Atmospheric Formaldehyde Monitoring in the Greater Houston Area in 2002

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A laser spectrometer based on difference frequency generation (DFG) was deployed for real-time long-term monitoring of HCHO concentrations at an environmental monitoring site located at Deer Park, Texas, in the Greater Houston area. Three HCHO concentration measurements were made during the periods of July 20–31 (period I), August 2–14 (period II), and August 24–September 25 (period III), 2002. In periods I and II, differences in HCHO concentrations are apparent between day and night measurements, with elevated concentrations during daylight hours. Most of the HCHO peak values are less than 20 ppbV except for two intense peaks on August 02 (~25 ppbV) and August 04 (~30 ppbV). The formaldehyde concentration levels in ambient air at the measurement site are produced mainly by the photochemical oxidation of volatile organic compounds (VOCs) caused by intense sunlight during periods I and II. This observation was made based on a comparison with the ozone concentration, solar radiation, temperature, relative humidity, and wind speed data obtained from the Texas Commission on Environmental Quality (TCEQ). During period III, data collected by a time-integrating wet-chemical technique are compared to the data collected by the spectroscopic instrument.

Index Headings: Formaldehyde detection; Laser absorption spectroscopy; Laser diodes; Difference frequency generation.

INTRODUCTION

Formaldehyde (HCHO) is an important and highly reactive component present in all regions of the atmosphere arising from the oxidation of biogenic and anthropogenic hydrocarbons. HCHO concentration levels range typically from ~2 to 45 ppbV (parts per billion in a given volume)[1–3] in urban settings that are mainly governed by primary emissions and secondary formation. Primary HCHO is emitted from motor vehicles and fugitive industrial emissions,[4,5] while secondary HCHO is produced by the photochemical oxidation of volatile organic compounds (VOCs) as the result of intense sunlight, especially during summer months.[6] In addition, it has been postulated that HCHO can be produced by reactions involving anthropogenic and naturally occurring alkenes.[7–9] In urban environments that commonly exceed ozone standards, such as the Greater Houston area, the monitoring of the HCHO concentrations over extended periods of time and the daily concentration cycle of HCHO is an important validation of air quality models that simulate the complex chemistry of ozone formation.

In this work, formaldehyde concentrations have been quantified using a wet chemical and a spectroscopic laser based absorption measurement technique. In the case of the wet chemical method, air samples containing formaldehyde are collected for a period of 4 h using a liquid impinger, followed by derivitization with pentafluorobenzylhydroxyamine (PFBHA) and subsequently analyzed by gas chromatography/mass spectrometry with a detection limit of 0.3 ppbV.[10] A second detection method permits the real-time long-term monitoring of HCHO based on infrared laser absorption spectroscopy. Precision laboratory and airborne measurements of atmospheric formaldehyde concentrations using tunable cryogenically cooled lead salt diode-laser absorption spectroscopy (TDLAS) at ~2831 cm^{-1} was reported by Fried et al.[11–14] In this study we employed a laser spectrometer based on difference frequency generation (DFG),[3,14–16] which was first deployed for real-time monitoring of HCHO in the 2000 summer field campaign in Houston, Texas.

For the 2002 summer field campaign described in this paper, various critical DFG spectrometer improvements as well as changes in the measurement protocol were implemented. A laboratory evaluation of the HCHO sensor showed that noise fluctuations for the DFG spectrometer could be limited to levels of ±0.5 ppbV. The DFG based gas sensor was successfully deployed at an environmental monitoring site located in the city of Deer Park, Texas, east of Houston in the summer of 2002. Three successful real-time HCHO concentration measurement periods were carried out from July 20–July 31 (period I), August 2–August 14 (period II), and August 24–September 25 (period III). During period III, time-averaged wet chemical based HCHO concentration measurements were performed to provide an intercomparison and validation of real-time DFG based HCHO monitoring and quantification.

DESCRIPTION OF LASER-BASED FORMALDEHYDE SENSOR

The DFG gas sensor configuration used in this work is shown in Fig. 1. The two primary mixing single-frequency diode lasers are a fiber-pigtailed 2-mW, 1561-nm distributed feedback (DFB) telecommunications diode laser and a fiber-coupled 12-mW, 1083-nm distributed Bragg reflector (DBR) diode laser. To saturate the gain of a 0.3 W Er/Yb fiber amplifier and a 0.9 W Yb amplifier, an Er-doped and Yb fiber preamplifier are used to increase the 1561-nm and 1083-nm power levels of both seed diode lasers, respectively.[3] The two amplified pump channels are then combined by a 2-port beam coupler into a single optical fiber. The fiber-delivered superimposed pump beams are imaged by a microscope into a
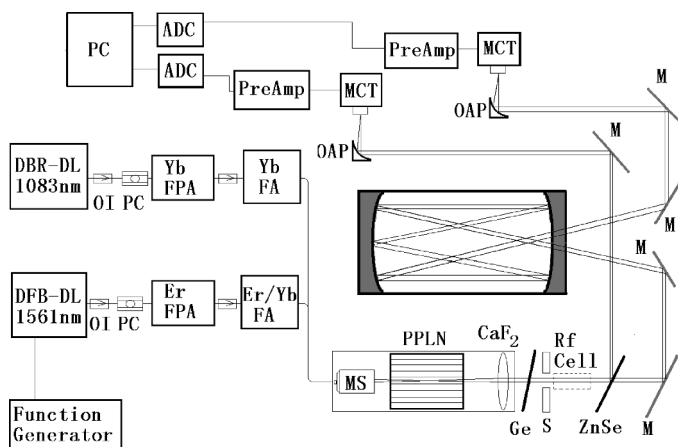
FIG. 1. Schematic of the DFG gas sensor: (OI) optical isolator; (DL) diode laser; (PC) polarization controller; (PPLN) periodically poled lithium niobate crystal; (MS) microscope; (M) plane mirror; (OAP) off-axis parabolic mirror; (MCT) Peltier-cooled HgCdTe detector; (WDM) wavelength-division multiplexer; and (ADC) analog-to-digital converter.)

FIG. 2. DFG based sensor calibration with a 5.00 ppbV HCHO permeation standard.

50-mm-long periodically poled lithium niobate (PPLN) crystal, which is temperature controlled by a thermo-electric controller. A 4-cm-focal-length CaF$_2$ lens re-collimates the DFG radiation at 2832 cm^{-1} exiting the PPLN crystal. A Ge filter rejects any unconverted near-infrared (NIR) pump radiation after exiting the PPLN crystal. The mid-infrared (MIR) power available for long-term HCHO monitoring is ~200 μW at the output of the DFG mixing stage.

A formaldehyde reference cell is inserted periodically into the collimated IR beam after the collecting lens using an electromechanical actuator. The reference calibration data is used in the fitting process of the acquired spectral data. Subsequently, the DFG beam is divided into a signal and reference beam with a ZnSe wedge. The signal beam enters an astigmatically compensated Herriott multipass cell with a 100-m path length and upon exiting is directed to a mercury cadmium telluride (MCT) detector. The reference beam is incident onto a second MCT. Both thermoelectric-cooled photoconductive MCT detectors are connected to custom-built preamplifiers with provision for stable long-term battery power in order to minimize electrical noise. This dual-beam technique allows optical fringes to be minimized by ratioing the signals of the two detection channels. Spectral lines are acquired by direct-current modulation of the 1561-nm diode laser with a triangular waveform at 119 Hz. The molecular HCHO transitions used in this sensor occur at 2831.6417 cm^{-1} (main peak) and 2831.6987 cm^{-1}, respectively, which were selected because they are free from potentially interfering molecular species such as H$_2$O, CO$_2$, and CH$_4$. The smaller HCHO peak at 2831.6987 cm^{-1} provides additional information for precise wavelength calibration when performing concentration measurements. The preamplified signals from the two channels are acquired simultaneously with two analog-to-digital converter (ADC) data acquisition cards and the digitized signals are recorded by a notebook computer, which can be accessed via a dedicated phone line.

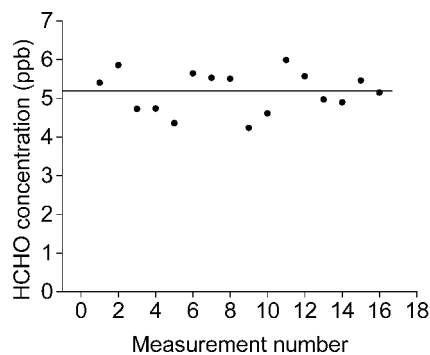The sample pressure for formaldehyde concentration measurements was set optimally at 40 torr by means of a gas-flow controller as a compromise between sensitivity and selectivity. The spectral line shape can be described as a convolution of Lorentzian and Doppler line shapes known as a Voigt profile. This line profile was fitted by employing the Levenberg–Marquardt nonlinear least-squares fitting algorithm available in the Labview VI code. The fitting algorithm first calculates the natural logarithm of the ratio of the detected intensity in the data channel versus intensity in the reference channel I_v/I_{vo}. This ratio gives the logarithm of the signal transmittance. Subsequently, the algorithm performs an additional Levenberg–Marquardt nonlinear least-squares fit to a cubic baseline polynomial. After this cubic baseline is removed, the Voigt line profile is fitted to determine the HCHO concentration. The two adjacent formaldehyde ro-vibrational transitions and the formaldehyde concentration are displayed simultaneously on the Labview VI code screen.[3,14,17] Such a DFG based sensor is capable of sensitive, selective, fast response and remote detection of HCHO at the ppb level, requiring no consumables, such as liquid nitrogen. For reference it should be noted that for 1 ppbV of formaldehyde (40 torr and 296 K) the peak absorbance (base e)[18] scaled to path length at 2831.6417 cm^{-1} is 3×10^{-9} cm^{-1}.

HCHO MONITORING PROCEDURES AT FIELD SITE

In July, 2002, the DFG gas sensor was moved into a trailer located at the environmental monitoring site (C35/139) in Deer Park, Houston, Texas, operated by the Texas Commission on Environmental Quality (TCEQ). Ambient air was sampled 4 m above the ground via a 5-m-long teflon tube and pumped into the multipass gas cell using an oil-free diaphragm pump. The teflon tube from the trailer inlet system was wrapped with heating tape in order to minimize removal of HCHO by possible water condensation inside the sample intake. The airflow intake provides a complete gas exchange in the 3.30 L multipass gas cell every 10 s. The sensor is configured to automatically acquire an HCHO concentration value every 100 s as an average of 2000 measured spectra. The DFG gas sensor is kept at a temperature of ~70 °F in the air-conditioned trailer, while the outside temperature varied between 68 and 95 °F during the field campaign. A 450 W UPS power supply was installed between the trailer power supply and the DFG based gas sensor to avoid any electrical disruptions caused by the occurrence of se-
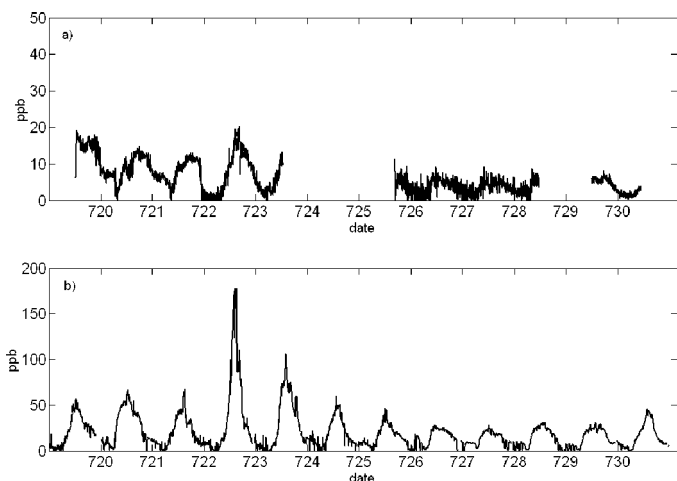
FIG. 3. (**a**) Formaldehyde and (**b**) ozone concentrations at Deer Park, TX, from July 20th to July 31st, 2002.

vere thunderstorms. During the real-time measurement campaign of HCHO concentrations we encountered unexpected meteorological events, such as intense rainfall, thunderstorms, and large temperature variations. We acquired HCHO data during three separate measurement periods. Prior to and upon completion of the field campaign the sensor was calibrated with a 5.00 ppb formaldehyde standard permeation tube,[19] which indicated an average value of 5.16 ppbV with a variance of 0.28 ppbV, as shown in Fig. 2.

RESULTS AND DISCUSSION

Time-resolved HCHO (top) and ozone (bottom) concentrations recorded at Deer Park, Texas, from July 20th

to July 31st, 2002 (period I), are shown in Fig. 3 where the ozone data were provided by the TCEQ.[20,21] The HCHO concentrations vary between day and night (peaks occur during day time). The peak values do not exceed 20 ppbV. The HCHO and O_3 concentrations are well correlated, with the HCHO concentration generally beginning to rise at the same time that the ozone concentration rises in late morning, but with its maximum value occurring after that of ozone. From the correlations of ozone and HCHO with ambient air temperature (Fig. 4c) and solar radiation TCEQ data (Fig. 4e), it can be inferred that the formaldehyde concentration levels in ambient air observed at the Deer Park, Texas, site are produced mainly by the photochemical oxidation of volatile organic compounds (VOCs) caused by intense sunlight in the day. This is consistent with the elevated concentrations of ground-level ozone, which indicates that photochemical smog formation is occurring during the sampling period.

Figure 5a shows the formaldehyde concentration levels from noon on August 2nd to 12:15 pm August 14th, 2002 (period II). In order correlate the source of HCHO with the urban smog process, we compare formaldehyde (top) and ozone (bottom) concentrations, as shown in Fig. 5. During this period, the correlation between ozone and formaldehyde observed during Period I is not as consistent, although correlation coefficient parameters are almost the same. When ozone and HCHO are both present in elevated concentrations, there is a closer match of the time of the peaks. In the later part of Period II, ozone peaks remain relatively high while the formaldehyde concentrations are low. Figure 5 also shows two intense peaks (>25 ppb) on August 2nd and 4th. In particular, the August 4th HCHO peak occurs rather early in the
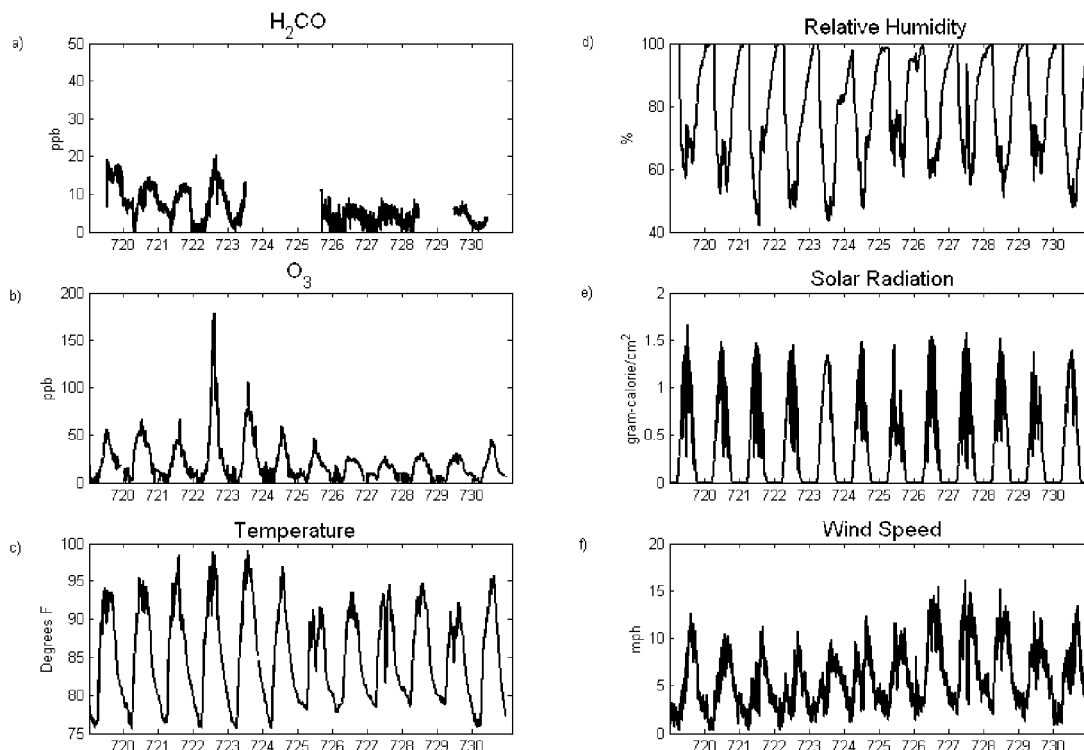

FIG. 4. Interrelationship of H_2CO data taken from July 20th to July 31st, 2002, at Deer Park, TX, with meteorological data supplied by Texas Commission on Environmental Quality (Austin, TX); (**a**) HCHO concentration, (**b**) O_3 concentration, (**c**) temperature of the corresponding period, (**d**) relative humidity, (**e**) solar radiation, and (**f**) wind speed.
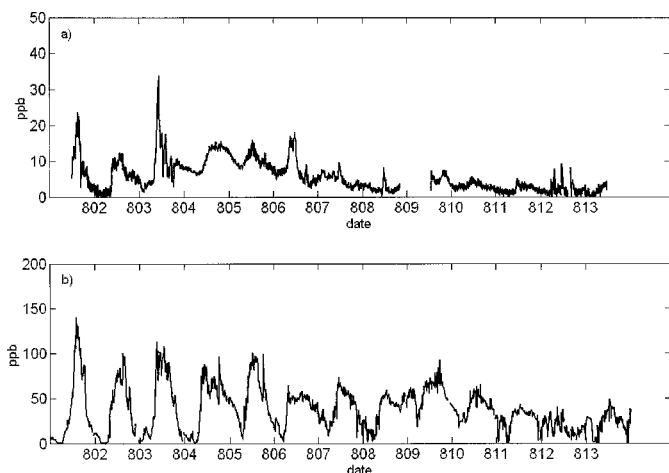
FIG. 5. (a) Formaldehyde and (b) ozone concentrations at Deer Park, TX, from August 2nd to August 14th, 2002.
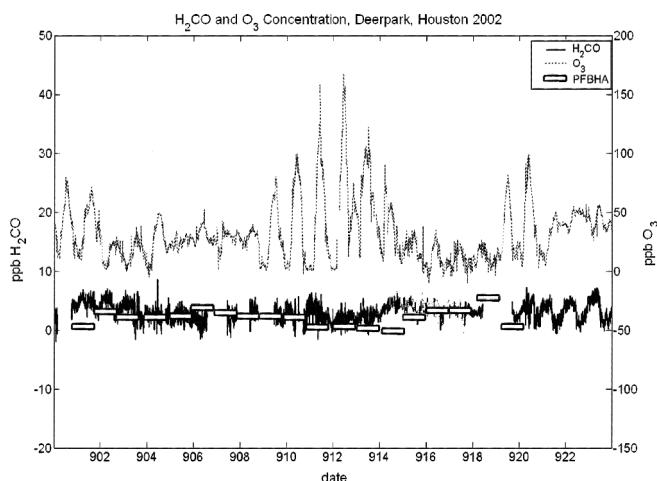

FIG. 6. Formaldehyde (dotted line) and ozone (thin line) concentrations (offset for clarity) at Deer Park, TX, from August 24th to September 25th, 2002. The horizontal bars represent the time-integrated average HCHO concentrations measured using the wet chemical quantification based on PFBHA analysis.

day, suggesting other formaldehyde formation processes in addition to the photochemical process during these two days. While the ozone concentrations during these two events (on August 2nd and 4th) are elevated compared to other days in period II, the ozone concentrations are not nearly as high as peak concentrations observed during events in July (where ozone concentrations were over 150 ppbV). These data suggest the complexity of photochemical smog formation. Most of the formaldehyde is formed by the photochemical oxidation of VOCs caused by intense sunlight. Ozone can be formed from the photochemical reactions of any reactive volatile organic compound, including olefins such as ethene or propene, as well as aromatic compounds that include toluene or the xylene compounds. On the other hand, HCHO formation in Houston has been shown to be directly related to oxidation of olefins, including propene and ethane.[22,23] To investigate the possibility of different precursor volatile organic compounds leading to ozone and HCHO formation, data collected periodically by the TCEQ on average VOC concentrations are compared between different periods. For example, periods of high olefin precursor concentrations correspond to periods of high levels of HCHO and ozone since both species are formed from the reactions of olefins. Aromatic VOC precursors form ozone but not HCHO and periods of high ozone and low HCHO should correspond to the presence of aromatic VOCs.

The formaldehyde (dotted line) and ozone (thin line) concentration data obtained in period III from August 24 to September 25 are shown in Fig. 6. The formaldehyde concentration levels are less than 7 ppbV during this period. Wet chemical data based on PFBHA analysis collected from August 31 to September 25, 2003, confirms this result. The difference between day- and night-time formaldehyde levels are noticeably reduced as compared to Periods I and II levels, and there is no apparent correlation between ozone and formaldehyde in this period. There were two time periods (early and late) in Period III where ozone levels were at a high level without a similar high HCHO concentration. While formaldehyde is known to be generated as a product of the photo-oxidation of almost all volatile organic compounds (VOCs),[24] recent studies in Houston suggest that HCHO

formation is dominated by reaction of olefins such as ethene and propene.[22,23] An explanation of the elevated ozone levels is that as a result of a change in the precursor VOCs that are present in the atmosphere in Period III, ozone formation is favored rather than HCHO formation.

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