

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

Airborne formaldehyde measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results

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Received: 9 June 2011 – Accepted: 30 June 2011 – Published: 21 July 2011

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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We present quantitative, fast time response measurements of formaldehyde (HCHO) onboard an aircraft using a Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS) instrument. The HCHO measurement by PTR-MS is strongly humidity dependent and therefore airborne measurements are difficult and have not been reported. The PTR-MS instrument was run in the normal operating mode, where about 15 volatile organic compounds (VOCs) are measured together with HCHO onboard the NOAA WP-3 aircraft during the CalNex 2010 campaign in California. We compare the humidity dependence determined in the laboratory with in-flight calibrations of HCHO and calculate the HCHO mixing ratio during all flights using the results from both. The detection limit for HCHO was between 100 pptv in the dry free troposphere and 300 pptv in the humid marine boundary layer for a one second acquisition time every 17 s. The PTR-MS measurements are compared with HCHO measurements using a DOAS instrument and a Hantzsch monitor at a ground site in Pasadena. The PTR-MS agreed with both instruments within the stated uncertainties. We also compare HCHO enhancement ratios in the Los Angeles basin and in the free troposphere with literature values and find good agreement. The usefulness of the PTR-MS HCHO measurements in atmospheric observations is demonstrated by following an isolated anthropogenic plume. The photochemical production of HCHO can be observed simultaneously with production of acetaldehyde and the photochemical degradation of aromatic compounds using the PTR-MS.

1 Introduction

Formaldehyde (HCHO) is one of the most abundant volatile organic compounds (VOCs) in the atmosphere. The mixing ratios range from about 100 pptv in remote areas (Sumner et al., 2002; Fried et al., 2008) to several tens of ppbv in polluted

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areas (Kormann et al., 2003; Dasgupta et al., 2005). The primary emission sources of HCHO include biomass burning (Yokelson et al., 1996; Holzinger et al., 1999) and anthropogenic sources such as vehicle exhaust (Dasgupta et al., 2005; Garcia et al., 2006; Zavala et al., 2009), but overall the primary emissions are small compared to the secondary production (Li et al., 1994; Garcia et al., 2006; Ban-Weiss et al., 2008). HCHO is produced in the atmosphere from many different compounds (Lee et al., 1998), where important precursors are alkenes such as ethylene (Gilman et al., 2009; Washenfelder et al., 2010) and isoprene, and alkanes such as methane (Finlayson-Pitts and Pitts, 1986). Isoprene, which has the largest global emissions of all VOCs (Guenther et al., 2000), produces HCHO as a first-generation product in the presence of NO_x and satellite measurements of HCHO can be used to estimate the isoprene emissions on large spatial scales (Palmer et al., 2006; Millet et al., 2008).

HCHO has a short lifetime of only a few hours during the day due to reactions with OH and photolysis, which makes it an important compound in the formation of ozone and the cycling of HO_x radicals. In an urban area the photolysis of HCHO is one of the most important radical sources sustaining photochemical ozone formation (Volkmann et al., 2010), which also makes HCHO one of the key indicators of atmospheric photochemical activity.

Various analytical techniques are available for ambient HCHO measurements. Commonly used instruments are tunable diode laser absorption spectrometer (TDLAS) (Fried et al., 2002; Wert et al., 2003), commercially available wet chemical sensors based on Hantzsch fluorometry (Kelly and Fortune, 1994; Junkermann and Burger, 2006), Fourier transform infrared spectroscopy (FTIR) (Yokelson et al., 1996), cartridges for 2,4-dinitrophenylhydrazine (DNPH) derivatization followed by off-line high pressure liquid chromatography (HPLC) analysis (Grosjean and Fung, 1982), and pulsed quantum cascade laser spectrometer (QCL) (Herndon et al., 2007). Other instruments that are commonly used are based on long-path techniques such as the differential optical absorption spectrometer (DOAS) (Lawson et al., 1990) and the multi-axes differential optical absorption spectroscopy (MAX-DOAS) (Heckel et al., 2005). A

table with instrumental details on most of the techniques listed above can be found in Wisthaler et al. (2008).

5 In a recent formal inter-comparison exercise at the SAPHIR chamber between five different HCHO analyzers using four different techniques it was found that significant analytical problems exist for most of the techniques (Wisthaler et al., 2008). Even though this inter-comparison varied humidity and ozone levels, it was nonetheless a laboratory simulation, which is one of the least challenging environments for the analyzers. Field measurements, especially aircraft measurements, present a much more challenging environment, complicating the HCHO measurements (Wert et al., 2003; 10 Herndon et al., 2007).

Recently Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS) has been used to measure HCHO in the atmosphere and laboratory settings despite various analytical challenges (Holzinger et al., 1999; Karl et al., 2003; Steinbacher et al., 2004; Inomata et al., 2008; Wisthaler et al., 2008; Vlasenko et al., 2010). Because the reaction of 15 H_3O^+ with HCHO is only slightly exothermic and the back reaction becomes important at typical PTR-MS instrument settings, the HCHO detection by PTR-MS is strongly humidity dependent and overall less sensitive than for other compounds (Hansel et al., 1997). To improve on the humidity dependence and the lowered sensitivity, in some measurements instrument settings were changed (Wisthaler et al., 2008) or the sample 20 stream was dried (Jobson and McCoskey, 2010), but might influence the ability of PTR-MS to measure multiple compounds important in atmospheric ambient measurements at the same time.

In this paper we will show that PTR-MS is capable of reliably measuring HCHO on board an aircraft together with all other VOCs typically measured by PTR-MS. The measurements were done on board the NOAA WP-3 aircraft during the CalNex campaign in California 2010 (California at the Nexus of Air Quality and Climate). The PTR-MS was run at the standard instrument settings and simultaneous measurements were made of oxygenated VOCs such as methanol and acetone, biogenic compounds 25 such as isoprene and monoterpenes and aromatics such as benzene and toluene. As

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a validation of the measurements we compare to HCHO measurements on a ground site in Pasadena during overflights. Furthermore, a plume study will be used to show the atmospheric HCHO production.

2 Experimental

2.1 PTR-MS instrument and HCHO detection

The PTR-MS instrument used in this study was described in detail by de Gouw and Warneke (2007) and was used in similar configurations in multiple aircraft and ground based experiments. Briefly, H_3O^+ is produced in a hollow cathode ion source and allowed to react with VOCs that have a higher proton affinity (PA) than H_2O in a reaction chamber. The resulting VOCH^+ ions are detected together with the primary ions using a quadrupole mass spectrometer. The instrument was operated at a pressure of 2.4 mbar and an electric field of 70 V cm^{-1} in the reaction chamber. During the flights 14 masses corresponding to different VOCs, including mass 31 for HHCHO^+ , were measured for one second each together with the primary ions resulting in a 16-s duty cycle. Instrument backgrounds were determined every 13 minutes for 1 min using a catalytic converter, which is described in more detail below.

HCHO has only a slightly higher PA than water ($165.2 \text{ kcal mol}^{-1}$ for H_2O and $170.4 \text{ kcal mol}^{-1}$ for HCHO), which is so small that the back reaction becomes significant:



The rate coefficients are $k_{\text{R1}} = 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ and $k_{\text{R1a}} = 3 - 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ molecule}^{-1}$ (Hansel et al., 1997; Vlasenko et al., 2010) and $[\text{HCHO}]$,

$[H_3O^+]$ and $[H_2O]$ are concentrations of HCHO, hydronium ions and water in the drift tube. The kinetics of the HCHO detection has been discussed in detail by Vlasenko et al. (2010) and we only summarize here. The humidity dependent concentration of $H \cdot HCHO^+$ ion concentration in the drift tube can be described as follows:

$$[H \cdot HCHO^+] = [H_3O^+] \frac{k_{R1}[HCHO](1 - e^{-k_{R1a}[H_2O]t})}{k_{R1a}[H_2O]}. \quad (2)$$

In Eq. (2) the $H \cdot HCHO^+$ concentration is dependent on the reaction time t , and at low water concentrations Reactions (R1) and (R1a) are not in equilibrium at standard PTR-MS conditions. This makes it clear that the detection of HCHO with PTR-MS is not only strongly humidity dependent, but also clearly less efficient than for other VOCs, where the back reaction rate coefficient is very small.

Besides the humidity dependence, the lowered sensitivity has made aircraft measurements of HCHO with PTR-MS very challenging. Our PTR-MS system has undergone constant improvements over the past years resulting in substantial increases in sensitivity, which are demonstrated in Fig. 1. The sensitivities and detection limits of methanol, benzene and acetone during five different aircraft missions in the past eight years have steadily increased to just over 1000 Hz ppbv⁻¹ for acetone, which is a compound with one of the highest sensitivities. The improvements include (1) changing from standard PTR-MS to high sensitivity PTR-MS, which adds a pumping station at the lens system of the quadrupole, (2) replacing the original ion source, (3) modifying the vacuum chamber to improve pumping of the quadrupole chamber and (4) the use of a different multiplier (ETP SGE 14140). Even at a reduced sensitivity, as expected for HCHO, the PTR-MS in its current configuration should be able to deliver measurements at adequate quality and time response for aircraft measurements, especially in a polluted location such as the Los Angeles basin.

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2.2 Aircraft inlet and calibration set-up

The aircraft inlet used for the PTR-MS during CalNex is shown in Fig. 2. The inlet is based on the one described previously by de Gouw and Warneke (2007) but was subsequently improved. The inlet was about a total 1.5 m long from the tip of the winglet to the drift tube, consisted partly out of PFA Teflon (1/8" O.D.) and PEEK (1/16" O.D.) tubing, and was temperature and pressure controlled at 75 °C and 120 mbar. Instrument background measurements are done using a catalyst made out of platinum wool at 250 °C, which was housed in the winglet sticking out of the aircraft, so that zero air can be generated as far forward in the sample stream as possible. Due to impurities in the catalyst that were picked up in the hangar during installations, nitric oxide (NO) was produced in the catalyst at the usual 350 °C setting. This artifact was avoided by setting the catalyst to 250 °C during the flights, which did not seem to have influenced its performance. In laboratory tests it was determined that the catalyst completely converts HCHO to CO₂ without changing the humidity making it an ideal background measurement for HCHO PTR-MS measurements.

Aldehydes including HCHO are not very stable in gas cylinders and therefore a permeation source was used to calibrate the PTR-MS during the flight. The permeation tube was housed in a Teflon cylinder at constant 20 sccm zero air flow, 50 °C and 2 bar, which keeps the permeation rate constant throughout the flight (Fried et al., 2003; Neuman et al., 2003). The permeation oven set-up was mounted in the aircraft rack about 3 h before the flights and kept under the constant conditions to ensure stable output at the beginning of the flight. In between flights, the set-up was kept under the same conditions in the hangar, where it was connected to the Mobile Organic Carbon Calibration System (MOCCS) that was recently developed (Veres et al., 2010). MOCCS consists of a catalytic converter (identical to the one used for PTR-MS background measurements) that converts the VOCs in the output of the permeation oven quantitatively to CO₂, which is then detected by a LiCor CO₂ analyzer. The LiCor was calibrated with 2, 5, 20, and 50 ppmv gas standards to be in the same range as the

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permeation source output converted into CO₂. The MOCCS can quantify the output of a permeation tube instantly forgoing the need to have the permeation tubes under constant conditions for very long periods of time usually months, so that the output can be determined gravimetrically. The same inlet and calibration set-up were used in the laboratory experiments conducted before CalNex as during the aircraft campaign.

2.3 CalNex aircraft campaign

During the CalNex campaign the NOAA WP-3 aircraft was stationed in Ontario, California during May and June 2010 and performed 20 research flights mainly over the Los Angeles (LA) basin and the Central Valley in California. The main goals of CalNex were emission quantification of greenhouse gases, ozone and aerosol precursors, the quantification of chemical transformations, and the transport of pollution. The NOAA WP-3 aircraft was equipped with a large suite of gas phase and aerosol measurements, but for this paper we only use the PTR-MS and CO data.

The Caltech/Pasadena ground site, 15 km northeast of downtown Los Angeles was located on a parking lot at the Caltech campus in an urban area 1.2 km from interstate 210. Multiple over-flights were performed during the campaign. The HCHO measurements made by PTR-MS onboard the aircraft will be compared to a DOAS instrument and a Hantzsch monitor at the ground site.

2.4 Other instruments

UCLA's long-path (LP) DOAS instrument (Stutz and Platt, 1997; Platt and Stutz, 2008) was located at the Pasadena ground site on the Caltech campus on the roof of the Millikan Library at 35 m above ground level (agl) (coordinates 34.1405–118.122). Four retro-reflectors were located northeast of the main instrument in mountains behind Altadena at 78 m a.g.l. (lowest; coordinates 34.17615, –118.092417), at 121 m a.g.l. (middle; coordinates 34.1789, –118.091883), at 255 m a.g.l. (upper; coordinates 34.190217, –118.08695) and at 556 m a.g.l. (highest; coordinates 34.193567,

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–118.09215). The average distance between the LP-DOAS telescope and the reflectors was about 6 km.

Spectral retrievals of HCHO mixing ratios were performed in the wavelength range between 324–346 nm using a combination of a linear and non-linear least squares fit, as described in Stutz and Platt (1996) and Alicke et al. (2002). Spectral absorption structures of O₃, NO₂, HONO, O₄, and HCHO were incorporated in the fitting procedure. Errors of HCHO mixing ratios were calculated as 1 σ statistical uncertainties by the analysis procedure for each individual spectrum and trace gas (Stutz and Platt, 1996). The campaign averaged statistical HCHO error during CalNex was ~150 ppt. The systematic errors of the reported trace gas mixing ratios are dominated by the uncertainties of the HCHO absorption cross sections of $\pm 5\%$ (Meller and Moortgat, 2000). The systematic error of the DOAS spectrometer was $<3\%$ (Platt and Stutz 2008).

Formaldehyde was measured on the Pasadena ground site in-situ using the fluorometric Hantzsch reaction (FHR, model AL4021, www.aerolaser.com). FHR based HCHO measurement instrumentation have been extensively field-used and validated (Gilpin et al., 1997; Cardenas et al., 2000; Hak et al., 2005; Apel et al., 2008; Wisthaler et al., 2008). The University of Houston has employed this technique both at ground sites (Rappengluck et al., 2010) and in airborne science missions (Boeke et al., 2011). The inlet was a funnel located at 4 m from the ground attached to 5.5 m of PFA Teflon (0.25 in OD) tubing. The instrument was calibrated weekly using a working gas standard (Air Liquide America Scott Specialty Gases LLC, Plumstead, PA; 5 ppm HCHO in N₂) and auto-zeroed every 90 min for 10 min. During the study the gas standard cylinder was hooked up to the MOCCS (Mobile Organic Carbon Calibration System; (Veres et al., 2010) for a duration of 18.5 hours, and a HCHO concentration of 6.86 ± 0.15 ppm was determined. In addition, the AL4021 was calibrated on-site using a HCHO permeation tube. The limit of detection for the HCHO instrument was 60 pptv (three times signal-to-noise ratio; 1 min averaging); the estimated uncertainty was $\pm 9.6\%$.

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Carbon monoxide (CO) was measured from the aircraft with a vacuum ultraviolet fluorescence instrument (Holloway et al., 2000). The overall uncertainty of the measurements is estimated to be about 5 % with a 2σ detection limit of about 1 ppbv.

Acetaldehyde was measured on the ground site using an in-situ gas chromatograph equipped with a mass spectrometer (GC-MS) and a Proton-transfer Ion Trap Mass Spectrometer (PIT-MS), which is an instrument similar to a PTR-MS. Instrumental details on the two instruments can be found elsewhere (Warneke et al., 2005; Gilman et al., 2010).

3 Instrument characterization

3.1 Interference test with GC-PTR-MS

Before the PTR-MS can be calibrated for HCHO on mass 31, it needs to be determined, if mass 31 is free of interferences. Fragmentation from larger compounds are the most probably source of interferences on mass 31. Inomata et al. (2008) have found small interferences from methyl hydroperoxide (CH_3OOH) and fragments of methanol and ethanol. In ambient air, the concentration of methyl hydroperoxide is expected to be very small compared to HCHO, so any associated interferences will be negligible.

Before the CalNex2010 campaign we tested the PTR-MS for interferences in the laboratory using GC-PTR-MS (Warneke et al., 2003). The basic principle is that a gas chromatographic (GC) column is used to pre-separate VOCs by their retention time before they are detected with PTR-MS. Any interferences on m31 will appear as distinct chromatographic peaks corresponding to the retention time of the parent compound. Various calibration standards containing a large number of VOCs, including methanol and ethanol, as well as ambient air samples with or without a standard addition of HCHO were tested with GC-PTR-MS to look for peaks on mass 31 in the chromatograms. HCHO was detected non-quantitatively with GC-PTR-MS on mass 31, but no other signal was detected on that mass. Formic and acetic acid that are not

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detectable with GC-PTR-MS were tested separately and no interferences were found. Methyl hydroperoxide is expected to be negligible compared to HCHO in ambient air. This shows that the minimum requirements of no substantial interferences for successful HCHO measurements with PTR-MS are most likely fulfilled.

3.2 Laboratory calibration

Laboratory calibrations with HCHO were performed before CalNex using the aircraft inlet and the permeation tube setup at different humidities. In Fig. 3a the PTR-MS signal on mass 31 is plotted versus the mixing ratio of HCHO generated by diluting the permeation tube output in synthetic air humidified to various degrees. Each line represents a separate calibration curve at a different humidity. In the PTR-MS reaction chamber ambient water vapor and water vapor from the ion source add up to determine the H₂O mixing ratio in Eq. (1) (Warneke et al., 2001; Vlasenko et al., 2010), which determines the measured distribution of the H₃O⁺ (mass 19) and H₃O⁺·H₂O (mass 37) ions (Warneke et al., 2001). In Fig. 3a the calibration curves are color coded with the mass 37/mass 19 ratio instead of the water mixing ratio, because this ratio is (1) directly related to Eq. 2, (2) measured by the PTR-MS simultaneously with HCHO on mass 31, and (3) takes the amount of H₃O⁺ primary ions into account. The relationship between the mass 37/mass 19 with the ambient water concentration is shown in Fig. 4. The data shown in Fig. 4 were taken during one research flight during CalNex and include data from the marine boundary layer off shore from the Los Angeles Basin and the free troposphere. This ambient measurement had mass 37/mass 19 ratios between 1–10 %.

In Fig. 3b the sensitivity of the PTR-MS towards HCHO (the slope from the calibration curves in Fig. 3a) is plotted versus the mass 37/mass 19 ratio. The atmospheric range observed during CalNex is indicated in Fig. 3b showing that the sensitivity ranged from 200 Hz ppbv⁻¹ in the free troposphere to around 60 Hz ppbv⁻¹ in the marine boundary layer. This is clearly lower than all other compounds that are usually between 400 Hz ppbv⁻¹ (methanol) and 1000 Hz ppbv⁻¹ (acetone), as shown in Fig. 1.

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During CalNex2010 the primary ion signal of the PTR-MS was around 30×10^6 Hz so that the range of the HCHO sensitivity normalized to the primary ion signal was about 2–7 ncps ppbv⁻¹ (also shown in Fig. 3b) and methanol and acetone were around 13.3 ncps ppbv⁻¹ and 33.3 ncps ppbv⁻¹, respectively. The sensitivity for HCHO is in the range of other VOCs during previous successful aircraft missions (see Fig. 1). A similar calibration curve and all the kinetic equations to calculate the humidity dependence of HCHO in the PTR-MS reaction chamber can be found in Vlasenko et al. (2010).

The detection limit is not only determined by the sensitivity, but also by the instrument background. Figure 3c shows the background measurements for mass 31 using the catalytic converter in the PTR-MS. The results in Fig. 3c are from laboratory measurements, but the instrument background was comparable during the aircraft mission. The instrument background changes with the mass 37/mass 19 ratio similarly as the sensitivity, but does not drop as fast. NO⁺ on mass 30 is produced in the ion source and the natural isotope from NO⁺ contributes about 50–100 Hz to the signal on mass 31. The NO⁺ signal is strongly dependent on the ion source setting and the humidity. The detection limit is calculated from the noise on the background (square root of the count rate (de Gouw and Warneke 2007)) on mass 31 and the sensitivity for HCHO. Figure 3c shows that the limits of detection at a conservative signal-to-noise of three (S/N = 3) ranged from 300 pptv in dry to 900 pptv in humid atmospheric conditions. This means that in the free troposphere or clean marine boundary layer 1-s measurements are challenging and some averaging should be applied, but in more polluted regions 1-s measurements are possible. Looking at previous campaigns and the earlier sensitivity of the PTR-MS (Fig. 1), the detection limit for HCHO for example during ICARTT2004 was roughly between 600 pptv and 1800 pptv. At such detection limits, aircraft measurements become difficult without long averaging times.

3.3 In-flight calibration

In-flight calibrations were performed during three separate research flights on 20 April, 21 April and 18 June 2010. The constant output of the HCHO permeation source was diluted into the inlet flow that varied from about 100 sccm at the highest flight altitude to about 600 sccm in the boundary layer. The results of the in-flight calibrations from all three flights are shown in Fig. 5a, where the background subtracted signal on mass 31 is plotted versus the inlet flow. Because of the humidity dependence, which is indicated with the color code in Fig. 5a, the observed signal is not linear with the inlet flow. The in-flight humidity dependence is compared to the one determined in the laboratory in Fig. 5b, where the calibrations factors are plotted versus the mass 37/mass 19 ratio. In-flight calibrations are less accurate than laboratory measurements due to the short amount of time that can be afforded on calibrations during the flight and due to the high concentrations of the calibration during the high altitude flight legs. Nevertheless the pre- and in-flight calibrations agreed to within 30 %. The calibrations performed on the ground during the campaign agreed with the ones from before and after the campaign performed in the laboratory to within 10 % and therefore the combined estimated uncertainty for the calibration is 30 %.

The determination of the HCHO calibration factor for all flights during CalNex2010 was done using the fit shown in Fig. 5b with the solid red line. Vlasenko et al. (2010) already noted that Eq. (2) does not describe the calibration data perfectly, especially at high humidity. One explanation is that the ligand switching reactions of the protonated water dimers also produces protonated HCHO after collisional dissociation of the HCHO water cluster (Jobson and McCoskey, 2010). Therefore the best fit to the calibration data in Fig. 5b is a double exponential fit. The expression we used to calculate the HCHO calibration factor for all flights is also given in Fig. 5b.

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4 Airborne results

4.1 Example flight

Here we demonstrate how the HCHO mixing ratio was determined from the raw PTR-MS data during CalNex2010 using an example flight on 19 May 2010. This flight was chosen, because it covered very different humidity conditions and pollution levels with flight tracks in the LA basin, off shore in the marine boundary layer, at high altitudes and over the high desert outside the basin.

The raw data (m31), background (bg 31) and ambient signal (raw data – background signal = ambient signal) are shown in Fig. 6a all normalized to the primary ion signal. From looking at the raw data it is clear that the PTR-MS HCHO detection does not only suffer from low and humidity dependent sensitivity, but also from high and humidity dependent background signals. The background was measured every 12 min and therefore has to be interpolated for subtraction from the ambient data. Due to the fast changes in humidity during flights a linear interpolation of the background data is not suitable. In Fig. 3c we already showed the humidity dependence of the mass 31 background signal. In Fig. 6b the mass 31 background signal is plotted against the mass 37/mass 19 ratio for this flight. The fit of this curve, shown with the yellow line in Fig. 6b, is used to calculate the background on mass 31 for the whole flight. The result is shown in Fig. 6a as a yellow line that connects the individual background measurements. The background is subtracted from the signal and the result is shown in Fig. 6a with the blue line.

The calibration factor is determined in Fig. 6c. The calibration factor is calculated as discussed earlier from the mass 37/mass 19 ratio using the fit and the expression given in Fig. 5b. The ambient mixing ratio is calculated in Fig. 6d by dividing the background-subtracted signal (blue line in Fig. 6a) by the calibration factor (red line in Fig. 6c). The mixing ratio is shown as a three point running average from the 1-s data (every 16 s).

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CO as an anthropogenic tracer is also shown in Fig. 6d. It is very clear that the HCHO mixing ratio is very well correlated with CO throughout the flight even in the free troposphere, where small changes in CO are tracked by HCHO.

4.2 Inter-comparison

5 Various over-flights during day and nighttime were performed for inter-comparison purposes over the ground site located in Pasadena. The aircraft flight altitude for all the over-flights was between 250 m and 500 m above ground level. The time series of the DOAS light paths at four different heights (from 35 m in Pasadena to 78 m, 121 m, 255 m, and 556 m at the reflectors) and the data from the Hantzsch monitor at the surface are shown in Fig. 7a together with the PTR-MS data averaged over a 10 km stretch around the ground site.

A scatter plot of the DOAS data versus the Hantzsch monitor and the PTR-MS over-flights is given in Fig. 7b. This inter-comparison features measurements from an aircraft (PTR-MS), from an instrument that gives a long-path regional average (DOAS) and from the ground (Hantzsch) and therefore local differences in mixing ratios will influence the inter-comparison. There are two other complicating factors: (1) The DOAS switches between the different elevation angles, which results in long time gaps between data points at the same elevation angle. The nearest data point, regardless of elevation angle, was used in the scatter plot in Fig. 7b. (2) During the nighttime flights, the aircraft usually did not get low enough into the nighttime surface layer and therefore the values at the ground are not representative of the values aloft. This is clearly demonstrated in Fig. 7c, which shows the inter-comparison of acetaldehyde from the aircraft PTR-MS measurements with the results from the ground-site using the GC-MS and the PIT-MS data. For acetaldehyde the daytime over-flights agree well within the measurement uncertainties with the ground site measurements, but the nighttime mixing ratios are clearly lower aloft. On some nights, the higher elevation angles of the DOAS show lower mixing ratios than the lower angles indicating that they might be more representative of the air mass sampled by the aircraft.

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Despite all these complications, all over-flights were included in the inter-comparison. The slope of the scatter plot shows that the PTR-MS is about 10 % higher than the DOAS, which is in turn about 35 % higher than the Hantzsch monitor. This means that the PTR-MS agrees well within the stated uncertainties with the DOAS and just within the uncertainties with the Hantzsch monitor. The agreement especially with the DOAS instrument gives further confidence in the validity of the aircraft PTR-MS HCHO measurements.

4.3 HCHO enhancement ratios in the LA plume and comparison with other data sets

Scatter plots of HCHO versus acetaldehyde and versus CO for the example flight on 19 May 2010 are shown in Fig. 8. Linear fits for all the data in the LA basin and the free troposphere are used to calculate the enhancement ratios $\Delta\text{HCHO}/\Delta\text{CO}$ and $\Delta\text{HCHO}/\Delta\text{acetaldehyde}$. The Los Angeles basin is characterized by a mixture of recirculated aged air and fresh anthropogenic emissions from a large variety of different sources such as vehicular and industrial emissions. An overall enhancement ratio of $12 \text{ pptv ppbv}^{-1}$ for $\Delta\text{HCHO}/\Delta\text{CO}$ and $1.5 \text{ ppbv ppbv}^{-1}$ for $\Delta\text{HCHO}/\Delta\text{acetaldehyde}$ was found in the LA basin for this flight. The free troposphere encountered during this flight was certainly impacted by aged pollution, which can be seen in the CO mixing ratios of up to 250 ppbv. Secondary production of HCHO resulted in a higher enhancement ratio of $\Delta\text{HCHO}/\Delta\text{CO}$ with $21 \text{ pptv ppbv}^{-1}$ and of $\Delta\text{HCHO}/\Delta\text{acetaldehyde}$ ratio with 3 ppbv ppbv^{-1} . Acetaldehyde also has large secondary sources (de Gouw et al., 2005), but a shorter lifetime than HCHO resulting in the observed increase of their ratio. The observations of CalNex can be compared to other data sets some of which are summarized by Herndon et al. (2007), who showed $\Delta\text{HCHO}/\Delta\text{CO}$ ratios ranging from $2\text{--}3 \text{ pptv ppbv}^{-1}$ for fresh emissions of light duty vehicles up to $50 \text{ pptv ppbv}^{-1}$ for very aged air masses. Over-flights of various US cities showed ratios between $10\text{--}25 \text{ pptv ppbv}^{-1}$. In the same publication $\Delta\text{HCHO}/\Delta\text{acetaldehyde}$ ratios ranging from 1 ppbv ppbv^{-1} for light duty vehicles up to 7 ppbv ppbv^{-1} for the aged air were

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observed. Over-flights of various US cities showed ratios between 2–3 ppbv ppbv⁻¹. The enhancement ratios observed during CalNex using the PTR-MS therefore agree well with the expected values from the literature.

4.4 HCHO production in an anthropogenic plume

5 In this section we demonstrate the usefulness of the airborne PTR-MS HCHO measurements for a field mission by looking at the photochemical production of HCHO and acetaldehyde in a pollution plume. On 12 May 2010 the NOAA WP-3 aircraft followed an isolated urban plume down the Central Valley. The flight track, shown in Fig. 9a, is color-coded with the HCHO mixing ratio and the plume intersects are marked with
10 numbers. The flight also included transects over San Francisco, which are marked with numbers 1 and 2 to give a starting point in the plume evolution. In the Central Valley the wind speed was very constant at about 7 m s⁻¹. The plume crossings were about 25 km apart and therefore the transport time between transects 3–7 was about one hour each. The observed mixing ratios in the plume were rather small and therefore
15 challenging the instrument more than the measurements in the LA plume that were presented above.

Aromatic hydrocarbons, such as benzene, toluene and C8-aromatics, are emitted mainly by vehicle exhaust with certain ratios in an urban environment (Warneke et al., 2007). With plume age the toluene/benzene and C8-aromatics/benzene ratios decrease because of the shorter lifetimes of toluene and the C8-aromatics compared to
20 benzene. HCHO and acetaldehyde have small primary emissions (Garcia et al., 2006; Ban-Weiss et al., 2008) and are produced in the plume, which causes their ratio with CO to increase with plume age. Figure 9b shows the scatter plot of HCHO versus CO for this flight. Each plume crossing is shown with a separate color. The slopes
25 from the scatter plot are shown in Fig. 9c together with the aromatics ratios that were determined in the same way. The aromatics ratios decrease until there are almost no detectable C8-aromatics in the plume. The HCHO/CO increases throughout the plume

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evolution, whereas the CH₃CHO/CO ratio initially increases and then decreases again, when the loss of acetaldehyde due to reactions with OH becomes more important than the photochemical production (de Gouw et al., 2005). This example shows the net photochemical production of HCHO from anthropogenic emissions.

Comparing those two photochemical clocks that were determined for an anthropogenic plume with low mixing ratios shows the ability of the PTR-MS to make accurate measurements of HCHO with a high time resolution onboard an aircraft together with many other VOCs.

5 Conclusions

In this paper we demonstrate fast time response measurements of HCHO from an aircraft using a PTR-MS instrument that was operated at standard instrument settings to detect its usual set of compounds including various oxygenated, biogenic and anthropogenic VOCs. HCHO was measured 1 s every 16 s. Aircraft HCHO measurements were made possible because of the recent improvements in the sensitivity of PTR-MS and by developing a specific calibration capability for HCHO. The humidity dependence of the PTR-MS HCHO detection was determined in the laboratory and agreed within 10 % with in-flight calibrations. The sensitivity of the PTR-MS for a 1-s measurement during the flights in the free troposphere was about 200 Hz ppbv⁻¹ and in the boundary layer about 60 Hz ppbv⁻¹ resulting in a detection limit (S/N = 1) of about 100 pptv and 300 pptv, respectively. The HCHO sensitivity is about 5–20 % of most other compounds detected by PTR-MS. Inter-comparisons with ground-based measurements and comparisons with other data sets validated the PTR-MS HCHO measurements. The usefulness of the PTR-MS measurements of HCHO together with many other VOCs is demonstrated by observing the photochemical processing in an anthropogenic plume.

The sensitivity of the HCHO detection with PTR-MS can be improved by using different instrument set-ups, which might influence the detection of other compounds. Dependent on the goal of the measurements an optimum setting can be used. Overall,

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the HCHO measurements are a very useful addition to the suite of compounds usually measured with PTR-MS. In many air quality studies, including aircraft missions, PTR-MS instruments are used and careful instrument calibrations and consideration of the humidity dependence can provide fast time response HCHO measurements.

- 5 *Acknowledgements.* The NOAA Climate Change and Air Quality programs supported this work. We would like to thank crew of the NOAA WP-3 aircraft.

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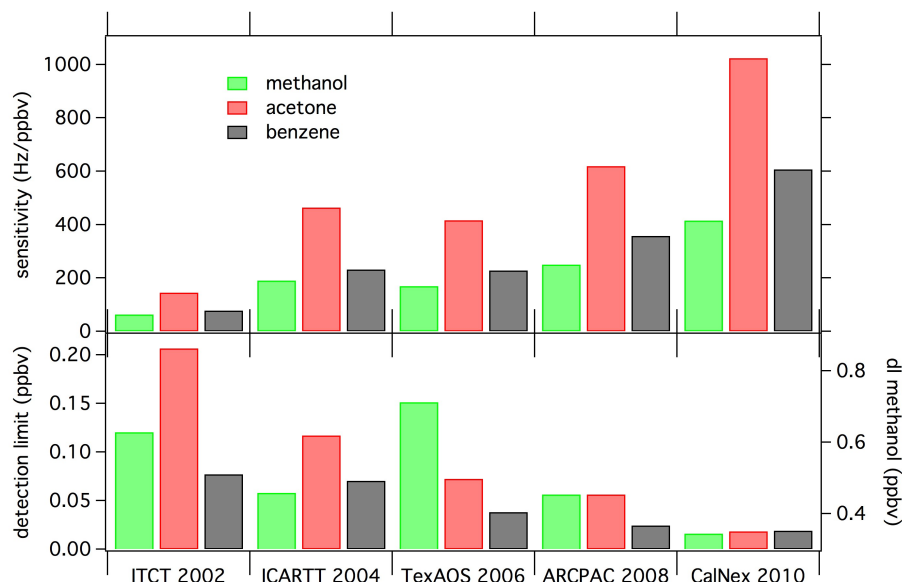


Fig. 1. The PTR-MS sensitivity and detection limits for methanol, benzene and acetone during five different aircraft missions during the past eight years: ITCT 2002 (de Gouw et al., 2004), ICARTT 2004 (Warneke et al., 2004), TexAQS 2006 (Warneke et al., 2010), ARCPAC 2008 (Warneke et al., 2010) and CalNex 2010.

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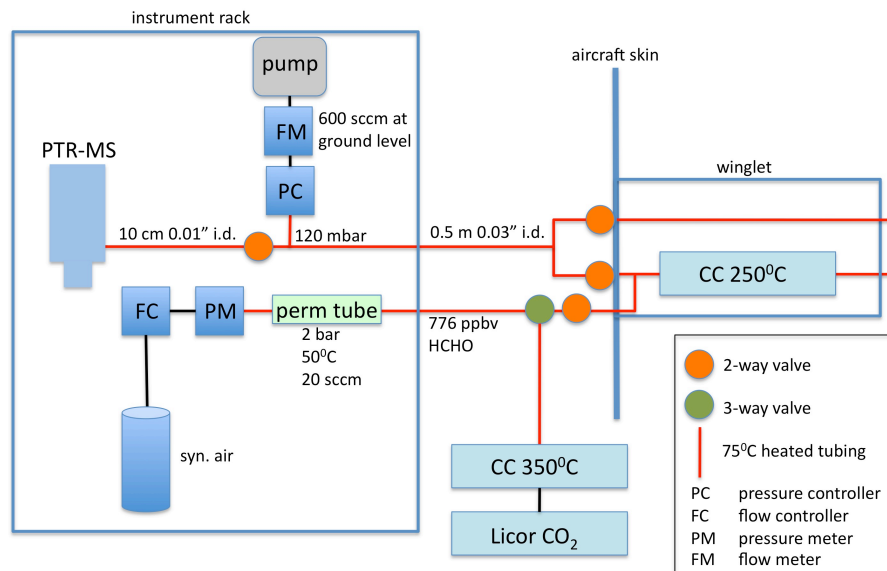


Fig. 2. Inlet and calibration system used during the CalNex 2010 campaign on the NOAA WP-3 aircraft.

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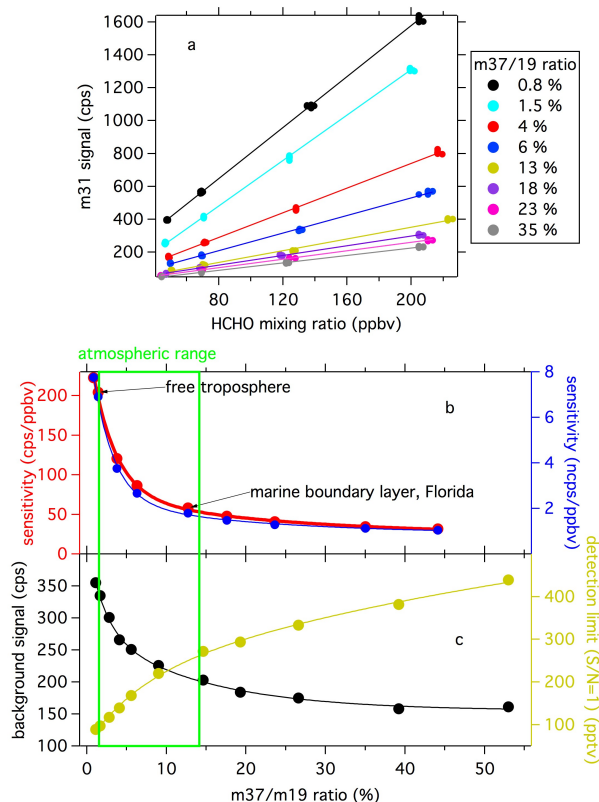


Fig. 3. (a) Calibration curves of the PTR-MS mass 31 versus HCHO mixing ratio (ppbv) at different humidities. (b) Sensitivity for HCHO dependent on the humidity. (c) The background signal and the detection limit for HCHO dependent on the humidity.

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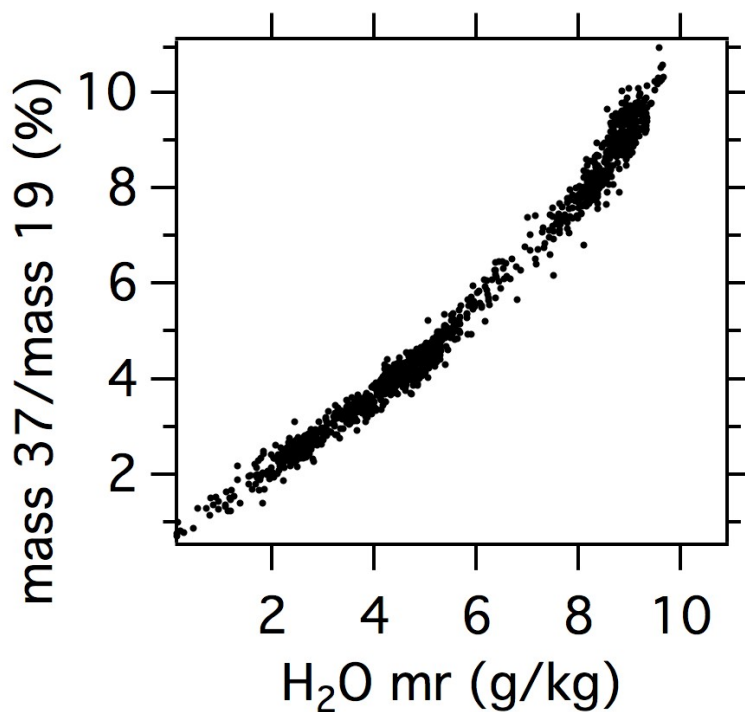


Fig. 4. The ratio of $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O} / \text{H}_3\text{O}^+$ (mass 37/mass 19) versus the ambient water mixing ratio (i.e. humidity) for a typical flight during CalNex 2010.

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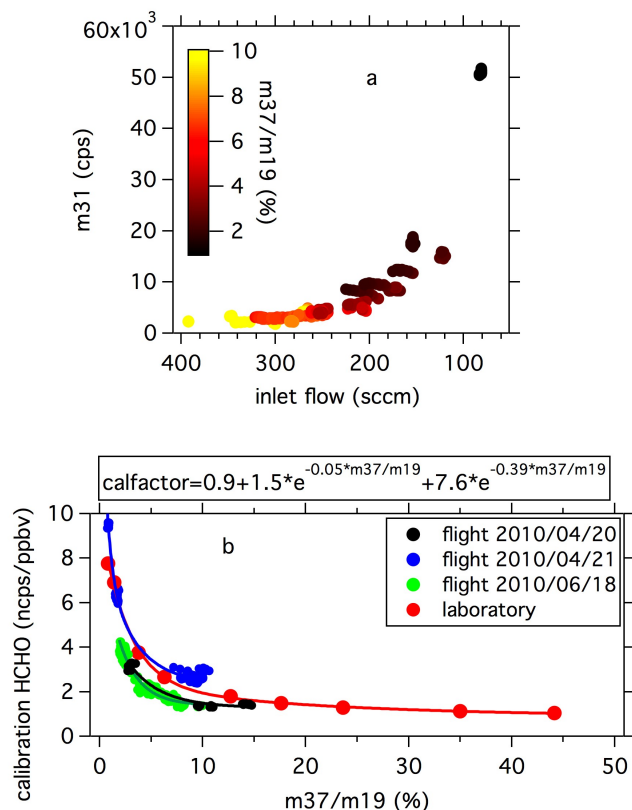


Fig. 5. (a) Background subtracted raw signals from the in-flight calibration of the PTR-MS for HCHO during flights on 20 April, 21 April and 18 June 2010 versus the inlet flow, which is proportional to the altitude. The color code represents the humidity (equivalent to the mass37/mass19 ratio). b) Laboratory and in-flight calibration of the PTR-MS for HCHO dependent on the humidity. A double exponential fit is used to describe the humidity dependence of the PTR-MS HCHO sensitivity.

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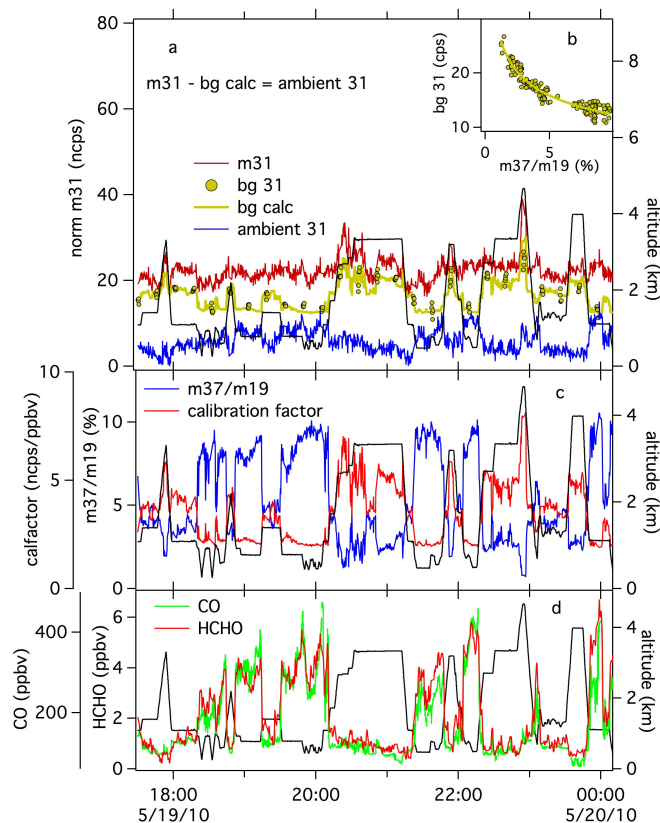


Fig. 6. Example flight on 19 May 2010 during CalNex 2010. **(a)** Raw signals (ambient and instrument backgrounds) of HCHO during the flight. **(b)** Humidity dependence of the instrument background signal. **(c)** Calibration factor estimated from the mass 37/mass 19 ratio. **(d)** HCHO mixing ratio together with CO.

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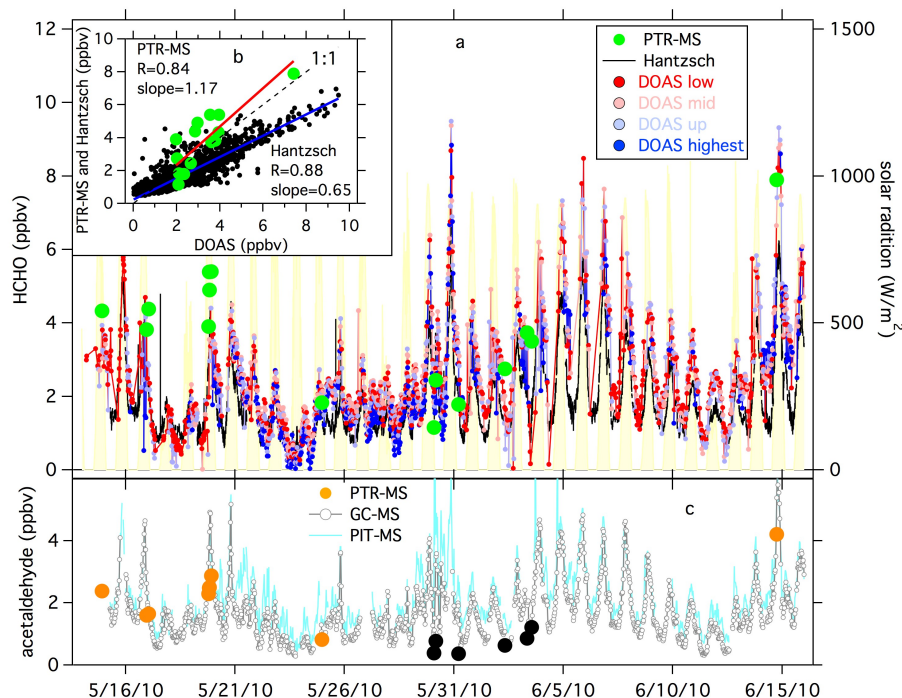


Fig. 7. (a) Inter-comparison of the airborne PTR-MS HCHO with measurements using a DOAS and a Hantzsch monitor at the Pasadena ground site. (b) Scatter plot of the PTR-MS and the Hantzsch versus the DOAS HCHO measurements. (c) Inter-comparison of the airborne PTR-MS acetaldehyde with measurements using a GC-MS and a PIT-MS on the Pasadena ground site. The color code of the aircraft data indicates the day- and nighttime measurements.

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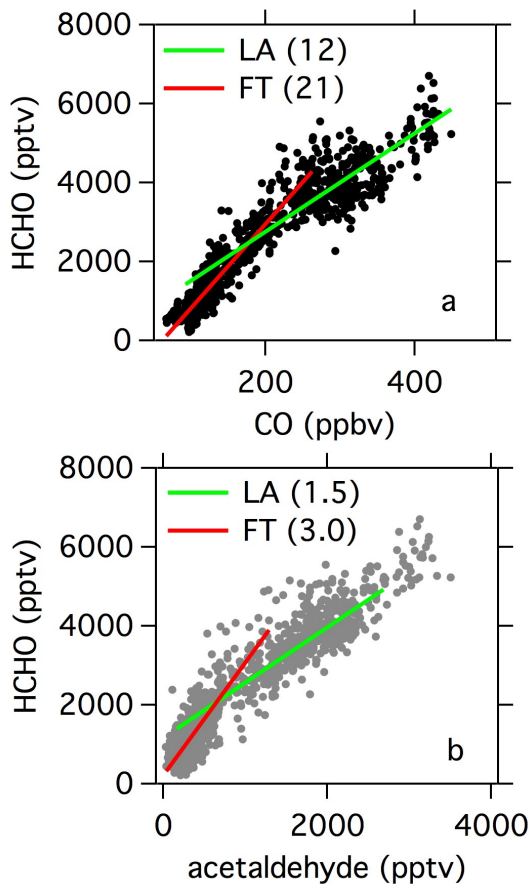


Fig. 8. Scatter plots of HCHO versus acetaldehyde and CO from a flight on 19 May 2010 in and around the Los Angeles basin including linear fits of data in the boundary layer over LA and in the free troposphere (FT). The values in the brackets are the slopes of the regression lines (in units of pptv/ppbv for CO and pptv/pptv for acetaldehyde).

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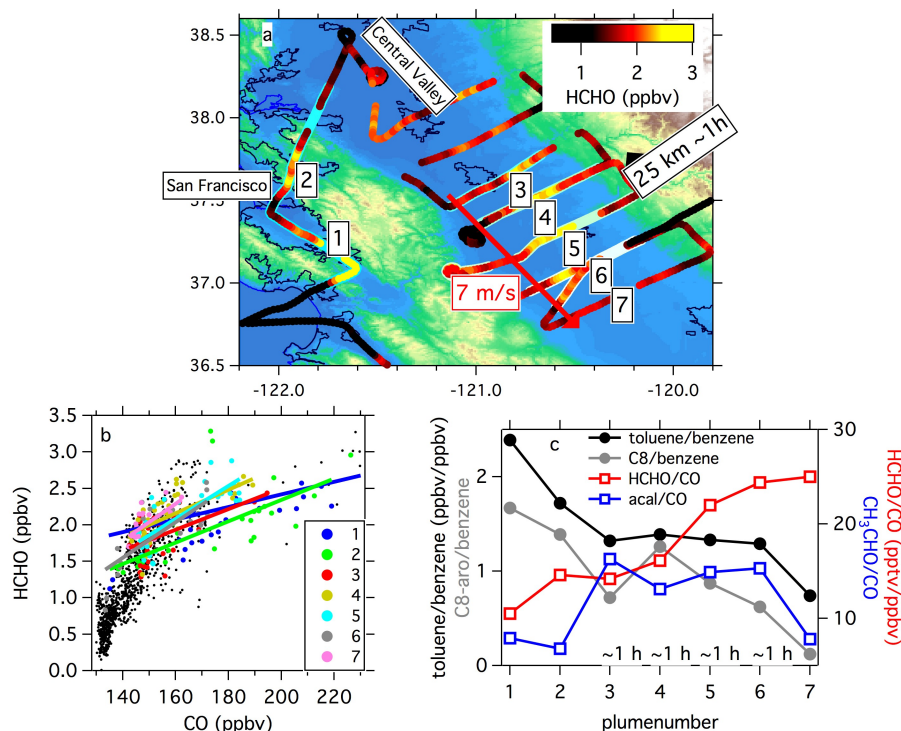


Fig. 9. (a) A map of the Central Valley with the flight track of the NOAA WP-3, which has been color coded by the HCHO mixing ratio. (b) Scatter plot of HCHO versus CO with individual plume crossings indicated in different colors. The linear fits for the individual plume crossings are also shown. (c) The increase of the HCHO/CO and CH₃CHO/CO ratios (slopes of the linear fits in (b)) together with the simultaneous decrease in toluene/benzene and C8-aromatics/benzene ratios during the processing of the anthropogenic plume travelling down the Central Valley.

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