canister samples, typically integrated over 8 s, were acquired on each flight at the discretion of the flight scientist; subsequent GC analysis provided an extensive suite of speciated VOCs (see Table 1) [Schauffler et al.,

**Table 1.** VOCs Measured by the NCAR Whole Air Sampler (WAS)

| Alkanes | Alkenes | Aromatics | Alkynes |
|---|---|---|---|
| methane | ethene | benzene | ethyne |
| ethane | propene | toluene | |
| propane | 1-butene | ethyl benzene | |
| isobutene | isobutene | *m*-xylene, *p*-xylene | |
| *n*-butane | *t*-2-butene | *o*-xylene | |
| isopentane | *c*-2-butene | styrene | |
| *n*-pentane | 1, 3-butadiene | isopropyl benzene | |
| *n*-hexane | 3-methyl-1-butene | *n*-propyl benzene | |
| 2, 2-dimethyl butane | 1-pentene | 1, 2, 3-trimethyl benzene | |
| 2, 3-dimethyl butane | isoprene | 1, 2, 4-trimethyl benzene | |
| 3-methyl pentane | *t*-2-pentene | 1, 3, 5-trimethyl benzene | |
| 2-methyl hexane | *c*-2-pentene | | |
| 3-methyl hexane | 2-methyl-2-butene | | |
| 2, 2, 4-trimethyl pentane | cyclopentene | | |
| *n*-heptane | α-pinene | | |
| *n*-octane | | | |
| *n*-nonane | | | |
| *n*-decane | | | |
| cyclopentane | | | |
| cyclohexane | | | |
| dimethyl cyclopentane | | | |
| dimethyl cyclohexane | | | |

1999]. In situ GC samples were acquired once every 15 min, measuring a different subset of VOCs, including a limited suite of oxygenates [*Goldan et al.*, 2000].

[9] Flights surveyed the greater Houston metropolitan area on 8 different days. Two days each were dedicated to exploring the Dallas–Fort Worth area, and power plant plumes throughout eastern Texas. Flight tracks usually involved multiple crosswind intercepts of one or several plumes at a number of distances downwind, in order to characterize the temporal evolution of the plume chemistry. The bulk of sampled plumes were either of mobile source (urban), petrochemical facility, or power plant origin, with many plumes representing some combination of these emission types. In order to capture midday photochemistry and the daily ozone maximum, flights typically took off between 1000 and 1100 CST, and lasted for about 6 hours.

## 2.2. TDLAS System

[10] The TDLAS and its forerunner systems have been described [*Fried et al.*, 1998, 2002] (B. P. Wert et al., Design and performance of a tunable diode laser absorption spectrometer for airborne formaldehyde measurements, submitted to *Journal of Geophysical Research*, 2002, hereinafter referred to as Wert et al., submitted manuscript, 2002), thus only a short summary is included here. Gas-phase CH$_2$O was measured by probing the 2831.6417 cm$^{-1}$ rovibrational line with a tunable diode laser coupled to a 100 m path length astigmatic Herriott absorption cell. Extensive field and laboratory analysis has shown that the TDLAS inlet and Herriott cell produce only minimal sampling artifacts under the conditions encountered during TexAQS [*Wert et al.*, 2002]. Frequent instrument zeros were acquired, and flowing gas-phase standards were generated via a permeation oven, the accuracy of which has been

determined to be ±6% [*Gilpin et al.*, 1997; *Fried et al.*, 1998, 2002]. During the first portion of the TexAQS intensive, ambient CH$_2$O measurements were made at 10 s resolution. Data integration was reduced to 1 s beginning on the 1 September flight, and this resolution was maintained for the remainder of the mission. Estimated TDLAS precision during the TexAQS mission was 120 parts per trillion by volume (pptv) for 10 s measurements, and 400 pptv for 1 s measurements (reported at the 2σ level) (Wert et al., submitted manuscript, 2002). Ambient measurements covered roughly 50% of the total flight time, excluding takeoff and landing.

[11] Extensive tests have found that only methanol (CH$_3$OH) interferes with this technique. Laboratory studies using the same TDLAS arrangement as in TexAQS have shown the methanol interference to be +3.8% at equal methanol and CH$_2$O concentrations [*Fried et al.*, 2002] (Wert et al., submitted manuscript, 2002), consistent with independent measurements made at Rice University [*Richter*, 2001]. Thus ambient methanol levels of 10 parts per billion by volume (ppbv) would cause the TDLAS CH$_2$O measurement to be too high by 380 pptv. TDLAS CH$_2$O data were corrected using an algorithm derived from 144 coincident measurements of methanol (in situ GC) and CH$_2$O made on the Electra. Given the 1–3 ppbv CH$_2$O boundary layer background in the Houston area, and the emphasis of the present study on plume chemistry, the methanol bias and associated correction were largely negligible for the data of interest (<10%). All analyses in this paper utilize methanol corrected data.

[12] Further evidence for the accuracy of the TDLAS CH$_2$O measurement was provided by comparison with UCLA's ground-based differential optical absorption spectrometer (DOAS) [*Stutz and Platt*, 1997; *Harder et al.*, 1997] during TexAQS; these two systems were also successfully compared throughout the SOS 99 campaign (Wert et al., submitted manuscript, 2002). During TexAQS the Electra aircraft conducted overflights of the La Porte airport, the site of extensive chemical instrumentation including the UCLA DOAS. TDLAS data was averaged for a 5–10 s period of closest approach in all but one case, corresponding to a path comparable in length (0.5–1 km) and height (40–60 m flight altitude) to that of the DOAS (1.9 km path length, 2–50 m height above ground). Ground-based O$_3$ and CO measurement variability was acceptably small during the DOAS integration periods (20 min to 1 hour). Bivariate regression of the TDLAS and DOAS CH$_2$O data produced the relationship: (TDLAS CH$_2$O) = 0.95 * (DOAS CH$_2$O) − 0.70 ppbv (n = 6, $\chi^2$ = 5.5), with slope and intercept uncertainties of 0.15 and 0.65, respectively (see Figure 2). CH$_2$O measurements made by three separate DOAS paths at La Porte (0.75, 1.9, and 5.5 km path lengths) agreed well during all overflight periods but one, indicating good mixing. The overflight associated with conditions of poor mixing was that which yielded the high concentration point. Removal of this point produces a slope of 1.23 (±0.29). These results suggest that systematic measurement errors associated with the two different techniques are small (< ≈10%).

## 2.3. Photochemical Model

[13] The photochemical model used in the current study is similar to earlier plume simulations by, for example, *Hov*
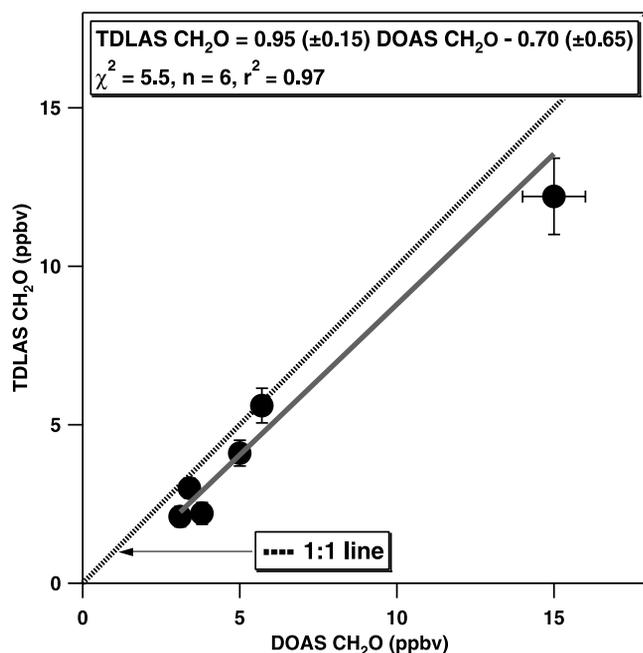
**Figure 2.** Bivariate regression of CH$_2$O measurements made by the NCAR TDLAS on the Electra aircraft and the UCLA DOAS at the La Porte site during close overflights.

*and Isaksen* [1981] and *Sillman* [2000], where the plume of a power plant was followed in an idealized Lagrangian fashion and the vertical and horizontal spreading were explicitly described. In the present model the vertical dispersion of the plume was controlled by the growth of the planetary boundary layer (PBL), and diffusive vertical transport was calculated as described by *Trainer et al.* [1991]. The maximum height of the PBL was scaled to approximate observed conditions. Horizontal spreading of the plume was described by a diffusion coefficient chosen to approximate the observed growth in plume width as a function of distance. The advective wind was a free parameter that controlled the peak concentration in the plume, and was chosen according to measurements aboard the aircraft, or radar profile measurements made from the ground. Horizontal grid resolution was fixed at 500 m and the plume was emitted into a 100 × 500 × 500 m grid cell. Plume spreading and photochemistry were concurrently calculated within this grid framework. The chemistry was based on the studies of *Trainer et al.* [1987, 1991] where the reaction rates and products were updated according to JPL97 [*DeMore et al.*, 1997] and to the study of *Atkinson* [1997]. Photolysis rates were calculated by the TUV radiative transfer model of *Madronich* [1987] and validated by comparison with actinic flux measurements made on the Electra. The TUV model is based upon the discrete ordinates model modified to solve the radiative transfer equation in pseudospherical coordinates [*Dahlback and Stamnes*, 1991].

## 3. Results

### 3.1. TexAQS CH$_2$O Distributions

[14] As depicted in Figure 3, the vertical distribution of CH$_2$O measured during TexAQS shows a rapid decay above the boundary layer (0.5–2.5 km) (C. Senff, private communication, 2001), indicative of surface CH$_2$O precursor sources and the short lifetime of CH$_2$O under summer conditions. The regional distribution of CH$_2$O maximums observed below 1000 m flight altitude is shown in Figure 1, at a grid cell resolution of 0.2° latitude by 0.2° longitude (22 × 19 km, respectively). Of primary interest to the present study are the high CH$_2$O levels found in the greater Houston metropolitan area on many days. These large mixing ratios of between 10 and 32 ppbv were observed in plumes substantially smaller in spatial extent than the Houston metropolitan area. In contrast to Houston, Dallas–Fort Worth had CH$_2$O levels that were much lower (2–6 ppbv) and more spatially uniform. Measurements of the Dallas–Fort Worth plume are compared with those from Houston, as the populations of the cities are similar (Dallas–Fort Worth: Dallas and Tarrant counties, 3.6 million people; Houston: Harris, Fort Bend, Brazoria, and Galveston counties, 4.2 million people) [*U.S. Census Bureau*, 2000]. The only power plant plumes with CH$_2$O levels significantly above background were those from the Welsh and Monticello plants (up to 17 ppbv CH$_2$O over a very limited area), which encountered strong biogenic isoprene emissions (see Figure 1).

### 3.2. Houston Area CH$_2$O Precursor Distributions

[15] To provide an assessment of the relative CH$_2$O production expected from measured VOCs, the present analysis calculates the "CH$_2$O production potential" of individual VOC samples [*Lee et al.*, 1998b]. For a given VOC mixture, the CH$_2$O production potential is here expressed as $\Sigma(k_xOH * [VOC_x] * (\gamma CH_2O_{(VOCx)}))$. Note that in this analysis the CH$_2$O yield term ($\gamma CH_2O$) reflects only the first generation products of OH-initiated VOC oxidation; production from moderately lived intermediates such as acetaldehyde (CH$_3$CHO) is not considered. Molar CH$_2$O yields used for the most abundant reactive CH$_2$O precursors were ethene (1.6) [*Niki et al.*, 1981], propene (1.0) [*Niki et al.*, 1978], and isoprene (0.6) [*Carter and Atkinson*, 1996]. For the alkanes yields of 0.1 to 0.3 were typically used (exceptions include methane (1) and isobutane (0.8)); the yields of alkynes and most aromatics were set to zero [*Lee et al.*, 1998b]. OH reaction rate constants were given by *Atkinson* [1990, 1997] and *DeMore et al.* [1997].

[16] CH$_2$O production potentials were calculated for 390 VOC samples collected in canisters aboard the Electra at flight altitudes less than 1000 m during TexAQS, producing the Houston–Galveston area distribution depicted in Figure 4. A distinct maximum in CH$_2$O production potential is clearly evident in the vicinity of the Houston Ship Channel. Of the VOC samples taken in this area, six yielded production potentials between 13 and 63 s$^{-1}$. Only two other samples acquired during TexAQS had CH$_2$O production potentials greater than 10 s$^{-1}$. One of these samples was taken in a plume downwind of Texas City, an area of concentrated petrochemical industry south of Houston (see Figure 1). The other was measured in a plume intercepted over eastern Texas, from a petrochemical facility that reported the largest ethene emissions in Texas (Eastman Chemical) [*TNRCC*, 1999]. On average, the terminal alkenes, largely ethene and propene, composed 95% of total
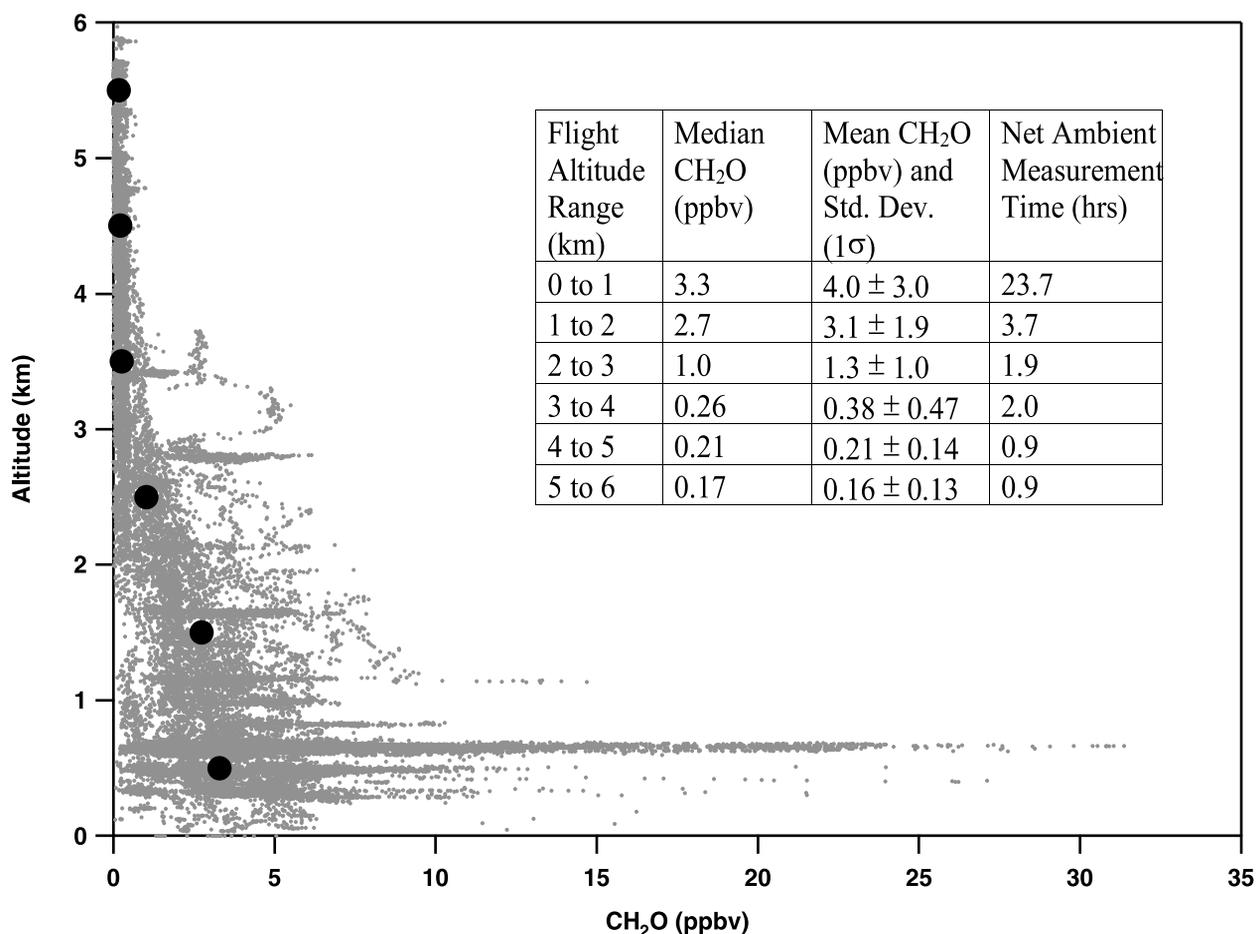
| Flight Altitude Range (km) | Median CH$_2$O (ppbv) | Mean CH$_2$O (ppbv) and Std. Dev. (1$\sigma$) | Net Ambient Measurement Time (hrs) |
|---|---|---|---|
| 0 to 1 | 3.3 | 4.0 $\pm$ 3.0 | 23.7 |
| 1 to 2 | 2.7 | 3.1 $\pm$ 1.9 | 3.7 |
| 2 to 3 | 1.0 | 1.3 $\pm$ 1.0 | 1.9 |
| 3 to 4 | 0.26 | 0.38 $\pm$ 0.47 | 2.0 |
| 4 to 5 | 0.21 | 0.21 $\pm$ 0.14 | 0.9 |
| 5 to 6 | 0.17 | 0.16 $\pm$ 0.13 | 0.9 |

**Figure 3.** The vertical distribution of CH$_2$O measurements made during TexAQS 2000. Median CH$_2$O values for 1000 m flight altitude bins are denoted by the solid circle symbols.

CH$_2$O production potential and 91% of total hydrocarbon OH reactivity in these eight highly polluted samples. Additional sources of substantial CH$_2$O production potential were the Sweeny, Freeport, and Chocolate Bayou petrochemical facilities south of Houston (2–9 s$^{-1}$); these three facilities will be collectively referred to as the "isolated petrochemical facilities." The forested region northeast of Houston also featured somewhat elevated CH$_2$O production potentials (1–3 s$^{-1}$) due largely to isoprene. In all such cases, the bulk of the CH$_2$O precursors must have been emitted within about an hour prior to sampling, given the rapid midday summertime photochemistry.

[17] The industrial origin of the eight highest CH$_2$O production potential samples (>10 s$^{-1}$) was confirmed by ethene/ethyne and propene/ethyne ratios (T. B. Ryerson et al., Effect of co-located petrochemical industrial emissions of reactive alkenes and NO$_x$ on tropospheric ozone formation, in preparation, 2002, hereinafter referred to as Ryerson et al., in preparation, 2002). Strong industrial signatures (ethene/ethyne $\geq$ 3 and/or propene/ethyne $\geq$ 1) were identified in 98 canister samples acquired over the greater Houston metropolitan area. These samples had a median ethene/ethyne ratio of 4.9, propene/ethyne ratio of 1.6, CH$_2$O production potential of 2.9 s$^{-1}$, and OH hydrocarbon reactivity of 3.1 s$^{-1}$. The CH$_2$O production potential of these 98 samples was due largely to the terminal alkenes (78%),

with ethene contributing 30%, propene 22%, and isoprene 14% (1-butene, isobutene, 1, 3 butadiene, 3-methyl-1-butene, and 1-pentene also contributed to a lesser degree). Terminal alkenes were also responsible for a majority (71%) of the total OH hydrocarbon reactivity of these samples.

[18] Seven VOC samples, acquired on 5 different days between 1130 and 1600 CST were selected as representative of Houston mobile source emissions based upon chemical ratios (ethene/ethyne < 1.7 and propene/ethyne < 0.5), CO mixing ratios (>150 ppbv), CO$_2$ mixing ratios (<375 ppmv), location over the Houston urban core, and wind direction. Median CH$_2$O production potential (0.6 s$^{-1}$) and OH hydrocarbon reactivity (0.7 s$^{-1}$) for these samples were substantially lower than seen in the industrially influenced samples. All nine canister samples acquired over the Dallas–Fort Worth metropolitan area yielded similar signatures, consistent with the lower, more spatially uniform CH$_2$O levels measured throughout the Dallas–Fort Worth plume (see Figure 1). These observations suggest that the CH$_2$O species should represent an excellent proxy for the important reactive VOCs in the Houston atmosphere, the utility of which is explored in the remainder of this paper.

### 3.3. Houston Area Plumes

[19] Measurements of CH$_2$O in the Houston area are now examined for consistency with the precursor distributions
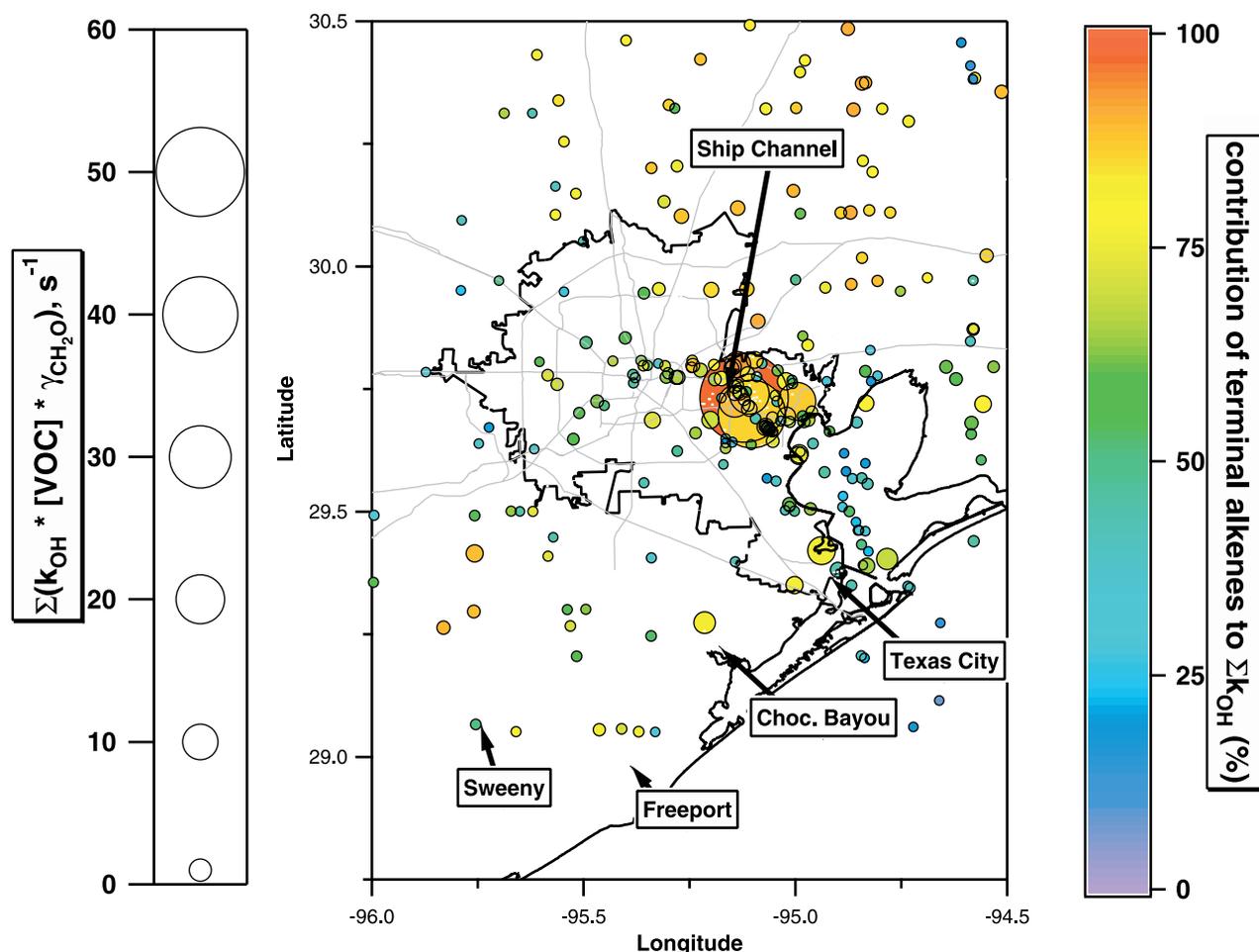
**Figure 4.** Measured Houston–Galveston VOC distribution coded by size for $CH_2O$ production potential and by color for the percentage of terminal alkene contribution to total OH hydrocarbon reactivity.

discussed above. Complicating this however, lifetimes of ethene (3–8 hours) and propene (1–2.5 hours) are short (lifetime ranges calculated for OH = $1 \times 10^7$ mol $cm^{-3}$, $O_3$ = 120 ppbv, and OH = $4.5 \times 10^6$ mol $cm^{-3}$, $O_3$ = 60 ppbv, respectively) [*Atkinson*, 1997]. Therefore, regressions of $CH_2O$ versus $CH_2O$ production potentials did not yield strong correlations; this lack of correlation was accentuated by variable meteorology and limited VOC measurements.

[20] Instead, levels of $CH_2O$ in Houston area plumes are compared for transects of roughly equivalent photochemical age. Plume sources were determined using tracers including $SO_2$, CO, and $CO_2$ [*Brock et al.*, 2003; Ryerson et al., manuscript in preparation, 2002]. Based on these tracers, distinct power plant (W.A. Parish), mobile source (Houston urban), and petrochemical (Ship Channel) dominated plumes were identified in the 28 August, 30.1° latitude E-W flight transect appearing in Figures 5 and 6. These plumes had passed over the core of the Houston metropolitan area 2.5–3 hours (40 km) previously. Peak $NO_y$ levels in each of the three plumes were roughly comparable (9–14 ppbv), and consistent $NO_x/NO_y$ ratios (0.21–0.27) indicated that the three plumes were well processed and of similar photochemical age. As shown in Figure 6, levels of $CH_2O$ in the petrochemically dominated plume were much higher (up to

13 ppbv) than those of the mobile source (up to 4.5 ppbv) and power plant plumes (up to 3 ppbv).

[21] Within individual plumes transects, tight positive correlations were found between $CH_2O$ and directly emitted species (CO, $CO_2$, and $NO_y$), as well as secondary photoproducts (ozone, $HNO_3$, and acetaldehyde), as listed in Table 2 for two petrochemically dominated plumes. Figure 7 depicts such relationships, showing $CH_2O$ and coincidentally measured $NO_y$ and ozone from a Ship Channel dominated plume transect. Associated correlation coefficient ($r^2$) values were greater than 0.95 for the 20-km-wide plume cross section, indicating that the relationship of $CH_2O$, $NO_y$, and ozone was very uniform throughout the plume (see Table 2). Note that these good correlations are largely the result of mixing/dilution, as will be discussed below.

[22] When comparing plumes of different sources, large differences were observed in such $CH_2O$/"tracer" relationships. This is clearly evident in the survey of petrochemical, mobile source (urban), and power plant plumes presented in Table 3. $CH_2O/NO_y$ slopes for petrochemical plumes, including the Ship Channel plume (see Figure 7b), were between 0.8 and 3.1. In contrast, $CH_2O/NO_y$ slopes ranged from 0.2 to 0.4 for the Houston and Dallas–Fort Worth
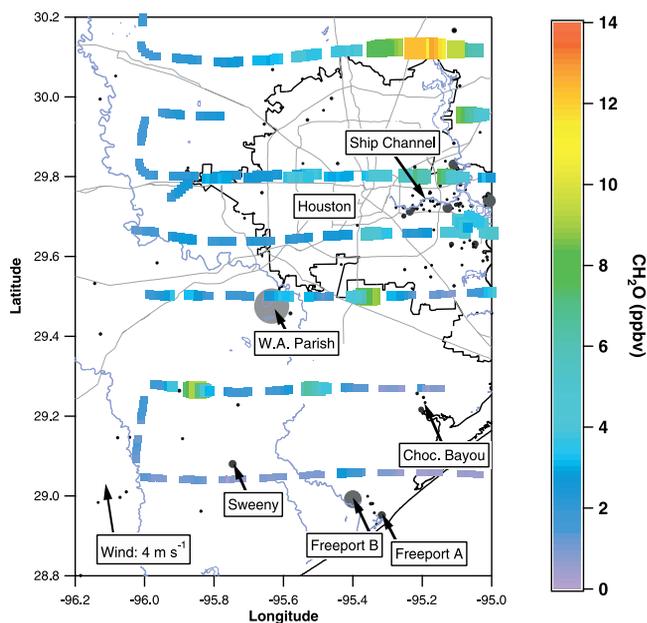
**Figure 5.** Measurements of $CH_2O$ in the Houston area on 28 August below 1000 m flight altitude. The solid circles show the location of $NO_x$ emitters and are sized according to reported $NO_x$ emissions. General wind direction is shown by the arrow in the bottom left corner.

plumes (mobile source dominated), and the W. A. Parish plume (power plant). Reported $CH_2O$/tracer slopes were determined from individual plume transects where $NO_x$/$NO_y$ ratios were generally between 0.2 and 0.3. Some uncertainty in this comparison arises due to $HNO_3$ loss [*Trainer et al.*, 2000], and the relatively short lifetime of $CH_2O$ that will cause such ratios to change significantly with the photochemical age of the air mass (see Table 2). Nonetheless, the striking and consistent $CH_2O$/$NO_y$ slope differences found between plumes of different source types on multiple days provides further evidence that petrochemical emissions are indeed the dominant source of extreme $CH_2O$ concentrations in Houston.

[23] The tightly positively correlated $CH_2O$/$O_3$ slopes repeatedly measured in mobile source, power plant, and petrochemical plumes (see Tables 2 and 3 and Figure 7c), suggest that oxidation of $CH_2O$ precursors (including photolysis of $CH_2O$ itself) played a major role in ozone production. This is consistent with the observation that $CH_2O$ precursors were responsible for a substantial fraction of total OH hydrocarbon reactivity, especially in the most polluted VOC samples. As depicted in Figure 6, $CH_2O$ and ozone levels observed the same basic trends in the 28 August Houston plumes. Measurements from 1 September, a highly polluted day (see Figures 7a and 7c and 8a and 8b), also show $CH_2O$ and ozone tracking one another. It should be noted that a spatial (temporal) offset was observed between the $CH_2O$ and ozone gradients, as expected, due to the longer lifetime and slower relative net production rate of ozone. Throughout the TexAQS campaign, high $CH_2O$ levels, often 10–20+ ppbv above background, were always found coincident with exceedance levels of ozone (>120 ppbv).

### 3.4. Isolated Petrochemical Facility Plumes

[24] Using the model discussed above, we now analyze several petrochemical plumes to determine if measured ethene and propene emissions can account for the majority of observed $CH_2O$ and ozone, and if measurements are consistent with $NO_x$ and VOC inventories. For this exercise, plume measurements from the isolated petrochemical facilities, Freeport, Sweeny, and Chocolate Bayou are used [*Brock et al.*, 2003; Ryerson et al., manuscript in preparation, 2002]. These facilities primarily conducted olefin-producing processes, and are analogous to many of the larger petrochemical facilities located along the Houston Ship Channel (C. Wiedinmyer and G. Frost, personal communication, 2001). On 27 and 28 August, plumes from these facilities were superimposed on clean background air, the result of prevailing winds from the Gulf of Mexico (see Figure 5). This kept the plumes largely unperturbed by other emission sources for several hours. Plume model results presented here are for 28 August, as intermittent $CH_2O$ instrument problems were encountered on 27 August. Sufficient $CH_2O$ data were collected on 27 August to demonstrate that the Freeport and Sweeny plumes exhibited consistent behavior on both days. Emission estimates inferred from aircraft observations are reported for Freeport and Sweeny, but not Chocolate Bayou, as VOC data were collected only on the very edge of the Chocolate Bayou plume. Measurements of acetaldehyde and $CH_2O$ were used to apportion emissions of ethene and propene, since propene oxidation produces acetaldehyde while ethene oxidation does not [*Niki et al.*, 1978, 1981; *Grosjean and Grosjean*, 1996; *Grosjean et al.*, 1996; *Calvert et al.*, 2000; *Bacher et al.*, 2001].

[25] Model $NO_x$ and VOC inputs were derived from observations made 1–2 hours downwind of the petrochemical complexes on both 27 and 28 August, between about 1200 and 1300 CST. It was assumed that by this time the boundary layer was well mixed vertically and the measurements at the flight altitude of 500–600 m were representative of the whole boundary layer (species ratios were constant). Uncertainty in estimated $NO_x$ emission rates for the isolated petrochemical facilities was largely due to model parameters such as wind speed ($\pm1$ m s$^{-1}$), and boundary layer heights. Considering these uncertainties, the adopted and reported $NO_x$ emission rates for the isolated petrochemical complexes compared favorably (see Table 4). Previous plume studies provide precedent for this good agreement [*Ryerson et al.*, 1998].

[26] Estimates of VOC emissions were derived using measured plume VOC/$NO_x$ ratios, with corrections applied for VOC and $NO_x$ losses occurring between the point of emission and measurement. For the Freeport plume, six separate VOC measurements were made at a variety of downwind distances. One VOC sample apiece was collected from the Sweeny and Chocolate Bayou plumes. Due to the dominance of ethene and propene in these samples, the model assumed that VOC emissions for each facility were composed exclusively of these two terminal alkenes. Isoprene was also measured in all plumes, the majority of which was attributed to biogenic emissions from the discontinuous forests of the region, based upon VOC samples taken outside of the plumes and biogenic inventories [*Wiedinmyer et al.*, 2001]. A background isoprene flux
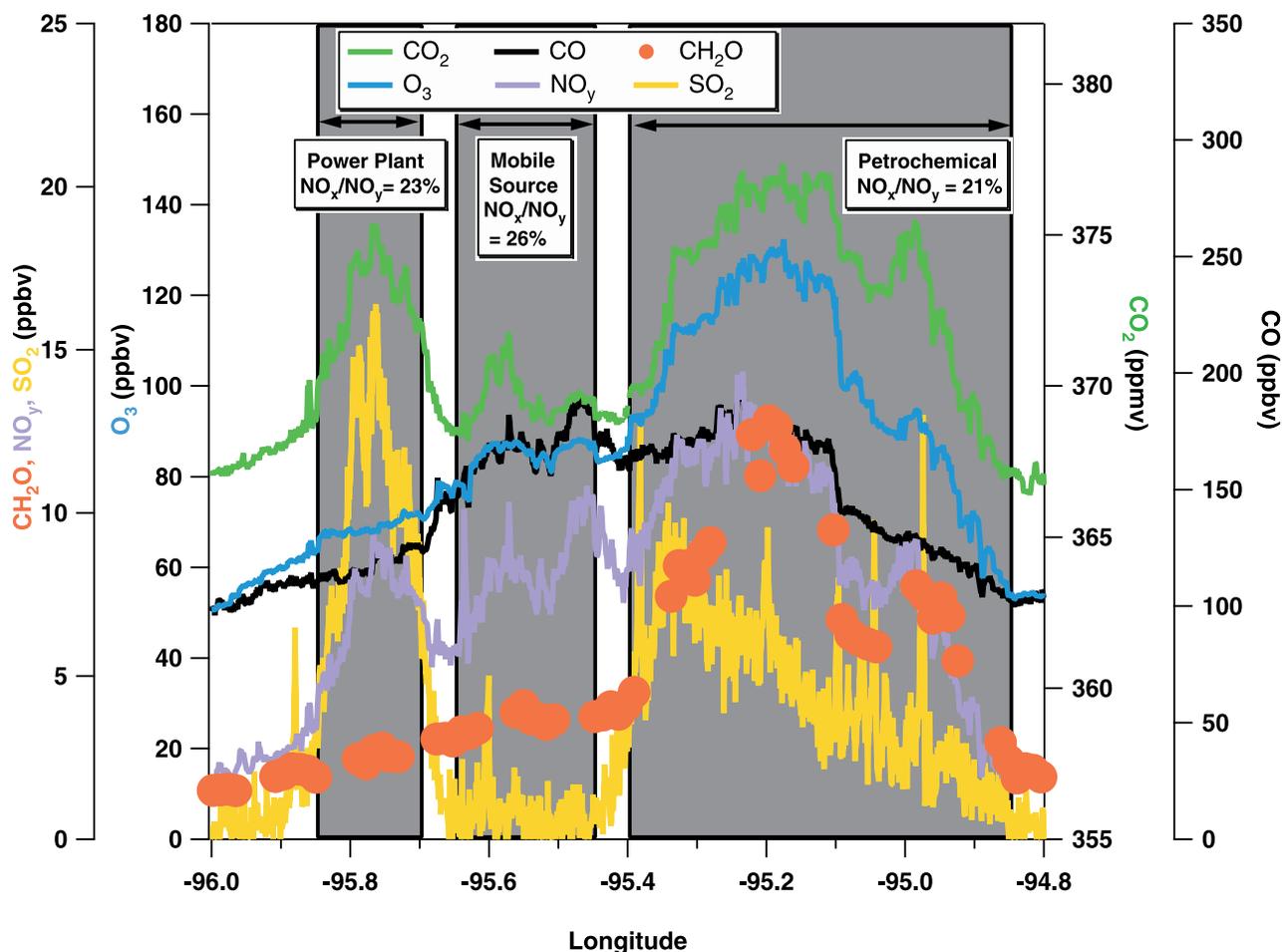
**Figure 6.** Mixing ratios of $CH_2O$ and other species in a cross section of the Houston plume acquired at $30.1°$ latitude on 28 August, showing distinct power plant (W. A. Parish), mobile source (Houston urban), and petrochemical (Ship Channel) dominated plumes.

common to all of the plumes was therefore included in the model ($5.2 \times 10^{15}$ mol m$^{-2}$ s$^{-1}$).

[27] Using these observationally derived $NO_x$ and VOC emission values, the model accurately replicated measured ethene, propene, $CH_2O$, acetaldehyde, ($NO_y - NO_x$), ($NO_y - (NO_x + HNO_3)$)), and ozone concentrations. As noted above, observationally derived $NO_x$ values were effectively equivalent to inventory values. Figure 9 provides an overview of results for the $29.3°$ latitude intercept of the Sweeny and Freeport plumes. Not only did the model successfully simulate the rapid $CH_2O$ enhancement in the plume, it also accurately captured the $CH_2O$ background due to the area-wide isoprene emissions (see Figure 9b). Ethene and propene emission apportionment was corroborated by agreement with both $CH_2O$ and acetaldehyde (Figures 9b and 9c). It is important to note that in all cases the model needed only standard OH-initiated VOC oxidation to achieve good agreement with observations. The observed "shoulder" feature seen on the east side of the Freeport plume, particularly apparent in the ozone measurement (Figure 9d), was due to incursion of the Freeport A complex plume into the Freeport B complex plume. The model only attempted to replicate the larger Freeport B plume (see Figure 5).

[28] The Freeport and Sweeny plumes were also modeled using $NO_x$ and VOC emissions taken directly from TNRCC inventories, along with the measurement-inferred biogenic isoprene background. Note that the only real difference between this and the previously discussed model case was the magnitude of the industrial VOC inputs (see Table 4). When using inventory inputs, less than 10% of the measured $CH_2O$, and 40% of the measured ozone enhancement over background levels were predicted (see Figures 9b and 9d, dotted gray lines). In this case, modeled $CH_2O$ and ozone production was largely due to the presence of the isoprene background, with TNRCC inventory VOCs contributing minimally. On a related note, inclusion of a large measured isobutane emission to the ethene, propene, and isoprene mix used to model the Chocolate Bayou plume (not depicted) produced very little additional $CH_2O$ and ozone, due to the much lower reactivity of alkanes.

[29] One potential weakness of the above analysis was its reliance on just a handful of canister measurements to characterize the VOC emissions of the isolated petrochemical facilities. However, since $CH_2O$ is efficiently produced by the dominant reactive VOCs in these plumes, it represents a good surrogate for plume VOCs. The very

**Table 2.** Slopes of CH$_2$O Versus Several Other Species Measured in the 1 September Ship Channel Dominated Plume and the 28 August Freeport Plume

| Distance (km) | Age (hours) | NO$_x$/NO$_y$ | CH$_2$O/NO$_y$ | $r^2$ | CH$_2$O/CO | $r^2$ | CH$_2$O/O$_3$ | $r^2$ | CH$_2$O/HNO$_3$ | $r^2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | *1 September Ship Channel Dominated Plume* | | | | | | | |
| 10 | 0.8 | 0.69 | 0.47 | 0.73 | 0.21 | 0.89 | 0.68 | 0.87 | 7.7 | 0.87 |
| 25 | 2 | 0.49 | 0.79 | 0.99 | 0.18 | 0.95 | 0.41 | 0.96 | 5.0 | 0.94 |
| 50 | 4 | 0.29 | 0.73 | 0.84 | 0.13 | 0.92 | 0.16 | 0.86 | 2.5 | 0.80 |
| 75 | 6 | 0.24 | 0.87 | 0.98 | 0.09 | 0.97 | 0.15 | 0.98 | 2.8 | 0.96 |
| 100 | 8 | 0.22 | 0.74 | 0.89 | 0.05 | 0.91 | 0.12 | 0.86 | 1.9 | 0.77 |
| | | | *28 August Freeport Plume* | | | | | | | |
| 8 | 0.6 | 0.77 | 0.14 | 0.90 | 0.07 | 0.50 | na | na | na | na |
| 33 | 2.3 | 0.36 | 1.35 | 0.95 | 0.31 | 0.94 | 0.25 | 0.99 | 3.7 | 0.92 |
| 60 | 4.2 | 0.29 | 0.87 | 0.93 | 0.10 | 0.84 | 0.15 | 0.95 | 2.2 | 0.85 |

robust positive CH$_2$O/tracer correlations measured in the plumes (see Tables 2 and 3) show that facility emissions were sufficiently collocated, and atmospheric mixing adequately strong, as to rapidly (0.5–1 hour) produce plumes of constant species ratios, despite the fact that the facilities were not perfect point sources. The strong boundary layer mixing necessary to create this measured horizontal uniformity would also be expected to produce

vertically homogeneous species ratios as well. Therefore, plume VOC/NO$_x$ ratios measured at flight altitudes of 500–600 m by the Electra should be representative of the entire boundary layer vertical profile, except for very fresh plumes (<0.5 hour under moderate winds) and perhaps for plumes affected by special meteorological conditions such as coastal effects. Support for this conclusion is provided by airborne LIDAR ozone measure-
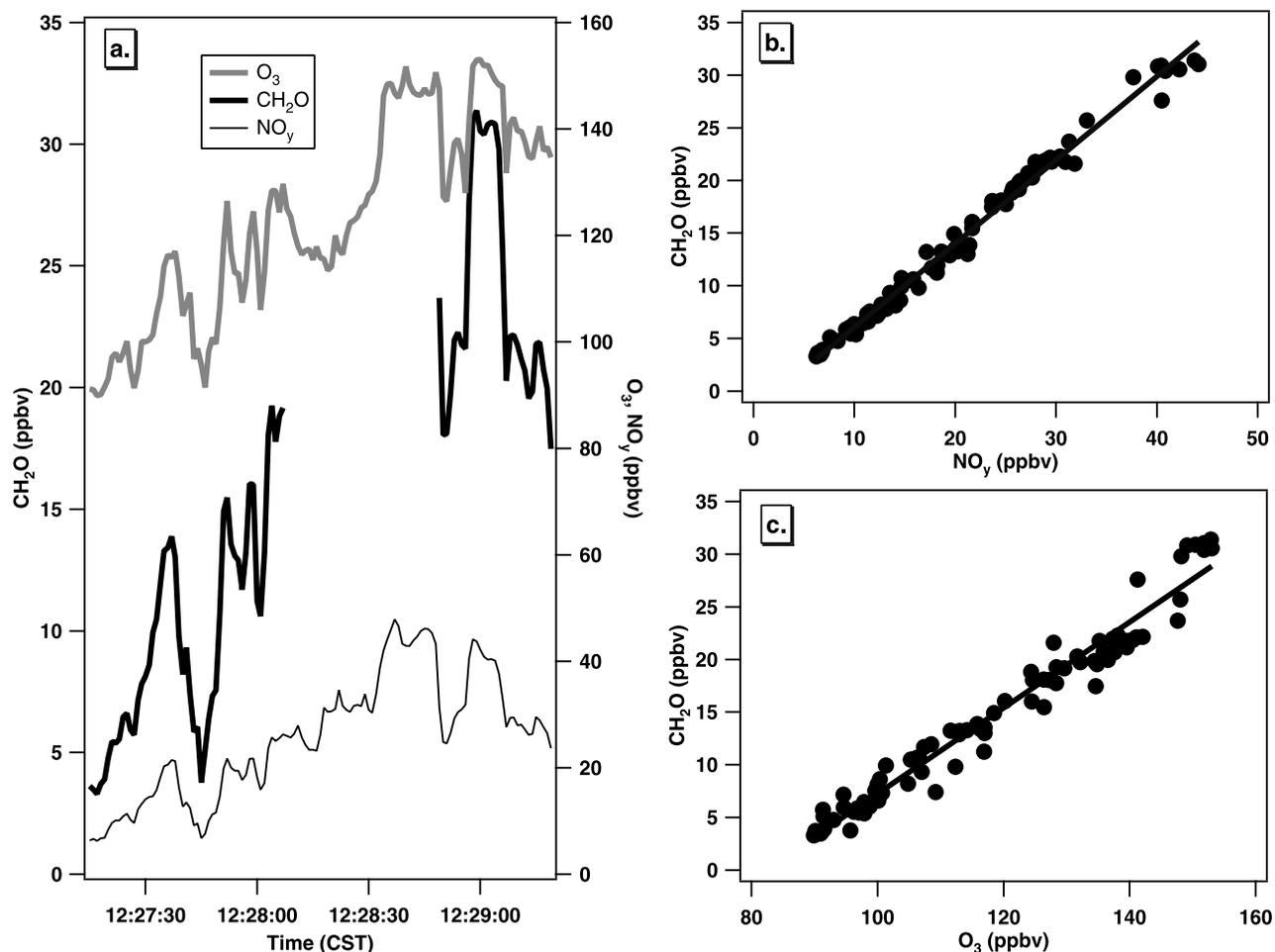


**Figure 7.** Measurements of CH$_2$O, NO$_y$, and ozone in a cross section of the 1 September Ship Channel dominated plume, 2 hours downwind of the Ship Channel (a). Regressions of CH$_2$O versus NO$_y$ (b) and ozone (c) (see Table 2 for slopes and correlation coefficients).

**Table 3.** Slopes of CH$_2$O Versus NO$_y$ and Ozone Measured in Plumes of Petrochemical, Mobile Source (Urban), and Power Plant Origin

| Plume Source | Date | NO$_x$/NO$_y$ | CH$_2$O/NO$_y$ | $r^2$ | CH$_2$O/O$_3$ | $r^2$ |
|---|---|---|---|---|---|---|
| *Petrochemical* | | | | | | |
| Freeport | 27 August | 0.37 | 0.85 | 0.93 | 0.19 | 0.97 |
| Freeport | 28 August | 0.36 | 1.35 | 0.95 | 0.25 | 0.99 |
| Freeport | 6 September | 0.31 | 1.30 | 0.78 | 0.18 | 0.84 |
| Sweeny | 27 August | 0.27 | 1.85 | 0.92 | 0.11 | 0.85 |
| Sweeny | 28 August | 0.32 | 1.66 | 0.99 | 0.12 | 0.97 |
| Chocolate Bayou | 28 August | 0.29 | 3.13 | 0.98 | 0.33 | 0.99 |
| Ship Channel | 27 August | 0.24 | 1.28 | 0.96 | 0.15 | 0.91 |
| Ship Channel | 28 August | 0.29 | 0.92 | 0.82 | 0.13 | 0.88 |
| Ship Channel | 1 September | 0.24 | 0.87 | 0.98 | 0.15 | 0.98 |
| | | | | | | |
| *Mobile Source (Urban)* | | | | | | |
| Houston | 28 August | 0.21 | 0.36 | 0.81 | 0.11 | 0.53 |
| Dallas–Ft. Worth | 7 September | 0.28 | 0.25 | 0.86 | 0.095 | 0.80 |
| | | | | | | |
| *Power Plant* | | | | | | |
| W.A. Parish | 28 August | 0.21 | 0.24 | 0.83 | 0.08 | 0.94 |

ments made during TexAQS that showed strong vertical mixing (C. Senff, private communication, 2001) as well as limited in situ measurement profiles made by the Electra.

[30] Measurement derived VOC emissions for the Freeport and Sweeny plumes used in this model exercise were estimated to be accurate within at least a factor of 2. This was based upon the high degree of agreement achieved between predicted and measured secondary photoproducts, particularly CH$_2$O and acetaldehyde, and the plume species ratio uniformity demonstrated by CH$_2$O/tracer relationships. Also accounted for were the uncertainties associated with NO$_x$ emissions, wind speeds (plume ages), and boundary layer heights. Consistent CH$_2$O/tracer slopes were found on each day the Freeport (3 days) and Sweeny plumes (2 days) were intercepted, as listed in Table 2 for intercepts of comparable photochemical ages (NO$_x$/NO$_y$ ratios), suggesting that the VOC emissions deduced here were the consequences of standard operations rather than unreported unusual emission events ("upsets"). As seen in Table 4, derived ethene and propene emissions for the Freeport and Sweeny facilities are 50–100 times larger than reported (1999 TNRCC VOC inventory), and in sum about 20 times larger than total reported VOC emissions. Analysis of the Chocolate Bayou plume produced similar disparities.

### 3.5.  Primary CH$_2$O Emissions

[31] The isolated petrochemical facility plumes were also used to assess the importance of primary petrochemical CH$_2$O emissions. If primary emissions were large, they would need to be considered in assessments of emissions and photochemistry made using CH$_2$O data. However, only small enhancements of CH$_2$O were found in close proximity intercepts of the isolated petrochemical facility plumes, providing an upper limit on direct emissions. In the Freeport plume, CH$_2$O levels were 1–2 ppbv above background about 20 min downwind (8 km), on both 27 and 28 August (see the 29.1° latitude pass in Figure 5). A similar enhancement was also measured 30 min (7 km) downwind of the Chocolate Bayou facility on 27 August. In all cases, plume CH$_2$O levels dramatically

increased downwind of these initial intercepts despite dilution, consistent with rapid photochemical production of CH$_2$O from emitted VOCs, rather than primary emission. In addition, the model achieved good agreement with observations invoking only photochemistry. The dominance of in situ CH$_2$O production was also supported by extensive, continuous PTRMS measurements of propene, acetaldehyde, and CH$_2$O made at the La Porte ground site near the Ship Channel (T. Karl et al., The use of proton-transfer mass spectrometry to characterize VOC sources at the La Porte super site during the Texas Air Quality Study 2000, manuscript in preparation, 2002). Direct CH$_2$O emissions from mobile sources are not expected to have contributed importantly to peak daytime Houston CH$_2$O abundances either, based upon work by *Zweidinger et al.* [1988], *Altshuller* [1993], and others, and the much lower measured CH$_2$O levels in the Houston and Dallas–Fort Worth mobile source plumes.

### 3.6.  Photochemistry of a Highly Polluted Plume

[32] Ozone exceedance events measured over Houston by the Electra typically involved ozone enhancements of 60–150+ ppbv above background. In comparison, ozone
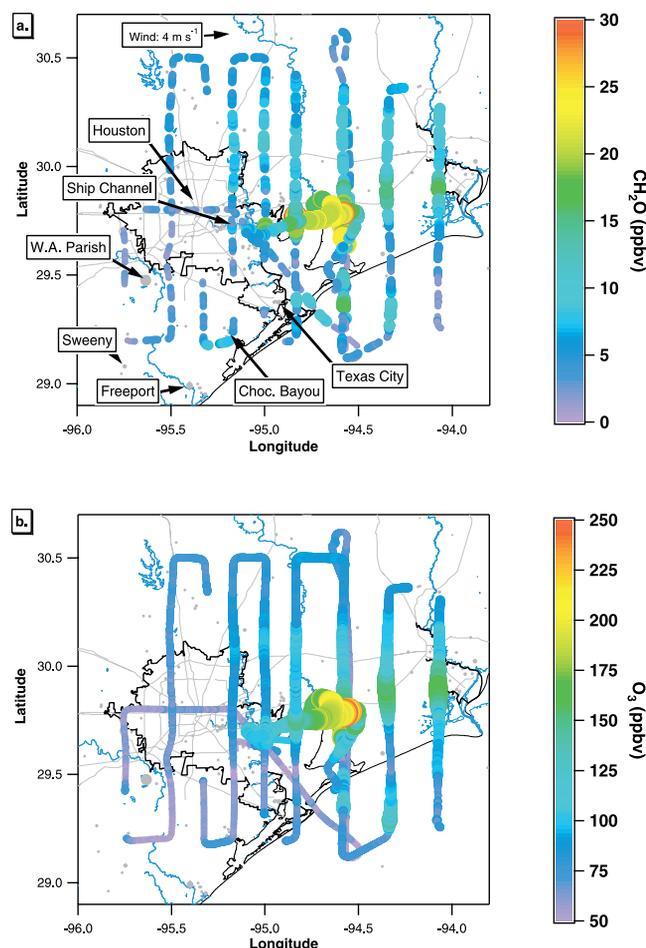


**Figure 8.** Measured CH$_2$O (a) and ozone (b) mixing ratios in the Houston–Galveston area on 1 September at flight altitudes less than 1000 m. General wind direction is shown by the arrow in the upper left corner of (a).

**Table 4.** Measurement-Derived Emissions Used for Modeling the Freeport and Sweeny Plumes (28 August) Along With Corresponding Inventory Values[a]

| Petrochemical Facility | Measurement-Derived Emissions (kmol hr$^{-1}$) | | | Inventory Emissions (kmol hr$^{-1}$) | | | |
|---|---|---|---|---|---|---|---|
| | NO$_x$ | Ethene | Propene | NO$_x$ | Ethene | Propene | Total VOCs |
| Freeport B | 30 | 45 | 15 | 31 | 0.9 | 0.3 | 3.1 |
| Sweeny | 15 | 54 | 30 | 14 | 0.5 | 0.3 | 3.7 |

[a]Inventory numbers from the 1999 and 2000 TNRCC Point Source Database. Freeport B = 6 sources, $28.94° \leq$ latitude $\leq 29.02°$, $-95.44° \leq$ longitude $\leq -95.36°$; Sweeny = 5 sources, $29.04° \leq$ latitude $\leq 29.10°$, $-95.80° \leq$ longitude $\leq -95.7°$.

enhancements associated with the isolated petrochemical facility plumes did not exceed 30 ppbv above background. Therefore to test the premise that petrochemical ethene and propene emissions are central to Houston's most extreme ozone pollution, the 1 September Houston plume (see Figures 7 and 8 and Table 2) was modeled using an approach similar to that employed with the isolated petrochemical plumes. This plume was dominated by Ship Channel emissions and had maximum observed ozone levels of 245 ppbv and CH₂O levels of 32 ppbv.

[33] Emission estimates for the 1 September plume were complicated by the diversity and size of the petrochemical source area, and the mobile source emission background, which although of secondary importance was still substantial. Based on a survey of VOC/NO$_x$ measurements made in the plume, corrected for differential losses, an equal molar emission rate for NO$_x$, ethene, and propene (252 kmol hr$^{-1}$ each) was estimated. Nonmethane hydrocarbons (NMHCs) other than ethene and propene contributed only weakly to total hydrocarbon OH reactivity measured in the plume and were left out. The point of this modeling exercise was to assess whether the oxidation of observed ethene and propene could alone account for the general rate and magnitude of extreme CH₂O and ozone production, rather than to provide a detailed check of emission inventories. Use of these simplified inputs yielded good measurement–model
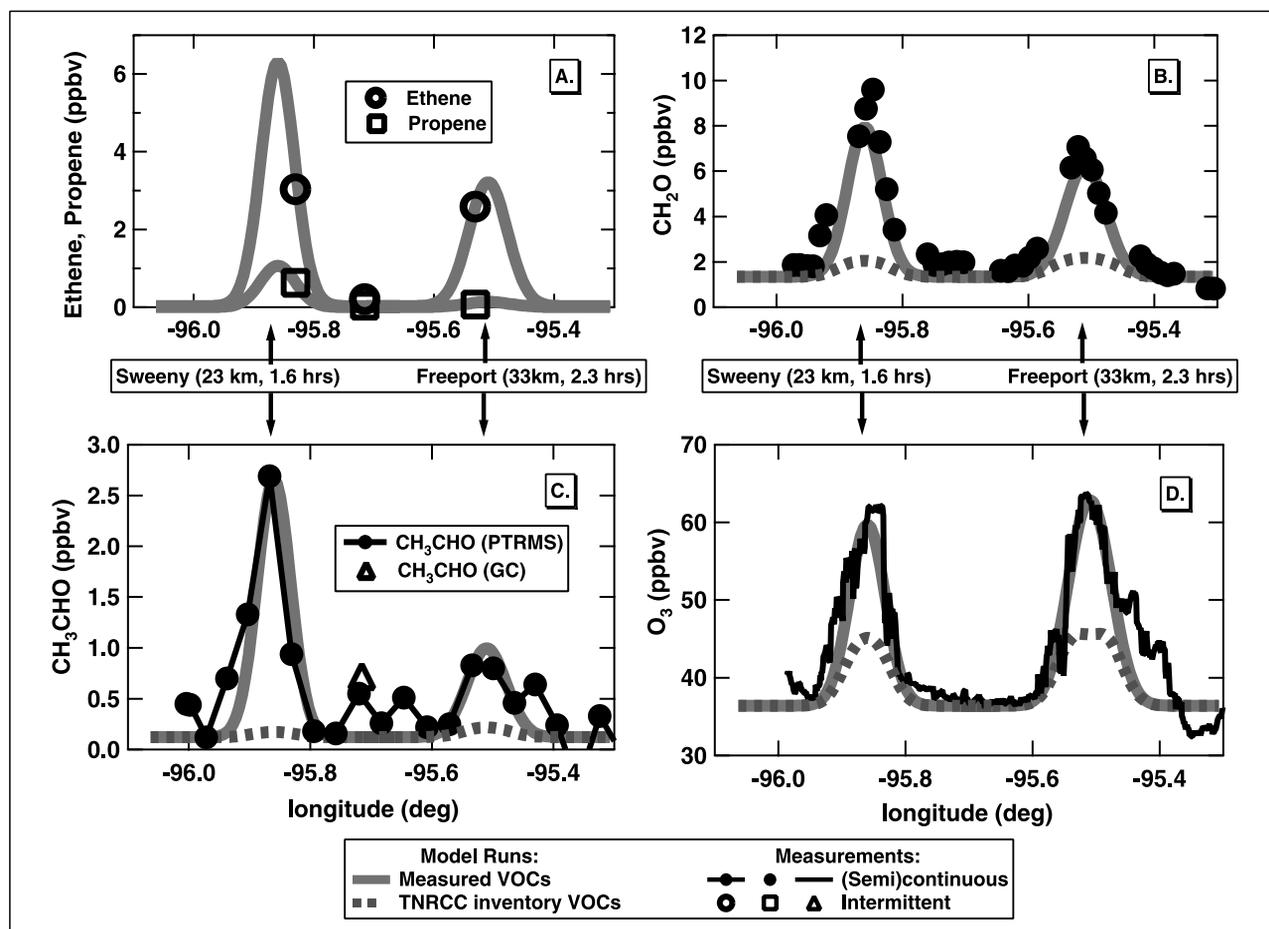


**Figure 9.** Measurements and corresponding model results for the 29.3° latitude intercept of the Sweeny and Freeport plumes (2.3 hours downwind of Freeport). Shown are ethene and propene (a), CH₂O (b), acetaldehyde (c), and ozone (d) mixing ratios.
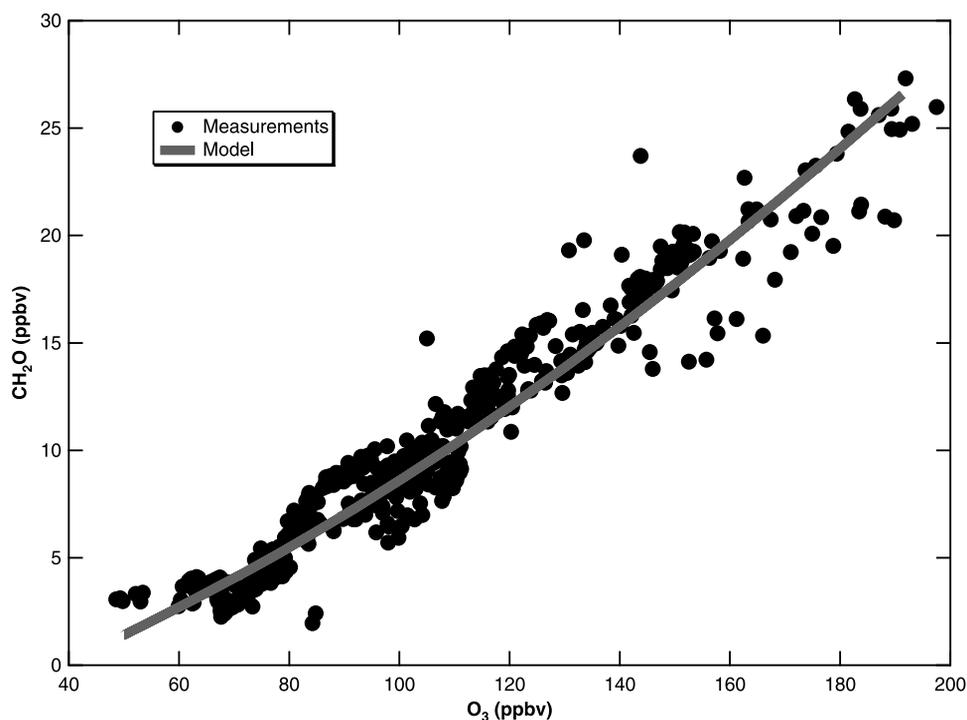
**Figure 10.** Measured and modeled $CH_2O$ versus ozone for the 1 September intercept of the Ship Channel dominated plume at $-94.6°$ longitude (4 hours downwind of the Ship Channel).

agreement. Figure 10 depicts results for the 94.6° longitude, 4 hours (50 km) downwind intercept (see Table 2), featuring $CH_2O$ concentrations of 3–27 ppbv, and ozone of 50–200 ppbv; $NO_y$ partitioning (not shown) was also accurately replicated.

## 4.  Summary and Conclusions

[34]  TDLAS $CH_2O$ measurements made during TexAQS 2000 yielded several important insights concerning terminal alkene emissions and photochemistry in Houston. These insights were amplified by the high resolution (1 and 10 s) of the measurements, the first time such resolution has been achieved in the field for $CH_2O$.

[35]  Results reported here indicate that measured petrochemical ethene and propene levels were alone sufficient to explain the highest $CH_2O$ and ozone levels measured in several Houston area plumes, including levels over 30 and 200 ppbv, respectively. No evidence was found for strong direct emissions of $CH_2O$ relative to secondary production. While enhanced concentrations of VOCs other than ethene and propene were measured in Houston, their lower reactivities rendered them far less important to rapid ozone formation. In addition, the successful modeling indicates that OH-initiated terminal alkene oxidation is the dominant source of ozone in Houston, and that other oxidants such as Cl radicals (and thereby alkanes) play a comparatively modest role, consistent with studies by P. L. Tanaka et al. (Direct evidence for chlorine-enhanced urban ozone formation in Houston, TX, submitted to *Environmental Science and Technology*, 2002).

[36]  Modeling of the isolated petrochemical facilities using measurement derived VOC emissions confirms that ethene and propene emissions are far larger than inventories indicate. Given that these facilities are expected to be representative of the Houston petrochemical industry, and that similar disparities exist between inventory and measured VOC/$NO_x$ ratios for the Ship Channel, it is highly likely that VOC emission inventory deficits are widespread in Houston. Accurate emission inventories will be critical to the success of three-dimensional modeling efforts and the development of efficient ozone control strategies for Houston.

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