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Instrument inter-comparison of glyoxal, methyl glyoxal and NO_2 under simulated atmospheric conditions

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Abstract

The α-dicarbonyl compounds glyoxal (CHOCHO) and methyl glyoxal ($CH_3C(O)CHO$) are produced in the atmosphere by the oxidation of hydrocarbons, and emitted directly from pyrogenic sources. Measurements of ambient concentrations inform about the rate of hydrocarbon oxidation, oxidative capacity, and secondary organic aerosol (SOA) formation. We present results from a comprehensive instrument comparison effort at 2 simulation chamber facilities in the US and Europe that included 9 instruments, and 7 different measurement techniques: Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS), Cavity Enhanced Differential Optical Absorption Spectroscopy (CE-DOAS), White-cell DOAS, Fourier Transform Infra-Red Spectroscopy (FTIR, two separate instruments), Laser Induced Phosphoresence (LIP), Solid Phase Micro Extraction (SPME), and Proton Transfer Reaction Mass Spectrometry (PTR-ToF-MS, two separate instruments; only methyl glyoxal as no significant response was observed for glyoxal). Experiments at the National Center for Atmospheric Research (NCAR) compare 3 independent sources of calibration as a function of temperature (293 K to 330 K). Calibrations from absorption cross-section spectra at UV-visible and IR wavelengths are found to agree within 2 % for glyoxal, and 4 % for methyl glyoxal at all temperatures; further calibrations based on ion-molecule rate constant calculations agreed within 5 % for methyl glyoxal at all temperatures. At the EUropean PHOtoREactor (EUPHORE) all measurements are calibrated from the same UV-visible spectra (either directly or indirectly), thus minimizing potential systematic bias. We find excellent linearity under idealized conditions (pure glyoxal or methyl glyoxal, $R^2 > 0.96$), and in complex gas mixtures characteristic of dry photochemical smog systems (o-xylene/NO_x and isoprene/NO_x, $R^2 > 0.95$; $R^2 \sim 0.65$ for offline SPME measurements of methyl glyoxal). The correlations are more variable in humid ambient air mixtures (RH > 45 %) for methyl glyoxal ($0.58 < R^2 < 0.68$) than for glyoxal ($0.79 < R^2 < 0.99$). The intercepts of correlations were insignificant for the most part; slopes varied by less than 5 % for instruments that also measure NO_2. For glyoxal and methyl glyoxal the slopes varied

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by less than 12 % and 17 % (both 3-sigma) between inherently calibrated instruments (i.e., calibration from knowledge of the absorption cross-section). We find a larger variability among in situ techniques that employ external calibration sources (75 % to 90 %, 3-sigma), and/or techniques that employ offline analysis. Our inter-comparison reveal existing differences in reports about precision and detection limits in the literature, and enables comparison on a common basis by observing a common airmass. Finally, we evaluate the influence of interfering species (e.g., NO_2, O_3 and H_2O) of relevance in field and laboratory applications. Techniques now exist to conduct fast and accurate measurements of glyoxal at ambient concentrations, and methyl glyoxal under simulated conditions. However, techniques to measure methyl glyoxal at ambient concentrations remain a challenge, and would be desirable.

1 Introduction

The α-dicarbonyl compounds, specifically glyoxal (CHOCHO, GLY) and methyl glyoxal ($CH_3C(O)CHO$, MGLY), are produced in the atmosphere by the oxidation of hydrocarbons from biogenic (isoprene), anthropogenic (toluene, xylenes, acetylene) and pyrogenic sources (Volkamer et al., 2007; Fu et al., 2008; Myriokefalitakis et al., 2008; Stavrakou et al., 2009; Washenfelder et al., 2011). Time resolved measurements indicate the rate of hydrocarbon oxidation (Volkamer et al., 2005a), and provide information about oxidative capacity (Huisman et al., 2011). Glyoxal and methyl glyoxal are further building blocks that actively participate in the formation of secondary organic aerosol (SOA) in aqueous aerosol particles (Volkamer et al., 2007, 2009; Ervens et al., 2008; Galloway et al., 2009; Hennigan et al., 2009; Ervens and Volkamer, 2010; Hamilton et al., 2013) and cloud droplets (Nozière et al., 2008; Yu et al., 2011; McNeill et al., 2012; Topping et al., 2013). Recent findings also show that the uptake of glyoxal is enhanced by the presence of some inorganic salts (Kampf et al., 2013). SOA formation from the uptake and multiphase chemistry of small oxygenated molecules is receiving increasing attention in recent years, and could be an important pathway to explain

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elevated field observations of high oxygen-to-carbon ratios in ambient organic aerosol that cannot be explained by traditional SOA formation mechanisms (Waxman et al., 2013).

Glyoxal and methyl glyoxal measurements have been conducted for almost 30 years (Tuazon and Atkinson, 1990a; Yu et al., 1997), but sensitive and robust in-situ techniques suitable to measure these compounds with high time resolution as part of field observations have only become available over the past decade (Volkamer et al., 2005a; Washenfelder et al., 2008; Huisman et al., 2008; Thalman and Volkamer, 2010; Baidar et al., 2012; Henry et al., 2012; DiGangi et al., 2012; Ahlm et al., 2012). Methods span a variety of analytical techniques, in particular: infrared (IR) absorption spectroscopy (Tuazon and Atkinson, 1990b; Profeta et al., 2011), ultraviolet-visible (UV-vis) absorption spectroscopy (Volkamer et al., 2005a; Sinreich et al., 2007; Washenfelder et al., 2008; Thalman and Volkamer, 2010), chromatographic analysis of derivatization by O-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) (Bao et al., 1998; Ho and Yu, 2002; Baker et al., 2005; Ip et al., 2009; Alvarez and Valcárcel, 2009; Pang et al., 2013, 2014) or DNPH (Grosjean et al., 1996) via C-18 packed columns or solid-phase micro-extraction and detection by mass spectrometry or flame ionization, phosphorescence (Huisman et al., 2008; Henry et al., 2012); and in the case of methyl glyoxal also chemical ionization mass spectrometry (H_3O^+, O_2^+ or NO^+) (de Gouw et al., 2003; Michel et al., 2005; Guimbaud et al., 2007; Karl et al., 2009). To our knowledge there has been no previous systematic effort to compare multiple techniques for quantifying α-dicarbonyls under conditions that resemble the polluted urban or pristine atmosphere. Furthermore, there are several methods and conventions to report detection limits for the different instruments in the literature, which complicates a direct comparison between instruments. This work addresses these issues of common language for limits of detection, assesses some likely measurement interferences, calibration standards and general instrument performance in a series of simulation chamber experiments carried out at the National Center for Atmospheric Research (NCAR) reaction chamber in Boulder, Colorado, USA and the Instituto Universitario Universitas

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2 Instrumentation and experimental conditions

2.1 Instruments

The various instruments used at both the NCAR and EUPHORE facility are listed in Table 1, and described in the following subsections in more detail.

2.1.1 NCAR Fourier transform infrared spectrometer (FTIR)

The FTIR instrument is integrated as part of the NCAR chamber, and measures along the long-axis of the chamber (2 m long, 16 passes, giving a total light path of 32 m). The spectrometer consists of a BOMEM DA3.01 FTIR, and was operated at 1 cm^{-1} resolution and collected and averaged 200 spectra between 800 and 4000 cm^{-1} over a period of 4 min. Standard spectra used for spectral subtraction were obtained using the same conditions as above, from scans of samples prepared via injection of known quantities of analyte into the chamber. Absorption cross sections quoted are derived from these standard spectra.

2.1.2 NCAR proton transfer reaction time of flight mass spectrometer (PTR-ToF-MS)

The NCAR chamber experiment involved measurements of VOCs by using a high resolution PTR-ToF-MS (Ionicon Analytik GmbH, Innsbruck, Austria) (Jordan et al., 2009). For detailed review of the instrumentation, refer to de Gouw and Warneke (2007). During the experiment, the PTR-ToF-MS was operated under H_3O^+ mode, which uses hydronium ions (H_3O^+) as the primary reagent ions to protonate VOC species. The ionization conditions in the drift tube were controlled by setting the drift voltage at 542 V,

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drift temperature at 60 °C and drift pressure at 2.3 mbar, resulting in an E/N value of about 120 Td (with E being the electric field strength, and N the gas number density; 1 Td = 10^{-17} V cm^2). The integration time was set to 1 s. A 1/16 inch OD capillary PEEK inlet (~ 1 m length) heated to 60 °C was used as a transfer line, with a flow rate of 100 sccm. The transfer line was connected to an unheated 1/8 inch OD PTFE line (~ 1 m length), which was connected to the chamber outlet through a dilution system. Standard gas calibration was performed by using a custom built calibration system. Zero air was produced by pumping ambient air through a catalytic convertor heated to 400 °C. A gravimetrically prepared gas standard containing isoprene (7.25 ppmv) and camphene (4.87 ppmv) was dynamically diluted by the zero air and analyzed by the PTR-ToF-MS.

2.1.3 University of Colorado light-emitting diode cavity enhanced differential optical absorption spectrometer (CE-DOAS)

The University of Colorado Boulder Light-emitting Diode Cavity Enhanced Differential Optical Absorption Spectrometer (CE-DOAS) consists of a high-power blue Light Emitting Diode (LED) coupled to a high finesse optical cavity (highly reflective mirrors, R = 0.999972 at 460 nm, cavity length, d_0 = 92 cm, useable range 430–490 nm) (Thalman and Volkamer, 2010). The CE-DOAS instrument was present for both the experiments at NCAR as well as those at EUPHORE and is here used as the comparative standard for purposes of cross-comparison. In the NCAR experiments 5 sccm (standard cubic centimetres per minute) of sample flow was sampled from the chamber through a mass flow controller (MKS) and diluted with 500 sccm of dry air before flowing through the optical cavity. At EUPHORE, the same CE-DOAS setup was connected directly to the chamber. The instrument sampled at 500 sccm from the chamber without dilution through 1 m long Teflon tubing with a 1 µm size 25 mm diameter Teflon filter (Pall) in a Teflon filter holder (Entegris) at the beginning of the line to remove aerosol. Spectra were acquired for 1 min and evaluated against a 5 min reference spectrum in pure nitrogen.

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Analysis of CE-DOAS spectra was performed for the retrieval of glyoxal, methyl glyoxal, NO_2 and O_4 as described in Thalman and Volkamer (2010). The mirror reflectivity was calibrated from the differential Rayleigh scattering of helium and nitrogen (Washenfelder et al., 2008) using the Rayleigh scattering cross-section values as described in Thalman et al. (2014). The mirror reflectivity curve was then used to calculate the absorption path in the empty cavity:

$$L(\lambda) = \frac{d_s}{1 - R(\lambda) + \alpha_{\mathrm{Ray}}^{\mathrm{Air}} d_0 + \sigma_{O_4} N_d^2 O_{2,\mathrm{mixing\,ratio}}^2 d_s + \sigma_i c_i d_s} = \frac{O_{4_{\mathrm{SCD}}}}{N_d^2 O_{2,\mathrm{mixing\,ratio}}^2}. \quad (1)$$

Where $L(\lambda)$ is the effective path length with respect to wavelength (cm), d_s is the sample length (cm), $R(\lambda)$ is the mirror reflectivity with respect to wavelength, α is the extinction due to the Rayleigh scattering in air (cm^{-1}), d_0 is the cavity length (cm), σ_i is the absorption cross-section of the corresponding gas, N_d is the density (molecules cm^{-3}), c_i is the concentration of the corresponding gas (molecules cm^{-3}), and $O_{4_{\mathrm{SCD}}}$ is the slant column density (concentration × pathlength of O_4, cm^{-5} $\mathrm{molecule}^2$). Absorption cross-sections are scaled by the path length (usually a maximum of 15 km for the sample path) as outlined in Thalman and Volkamer (2010). The Windoas software (Fayt and Van Roosendael, 2001) was used to adjust literature cross sections to the instrument resolution, and perform DOAS fitting of multiple reference spectra simultaneously. Literature absorption cross-sections for glyoxal (Volkamer et al., 2005b), methyl glyoxal (Meller et al., 1991), NO_2 (Vandaele et al., 2002), and O_4 (Hermans et al., 1999; Hermans, 2010) were used in fitting the spectra. The DOAS output in units of slant column density (SCD = concentration $\cdot L$) was then divided by the path length to get concentration. Measurements of O_4 SCDs as part of each spectrum at high signal-to-noise facilitate online control over cavity alignment and/or R. The path length calculated from Eq. (1) agreed with the O_4 calibration gas within 1 %. Equation (1) was solved iteratively to account for self-limitation until the concentrations converge (either for NO_2 (experiments 3, 4, 7, 9 and 10) or glyoxal (exp 1 and 8)). For experiments with

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high glyoxal concentrations, data were retrieved in two ways: (1) fitting of two cross-sections bounding the absorption range or (2) fitting of the weak absorption structures in the wavelength range 458.5–475 nm (instead of the normal glyoxal fit window is 435–465 nm). For Experiments N3, E9 and E10 (see Table 2) a NO_2 residual is fitted to account for systematic structures arising from extremely high NO_2 concentrations leading to a more stable retrieval of the glyoxal or methyl glyoxal concentrations.

2.1.4 University of Leicester broadband cavity enhanced absorption spectrometer (BBCEAS)

The University of Leicester Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS) instrument is based on predecessor BBCEAS instruments used to detect NO_2 in urban air (Langridge et al., 2008) and iodine in the marine atmosphere (Ball et al., 2010). In its present form, it has been deployed as the reference instrument for glyoxal and methyl glyoxal quantification in experiments at the EUPHORE chamber to test a micro-fluidic derivatisation instrument (Pang et al., 2014) and to investigate glyoxal uptake onto ammonium sulphate aerosol (Hamilton et al., 2013). The instrument uses a high power LED peaking around 455 nm to pump an optical cavity constructed from two high reflectivity plano-concave mirrors separated by 110.5 cm (peak reflectivity = 0.999817 at 462 nm). Gas mixtures were sampled from the EUPHORE chamber into the cavity through a PFA inlet line (1.2 m length, 6.35 mm outside diameter, 2 L min^{-1} flow rate) that passed through a bulkhead compression fitting in a flange in the chamber floor, close to the centre of the chamber (see Fig. 1b). The inlet line protruded 40 cm above the chamber floor in order to sample well-mixed gas. Because the BBCEAS instrument shared the same flange used to inject samples into the chamber, the instrument often measured elevated trace gas concentrations during and shortly after injections. Hence data within 5 min of any such trace gas injection have been excluded from the comparisons in this paper.

Spectra of the light intensity transmitted through the cavity and gas sample were recorded using a miniature spectrometer (Ocean Optics HR2000) housed inside

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a temperature stabilised enclosure. For this work, spectra were integrated for 10 s, and six spectra were averaged together and combined with $I_0(\lambda)$ reference spectra (obtained whilst flushing the cavity with dry synthetic air; averaged for 10 min) to produce BBCEAS spectra at a 1 min time resolution. Absorber concentrations were retrieved by fitting the molecular absorption features in the spectra between 430 and 486 nm using the same reference absorption cross sections as the other spectroscopic instruments (references in Sect. 2.1.3). Spectra were routinely fitted for glyoxal, methyl glyoxal, NO_2, oxygen's O_2–O_2 collision complex and a high order polynomial function (typically 6th order) to account for all remaining unstructured extinction contributions, such as extinction by secondary organic aerosol formed from VOC oxidation in the EUPHORE chamber. Spectra were also fitted for water absorption bands whenever water vapour had been admitted into the chamber (e.g. the ambient air experiment E6). The highly structured glyoxal, NO_2 and water cross sections (Rothman et al., 2009) were degraded to the instrument's spectral resolution (between 0.09 and 0.13 nm half width at half maximum) using asymmetric line shape functions deduced at some 20 wavelengths across the spectrometer's bandwidth by recording and fitting atomic emission lines from argon and krypton calibration lamps. Spectra were not explicitly fitted for ozone or biacetyl absorption, even for experiments where these species were known to be present (see Sect. 4.3); both these molecules have broad, relatively unstructured absorptions within the instrument bandwidth, and their absorptions were adequately fitted by the polynomial function.

Allan variance tests conducted on a long time series of BBCEAS spectra obtained whilst flushing the cavity with dry nitrogen showed that the measurement precision is dominated by random noise components for averaging times up to several hundred seconds. The instrument was subject to small long-term drifts over the ~ 12 h duration of the Allan tests that degraded the achievable precision. However these drifts were always smaller than the 1σ measurement precision for each molecular absorber for the 1 min averaging time, as also evidenced by the modest departures of the BBCEAS data's means from zero in the histograms in Figs. 9 and 10 below. For this deployment

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at the EUPHORE facility, $I_0(\lambda)$ reference spectra were obtained only at the start and the end of each experiment, whereas more frequent re-acquisitions of the reference spectra during experiments themselves, at time intervals informed by the Allan tests, would reduce the effects of instrument drift. The overall accuracy of the BBCEAS concentration measurements is estimated to be 7 % for glyoxal and NO_2 and 10 % for methyl glyoxal. Three main factors (which are comparable in size) control the accuracy: uncertainties in the reference absorption cross sections used to fit the molecular absorbers, uncertainties in determining the reflectivity of the cavity mirrors (this work used a combination of Rayleigh scattering in helium and nitrogen, and absorption by the O_2-O_2 dimer in pure oxygen samples), and uncertainties in determining the proportion of the cavity occupied by the gas sample (the cavity mirrors were flushed with synthetic air to prevent degradation of the mirror reflectivity during experiments). Daniels et al. (2014) provide a full discussion of the BBCEAS instrument and its performance.

2.1.5 University of Leicester proton transfer reaction mass spectrometer (PTR-ToF-MS)

A PTR-ToF-MS instrument (Series I, Kore, UK) was employed to detect methyl glyoxal during the EUPHORE experiments. The PTR-ToF-MS technique is based on the chemical ionization of trace VOCs present in atmospheric samples by proton transfer reactions with the hydronium reagent ion (H_3O^+) (Blake et al., 2009). The product is a protonated molecular ion $(VOC\text{-}H)^+$ for each VOC of suitable proton affinity which is then separated and quantified by time-of-flight mass spectrometry (Wyche et al., 2007; Blake et al., 2009).

The PTR-ToF-MS method can also measure oxygenated VOCs such as glyoxal and methyl glyoxal. However, one drawback to PTR-ToF-MS, common to mass spectrometric techniques, is isobaric interference between VOC species being sampled; glyoxal is isobaric with acetone and propanal while methyl glyoxal is isobaric with several oxidized C_4 species and also the protonated water cluster $(H_2O)_4 \cdot H^+$. A full discussion

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of the challenges and interferences for measuring glyoxal and methyl glyoxal are given in Pang et al. (2014).

With methyl glyoxal detection, moisture within an air sample can lead to an interference from water cluster adducts. As sample humidity increases the background signal from the protonated water cluster $(H_2O)_4 \cdot H^+$ increases, elevating background noise on the m/z 73 mass channel and changing the methyl glyoxal limit of detection. With calibration of the instrument response to changing chamber temperature and humidity it is possible to correct for interference from isobaric water clusters. In this study the $m/z = 73$ Da signal for methyl glyoxal-H^+ was used to analyse the concentration of methyl glyoxal. The linear range for methyl glyoxal is 1.5–172 ppbv by PTR-ToF-MS measurement with a limit of detection of 1.5_1 ppbv (3σ for 3 min averaging) using dry nitrogen as a carrier. The instrumental error on the methyl glyoxal measurement is $\pm 0.8_6$ ppbv.

2.1.6 University of Wisconsin, Madison laser induced phosphorescence (Mad-LIP)

The Mad-LIP light source is a pulsed, narrow bandwidth (< 0.00078 nm), doubled Ti:Sapphire laser (Photonix Ind.) that is operated at 3 kHz and 20–70 mW. It is further capable of rapid and reproducible wavelength tuning on the scale of the vibro-rotational absorption spectral features of glyoxal (~ 0.06 nm) that are exploited for its detection as discussed below. The emitted laser light is then directed through a White-type multi-pass cell, typically operated at 32 passes and 100 Torr. Gas is drawn through the cell via a scroll pump (Edwards) orthogonal to the laser beam path. During ambient operation, the gas flow is nominally ~ 20 SLM (standard liters per minute) that was reduced to ~ 3 SLM for the first half of the comparison to be increased to ~ 13 SLM in the later half for operational reasons. As a result of the initial flow being very different from standard field operating conditions, operational problems occurred during calibrations. These were accounted for after the fact but resulted in extensive instrument maintenance, which resulted in variability of the alignment of the multi-pass cell not observed

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during standard field operation. The variability of the alignment is reflected in variability of the calibration factors. The detection axis is orthogonal to both the laser and gas axis. The detector is a single photon counting photo-multiplier tube (PMT) guarded by a 520 ± 20 nm bandpass filter (Barr Associates). The interior of the detection cell was optically baffled to reduce laser and ambient light scattering and/or reflecting into the detector.

The Mad-LIP instrument detects both glyoxal and methyl glyoxal by phosphorescence. This is initiated in either analyte by absorption of the laser light, after which, they relax by emission of a phosphorescent photon or are quenched collisionally. As a result, the amount of phosphorescent photons emitted by either is linearly proportional to the optical cross section, which is a function of wavelength described by their respective absorption spectra, the intensity of light, and analyte number density. Both glyoxal and methyl glyoxal signals are normalized by laser power to account for its variation. The photons between 2.5 and 37.5 µs after each laser pulse during a period of integration are summed and recorded as the signal during this time. Due to this gate and delay photon counting combined with a 520 ± 5 nm bandpass filter, the effect from laser scatter and fluorescent photons are diminished, minimizing the signal background, and, in particular eliminating any detection of NO_2 fluorescence.

The PMT signal (S_{total}) is a linear combination of several components: dark counts (S_{dark}), light scatter (S_{scatter}), glyoxal phosphorescence (S_{gly}) and methyl glyoxal phosphorescence (S_{mgly}). The glyoxal mixing ratio ($\text{Glyoxal}_{\text{mr}}$) is proportional to the difference in S_{total} at two different wavelengths: one at high glyoxal absorbance ($\lambda_1 = 440.138$ nm) and another at low glyoxal absorbance ($\lambda_2 = 440.104$ nm, Fig. S4 in the Supplement, Eq. 3). S_{total} is expressed in Eq. (2), followed by the calculation of $\text{Glyoxal}_{\text{mr}}$ in Eq. (3).

$$S(\lambda)_{\text{total}} = S_{\text{dark}} + S_{\text{scatter}} + S(\lambda)_{\text{gly}} + S_{\text{mgly}} \tag{2}$$

$$\begin{aligned}\text{Glyoxal}_{\text{mr}} &= [S(\lambda_1)_{\text{total}} - S(\lambda_2)_{\text{total}}] \cdot \eta_{\text{gly}} \\ &= [[S_{\text{dark}} + S_{\text{scatter}} + S(\lambda_1)_{\text{gly}} + S_{\text{mgly}}] - [S_{\text{dark}} + S_{\text{scatter}} + S(\lambda_2)_{\text{gly}} + S_{\text{mgly}}]]\end{aligned}$$

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$$= \cdot \eta_{gly}$$
$$= [S(\lambda_1)_{gly} - S(\lambda_2)_{gly}] \cdot \eta_{gly} \quad (3)$$

Where η_{gly} is the calibration factor relating glyoxal mixing ratio to the net glyoxal signal ($S(\lambda_1)_{gly} - S(\lambda_2)_{gly}$). The intensity of dark counts is a characteristic of the PMT, and light scatter as well as methyl glyoxal absorption are the same at λ_1 and λ_2. The calibration factor is determined by introducing a known amount of glyoxal by diluting a calibration standard quantified by CRDS and introducing it into the White-type multi-pass cell. See the following sub-section for CRDS system description as well as theory of operation. A very high degree of selectivity for glyoxal is achieved using this wavelength dithering approach coupled with monitoring only phosphorescent emission. Only molecules that absorb at ~ 440 nm, phosphoresce at ~ 520 nm, and have similar absorption spectra to glyoxal would be able to interfere. To the authors' knowledge, the Mad-LIP instrument has not observed any interferences with glyoxal detection.

Because S_{gly} is proportional to the glyoxal optical cross section at λ_1 (1.02×10^{-18} cm^2 molecule^{-1}), and the net glyoxal signal is proportional to the difference in optical cross section at λ_1 and λ_2 (3.42×10^{-19} cm^2 molecule^{-1}, Volkamer et al., 2005b), the contribution of glyoxal at λ_1 is calculated in Eq. (4). This is then substituted into Eq. (2), and is solved for S_{mgly}, and related to the mixing ratio of methyl glyoxal (methyl glyoxal$_{mr}$) by a calibration factor (η_{mgly}).

$$S(\lambda_1)_{gly} = \left(\frac{\sigma(\lambda_1)_{gly}}{\sigma(\lambda_1)_{gly} - \sigma(\lambda_2)_{gly}} \right) \cdot (S(\lambda_1)_{gly} - S(\lambda_2)_{gly}) \quad (4)$$

$$\text{Methylglyoxal}_{mr} = \left[S(\lambda)_{total} - S_{dark} - S_{scatter} - \left(\frac{\sigma(\lambda_1)_{gly}}{\sigma(\lambda_1)_{gly} - \sigma(\lambda_2)_{gly}} \right) \cdot (S(\lambda_1)_{gly} - S(\lambda_2)_{gly}) \right] \cdot \eta_{mgly} \quad (5)$$

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The calibration factor for methyl glyoxal is determined in an analogous way as glyoxal via CRDS. Due to the lack of structured absorption of methyl glyoxal (Meller et al., 1991; also see Fig. S3 in the Supplement), Mad-LIP does not possess as high of selectivity for methyl glyoxal as for glyoxal. Additionally, the maximum absorption of methyl glyoxal is about 3 × lower than the maximum of glyoxal absorption at λ_1. Furthermore, the quantum yield of phosphorescence for methyl glyoxal is lower than that of glyoxal. Due to these three reasons, methyl glyoxal has a much higher limit of detection and is susceptible to interferences due to small concentrations of glyoxal.

Instrumental calibrations were performed using Cavity Ringdown Spectroscopy (CRDS), an absolute quantification method in that it relies only on well-documented absorption cross-sections. Further details about the theory of this method are described elsewhere (O'Keefe and Deacon, 1988).

A cavity 62 cm long and 0.635 cm in diameter was formed between two parallel, highly reflective mirrors with a radius of curvature of 1 m (99.995 % reflectance, Los Gatos Research Inc.). The bulk of the cavity was encased in a 3/8″ O.D., 1/4″ I.D. PTFE tube. Halfway along the cavity, a PTFE tee was used as an inlet for the calibrant gas. On each end of the cavity, the mirror mounts were coupled via metal bellows to a Teflon PTFE tee which coupled the cell to exhaust ports for the cell. The dead volumes between the exhaust ports and the mirrors were flushed with zero air through a 200 standard cubic centimeter per minute (sccm) flow controller (1779A, MKS Instruments) to prevent optics fouling as well as bias. This purging did not allow any sample gas to mix beyond the exhaust ports, fixing the physical absorber path length to 42 cm. This cell design is based on to the NOAA NO_3 ring-down cell design (Dube et al., 2006; Osthoff et al., 2006). The entire cavity length between, and including, the exhaust tee fittings was enclosed in a 1.5″ by 1.5″ block of aluminum which was maintained at a constant temperature (35 °C) to discourage analyte deposition inside the cavity.

A 10 sccm flow controller (MKS Instruments) supplied calibrant gas that was then diluted by zero air. The zero air was delivered by a 200 sccm flow controller (MKS Instruments) at a rate which made up the remainder to a total flow of 100 sccm of diluted

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calibrant. The purge was held at 100 sccm using a 200 sccm flow controller (MKS Instruments). To maintain a constant cell pressure and therefore achieve a stable baseline, both the purge and the diluted calibrant flows were held constant. Laser pulses were introduced into the cavity through one of the high-reflectivity mirrors. A beamsplitter placed between the light source and the White-type multipass cell supplied light to the CRDS cell. With each reflection of a laser pulse, a small quantity of light escaped through the mirrors. On the opposite side of this cavity, a PMT (Hamamatsu), guarded by a 440 nm bandpass filter, detected this escaped light. Loss of photons within the cavity is a first-order process, thus the light leaking from the cavity has the characteristics of an exponential decay. The number density of a chemical absorber (molecules cm^{-3}) can be determined by relating two determined lifetimes, those determined with and without the presence of the absorber, by the following equation:

$$N_d = \left(\frac{1-R}{\sigma l_a}\right)\left(\frac{\tau_o - \tau}{\tau}\right) \tag{6}$$

Where N_d is the number density of the absorber, R is mirror reflectivity, σ is the absorption cross-section (either (Volkamer et al., 2005b) or (Meller et al., 1991) for glyoxal and methyl glyoxal, respectively), l_a is the path length of the absorber, τ and τ_o are the lifetimes with and without the absorber, respectively (Zalicki and Zare, 1995).

2.1.7 CEAM white cell-DOAS (W-DOAS)

A Differential Optical Absorption Spectroscopy device using a White multi-reflection cell (W-DOAS) of 8 m base path-length is deployed at EUPHORE. The optical system employed a Xenon high pressure short-arc lamp (XBO-550 W) as the light source, coupled to a telescope that collimates the light into a narrow beam and sends it into the chamber. The multi-reflection cell used during th experiments consisted of a set of prisms and mirrors dielectrically coated, allowing an optical path of 1154 m with reflection of the beam in the range 389–469 nm, for the detection of glyoxal, methyl

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glyoxal and NO_2. Two laser diodes and web-cameras were used to adjust the path-length of the system. The beam is finally driven outside of the chamber where it is focused by a telescope onto the entrance slit of a spectrograph equipped photodiode array detector. A detailed description can be found in (Becker, 1996).

The system collected spectra every 80–110 s by co-addition of 100 samples. A blank spectrum taken at the beginning of each day in the clean chamber was used as background $I(\lambda)$. Also, during the experiment, the stray-light was corrected by subtracting a spectrum recorded by introducing an edge filter in the light beam. The resolution was set to 0.35 nm FWHM. The analysis of the data was performed using a fitting routine (Rodenas, 2008) adapted to process DOAS data which has been successfully tested in previous intercomparison exercises (Rodenas, 2008). The same literature cross-sections for glyoxal, methyl glyoxal and NO_2 as the other instruments were used.

2.1.8 CEAM Fourier transform infrared spectrometer (CEAM FTIR)

The EUPHORE chamber is equipped with a Fourier Transform Infrared system (FTIR). The spectrometer (NICOLET 550, MCT/B-detector) is coupled to a White-type multi-reflection cell installed into the chamber for the detection of gaseous reactants and products in the IR spectral range (400–4000 cm^{-1}). The gold-coated mirrors of the cell allow a total path length of 616 m (8.3 m base path). With FTIR, it is possible to calculate the concentration of a wide range of compounds and reaction products using absorption reference spectra previously collected and the corresponding calibration thereof. A detailed description of the instrument is given in Becker (1996).

The spectra were derived from the co-addition of 280 scans, collected over a 5 min period, with a resolution of 1 cm^{-1}. During the experimental campaign, concentration profiles of glyoxal and methyl glyoxal were determined using improved analysis software developed at CEAM (Rodenas, 2008) adapted to analyze infrared spectra, and applied to the region of 2700–2900 cm^{-1}. This program is based on a classical least squares fitting which also removes the spectral interfering broadband (formed due to the presence of aerosols, equipment instabilities or unknown broadband products) by

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including a curve that models and subtracts it locally. The software as been tested and used in previous works (Muñoz et al., 2011, 2012).

Reference spectra were previously collected with the instrument, and calibrated with the references used by the W-DOAS system (Sect. 2.1.3). Water, formaldehyde, methanol and other compounds show absorption bands in the same spectral region as glyoxal and methyl glyoxal. Together with these compounds, the instrument was used to report the evolution of most of the reactants and products forming the complex mixture in the experiments preformed. These compounds were present in the samples to a greater or lesser degree depending on the experiment carried out. The fitting was done using both the aldehydic C-H band and the region 770–1140 cm^{-1}. The list of compounds analyzed includes ozone, isoprene, nitric acid, *o*-xylene, and formic acid. SF_6 was also monitored by FTIR to quantify the dilution range of the chamber.

2.1.9 CEAM Solid-phase-microextraction (SPME)

Solid Phase Microextraction (SPME) methodology was used to determine glyoxal and methyl glyoxal through PFBHA on-fiber derivatization. A detailed description of the methodology used at the EUPHORE chambers can be found in the literature (Gómez Alvarez et al., 2007; Alvarez and Valcárcel, 2009). Briefly, the SPME device used in this work consisted of a holder assembly with 65 µm fibers coated with Polydimethylsiloxane/Divinylbenzene (PDMS/DVB), from Supelco, Bellefonte, PA (USA). These fibers were conditioned following the manufacturer's recommendations for at least 0.5 h at 250 °C to eliminate any impurities. Fibers were loaded with PFBHA derivatization reagent, for 2 min, through the headspace of a 4 mL opaque amber vial containing a 17 mg mL^{-1} PFBHA water solution.

Exposing the fiber to the air of the chamber was achieved by means of an aluminum adapter located in one of the flanges in the chamber floor. In the exposed position, fibers extend into the chamber by a few millimeters.

Samples were taken for several minutes and were subsequently analyzed by GC-FID by injecting the fiber directly into the GC injector. Sampling time ranged depending on

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the dicarbonyl concentrations. Whenever possible, identification of the peaks was also cross-checked using GC-MS. Chromatographic Conditions: 6890 HP Gas Chromatograph was used, coupled to a Flame Ionization detector (FID), equipped with a HP5-MS capillary column (30 m × 0.25 mm I.D. × 0.25 µm) and an inlet liner with a narrow internal diameter 0.75 mm I.D. Pre-drilled Thermogreen LB-2 septa for SPME were used. The chromatograph was programmed at 80 °C for 2 min, then ramped at a rate of 20 °C min^{-1} to 280 °C and held at 280 °C for 3 min. The injection port was held at 270 °C and detector at 300 °C. Samples were injected in splitless mode, using on column constant helium flow of 1 mL min^{-1}.

2.2 NCAR chamber and experimental conditions

A set of chamber experiments was carried out using the temperature controlled simulation chamber at the National Center for Atmospheric Chemistry (NCAR) to study the temperature dependence of glyoxal and methyl glyoxal calibrations (January–March 2011; March–April 2012). The chamber consists of a stainless steel cylinder (~ 47 L) connected to a Fourier transform infrared spectrometer, as previously described in the literature (Shetter et al., 1987; Orlando and Tyndall, 2002) (see Fig. 1a). The chamber was chilled by circulating ethanol to cool the chamber to 260 K or heated (320 K) by circulating water. See Table 1 for the list of experiments. Reactant gases (typical starting concentrations 3–7 × 10^{14} molecules cm^{-3}; 11–26 ppm) were injected from a calibrated bulb into the chamber via a gas line as described previously (Orlando and Tyndall, 2002). The chamber was pressurized above ambient pressure and a small amount of gas (20–30 sccm) was leaked from the chamber through one port and divided and diluted (a factor of 100 dilution for CE-DOAS and a factor of 50 dilution for PTR-ToF-MS) before going to the sampling instruments. Reaction chemistry was initiated by adding light from a filtered Xe arc lamp or by injection of O_3 in presence of an alkene.

In the NCAR chamber glyoxal was produced by the oxidation of acetylene (C_2H_2, ethyne) by either Cl or OH radicals. Starting gases (reactants, oxygen) were injected into the chamber and the entire volume was diluted with nitrogen to 800 Torr.

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Methyl glyoxal was produced in a similar fashion from the oxidation of hydroxyacetone ($CH_3C(O)CH_2OH$, HACET) by Cl atoms.

2.3 EUPHORE chamber and experimental conditions

The EUPHORE facility consists of two 200 m^3 hemispherical Teflon enclosures with retractable roofs to allow for ambient illumination of the chambers for radical production. Figure 1b shows the layout of the Chamber A of the EUPHORE facility during the experimental campaign including the locations of the various instrument sampling ports, gas injection and circulation. Samples were injected into the chamber via an air stream added through center ports and mixed in the chamber by two fans. The chamber was operated at ambient temperature and approximate pressure using scrubbed air and homogeneously mixed using two horizontally and vertically mounted fans (see Fig. 1b). Chamber dilution is followed throughout each experiment using an inert SF_6 tracer (Becker, 1996; Borrás et al., 2014).

At the EUPHORE facility 10 experiments were carried out from 24 June–6 July 2011. These experiments consisted of the injection of pure glyoxal (Exp. E1 and E8) or methyl glyoxal (Exp. E2) which were subsequently diluted in steps, as well as the simultaneous in situ production of these compounds from the (photo) oxidation of precursors (isoprene (Exp. E4, E7) and *o*-xylene, Exp. E3). Additionally, the instruments were tested for interferences in the chamber from other species, such as NO_2 (Exp. E9 and E10), biacetyl (butane-2,3-dione, $CH_3C(O)C(O)CH_3$; Exp. E3), aerosol (Exp E3) with filtered/unfiltered optical instruments and O_3 (Exp. E5, possible production of glyoxal from O_3 reacting with Teflon). The full list of experiments along with experiment objectives are listed in Table 2.

The photo-oxidation experiments (*o*-xylene and isoprene oxidation) are rapidly evolving, complex chemical systems and hence there is potential for interferences from a wide range of α-dicarbonyls (glyoxal, methyl glyoxal and biacetyl) co-products such as unsaturated 1,4-dicarbonyls and furanones (from *o*-xylene) and glycolaldehyde and

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hydroxyacetone (isoprene). In addition a reasonable amount of SOA is formed in the *o*-xylene experiment.

Glyoxal and methyl glyoxal were prepared as described in the literature: pure glyoxal monomer was prepared from the solid trimer-dihydrate using the methods described in (Feierabend et al., 2007) with minor modification. Pure methyl glyoxal monomer was prepared from 40 % aqueous solution after one night pumping to eliminate most of the water using the method describe in Talukdar et al. (2011) with minor modifications. Cold fingers containing pure samples of un-polymerized glyoxal or methyl glyoxal were temporarily kept at liquid nitrogen temperatures prior to experimental use. Glyoxal and methyl glyoxal were introduced into the chamber by passing a small flow of nitrogen through a gently warmed cold-trap.

3 Results

The data from all instruments was analyzed by the individual groups and then correlations were calculated with respect to CE-DOAS for the data from NCAR and between each instrument pair for the EUPHORE experiments. In order to account for differences in time resolution between different instruments the data points were averaged to the longest time interval of any given instrument pair (see Table 3 for time resolution of the instruments), and data points a few minutes after injection periods were removed to avoid any effects due to the instruments sampling unmixed gas from the chamber. Correlations were calculated in IGOR Pro (Wavemetrics) using the optimal distance regression (ODR) function, to account for uncertainty along both axes (y-y regression).

3.1 NCAR

The CE-DOAS, PTR-ToF-MS and FTIR instruments at NCAR used independent sources of calibration, and provide an opportunity to assess our understanding of the underlying absorption cross-section data at UV-visible and IR wavelengths, as well as

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compare these cross-sections with ion-molecule rate constants (in the case of methyl glyoxal). No signal was observed for glyoxal in the PTR-ToF-MS (up to 32 ppbv glyoxal was supplied to the PTR inlet after dilution). Correlation plots for glyoxal and methyl glyoxal did not show significant intercepts and independent of temperature (295 and 320 K). Correlations for NO_2 (for CE-DOAS and FTIR only) agreed within ±5 % ($R^2 = 0.99$) and were independent of temperature (260, 295 and 320 K) but had lower R^2 values (0.95) due to non-linearity in the FTIR when high concentrations ($> 4 \times 10^{14}$ molecules cm^{-3}) were included. The results of these correlations are shown in Table 3, and a time series of one methyl glyoxal experiment is shown in Fig. 2. Panels a–c of Fig. 2 include data from 20 different experiments for NO_2, and 5 experiments each for glyoxal and methyl glyoxal; averages are shown in Fig. 2.

3.2 EUPHORE

3.2.1 Glyoxal intercomparison

Experiments E1 and E8a consisted of the injection of pure glyoxal into the chamber followed by stepped dilution. Correlations of data segregated between high (0–15 ppbv) and low (0–2 ppbv) mixing ratio data are shown in Fig. 3. It should be noted that the W-DOAS instrument is affected by the distortion of the light beam during the flushing of the chamber (the air input of the flushing is in the center of the chamber and intersects the W-DOAS light path). Table 3 compares individual instruments to CE-DOAS; correlation matrices that compare each instrument pair-wise to each other instrument for Experiments E1 and E8a can be found in Tables S1–2 in the Supplement. The slopes varied between 0.76 and 1.09 between all instruments and both experiments. Mad-LIP defines the highest and lowest slopes observed, reflecting ∼ 33 % difference in separate calibrations between both experiments as well as different operating conditions (see Sect. 2.1.6). All other instruments agreed within 15 %.

Experiment E9 investigated the possible interference of a large amount of NO_2 on detection of glyoxal for instruments using visible (430–490 nm) light spectroscopy and

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found no scalable bias due to NO_2. In this experiment the Mad-LIP was used as the glyoxal reference to evaluate effects of NO_2 with the UV-visible absorption techniques as previous work by Huisman et al. (2008) had shown Mad-LIP to be insensitive to NO_2 interferences, tested up to 1 ppmv. Figure 4 shows the time series of glyoxal and NO_2 concentrations for Exp. E9. The initial glyoxal amount (0.6 ppbv) was diluted and left to stabilize around 0.3 ppbv in absence of NO_2, followed by stepped NO_2 additions up to ~ 180 ppbv. SF_6 was added and measured by FTIR as a tracer for dilution, and the SF_6 signal in Fig. 4 has been scaled to the initial glyoxal to show the theoretical decay according to dilution of the glyoxal signal, in good agreement with the Mad-LIP glyoxal data. Note that the error bars increase at high NO_2, more for CE-DOAS than for BBCEAS due to larger light losses at the longer absorption path in CE-DOAS. Deviations in glyoxal however were small for all instruments; they are marginally significant for BBCEAS and insignificant for CE-DOAS during periods when MAD-LIP data is available (see Fig. S5 in the Supplement). Deviations in the SPME concentrations were large but appear to be unconnected to the high NO_2 levels in the chamber. For both CE-DOAS and BBCEAS (Fig. 4) we do not find significant bias, i.e., an upper limit change in glyoxal due to NO_2 is derived as ±200 pptv glyoxal in the presence of 200 ppbv NO_2 (or 1 pptv glyoxal/1 ppbv NO_2).

3.2.2 Methyl glyoxal intercomparison

Experiment E2 compared methyl glyoxal measurements in a pure compound system. Approximately 25 ppbv of methyl glyoxal was injected into the chamber, and diluted in 6 discrete steps to less than 1 ppbv. Figure 5 shows correlation plots of data segregated into high and low (< 3 ppbv) concentrations, and the regression lines (see Table 3). The slopes varied between 0.97 and 1.40, with generally larger differences in slopes between instruments than for glyoxal. Mad-LIP showed the highest slope, while W-DOAS had the lowest slope. Experiment E10 tested the interference of NO_2 on methyl glyoxal, as previously described for glyoxal (Sect. 3.2.1). The initial level of methyl glyoxal was 5.3 ppbv (Fig. 6), and FTIR is used as the reference instrument, given

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that concentrations were high enough to obtain good signal, and the methyl glyoxal and NO_2 absorption are well separated at IR wavelengths. No significant deviations in methyl glyoxal were observed in CE-DOAS and BBCEAS, and excellent agreement is observed even in excess of 200 ppbv NO_2 (see Fig. S5 in the Supplement). We quantify the bias of 5.3 ppbv methyl glyoxal as ±1 ppbv methyl glyoxal in the presence of 200 ppbv NO_2 (or 5 pptv methyl glyoxal/1 ppbv NO_2; see Fig. 6).

3.2.3 Dry photochemical smog systems

Experiment E3 investigated *o*-xylene photo-oxidation by OH radicals in the presence of NO_x, as a source for highly variable concentrations of glyoxal, methyl glyoxal, biacetyl and NO_2 that are present simultaneously in the chamber. Figure 7 illustrates the time series, and correlation plots, and Table 3 gives the results of regression fits (correlation plots include data from before and after HONO addition and chamber opening). The slopes varied between 0.83–1.1 (glyoxal), 0.86–1.7 (methyl glyoxal), and 0.95–1.01 (NO_2), and most instruments agreed within 12, 30, and 5 %, respectively. These differences were similar or slightly larger than those observed in the pure compound experiments (Sects. 3.2.1, and 3.2.2.). Notably, differences of up to 8 % between BBCEAS and CE-DOAS for methyl glyoxal are observed despite excellent agreement (better than 1 %) for both glyoxal and NO_2. While Mad-LIP data show excellent correlation ($R^2 > 0.95$ for both α-dicarbonyls, Table 3) they also mark the largest (1.66 methyl glyoxal) and smallest (0.83 glyoxal) slopes for both α-dicarbonyls. Although FTIR performed well for methyl glyoxal, concentrations of glyoxal were close to the detection limit of the FTIR, and the measured concentrations did not scatter around zero as expected (Fig. 7a) most probably due to unknown interfering products formed because the chamber was exposed to light (ozone and HCHO formation were observed from walls). Hence, FTIR data were only considered for further discussion if values exceeded detection limits by at least a factor of 2.

In the isoprene/NO_x system (Exp. E7) results were generally similar. However, the variations in slopes were somewhat higher, i.e., 0.94–1.54 (glyoxal), and 0.7–2.2

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(methyl glyoxal), while most instruments agreed within 30 % for both species (see Table 3). Again, MAD-LIP data show excellent correlation ($R^2 > 0.98$), and systematic differences in slopes (up to a factor of 2.2 for methyl glyoxal). This is indicative of the calibration and stability issues present in the Mad-LIP instrument during the campaign (see Sect. 2.1.6) as well as the difficulty in differentiating the methyl glyoxal signal from a large glyoxal background.

Experiment E4 consisted of a higher NO_x isoprene oxidation experiment and has been excluded from these comparisons for operational reasons. The NO_x control system failed to maintain a stable NO_x concentration in the chamber and a dilution valve failed in the CE-DOAS system which prevented the retrieval of the data to compare with other instruments (dilution was not attempted on any of the other experiments).

3.2.4 Moist ambient air

For experiment E6, ambient air was added to a cleaned chamber, to assess possible interferences from other species. For example, water vapour absorbs light at blue visible wavelengths, and can create problems with the molecular spectroscopy in UV-visible absorption techniques. Further, the transfer of α-dicarbonyls through sampling lines can become complicated in presence of ambient levels of relative humidity. Aerosols can reduce path length with BBCEAS, and other species in ambient air may create further interferences. Figure 8 shows the time series: a clean chamber was exposed to sunlight, and ambient air was added; the chamber's roof was closed and ~ 100 ppbv O_3 was added. Some of the accelerated decrease in NO_2 during the following hour may indicate formation of NO_3 radicals, and subsequent N_2O_5 hydrolysis on aerosols and chamber walls. The roof was then opened, and after 1.5 h HONO was added in a defined way such that NO_x ($NO + NO_2$) remained constant. Finally, a small amount of isoprene (18 µL, ~ 25 ppbv in the chamber) was injected while NO_x was controlled via the HONO source. The RH varied between 45 % and 58 %, and NO_2 levels were below 16 ppbv at all times, while concentrations of α-dicarbonyls varied between 10 pptv < glyoxal < 1 ppbv, and 50 pptv < methyl glyoxal < 5 ppbv, with average

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concentrations of 380 pptv glyoxal, and 1.7 ppbv methyl glyoxal. The slopes of correlations (Table 3) varied between 0.95–1.5 (glyoxal), 0.68–1.83 (methyl glyoxal), and 0.995 (NO_2) – agreement between most instruments was on the order of 10 % for glyoxal, and 30 % for methyl glyoxal, with extreme slopes showing differences of 50 % in case of SPME-glyoxal, and 83 % in the case of MAD-LIP methyl glyoxal. Interestingly, CE-DOAS and BBCEAS slopes agreed within 2 % for NO_2, 5 % for glyoxal, but differed by 32 % for methyl glyoxal. We note that the range of methyl glyoxal concentrations is fairly limited (correlations are driven by essentially two levels of points one near 0 and the other near 2 ppbv). The cause for difference is not clear to the authors. A possible partial explanation may consist in the difference in sampling location from the chamber, as CE-DOAS sampled close to the wall of the chamber, and the rise in methyl glyoxal after 3 p.m. drives the CE-DOAS vs. BBCEAS correlation away from 1 : 1 could be an artefact of wall interaction (and not instrumental difference). Generally, correlations are slightly more variable in humid air, than in dry air, and were found to be slightly lower for methyl glyoxal ($0.58 < R^2 < 0.68$) than for glyoxal ($0.79 < R^2 < 0.99$).

3.2.5 Interference from O_3

Experiment E5 tested the effects of O_3 either by production of glyoxal on reaction with Teflon (walls of the chamber or sampling lines) or other VOCs in the chamber. In the first half of the experiment O_3 was injected into the chamber to three stable levels (0–2.5 ppmv) and then flushed out of the chamber (see Fig. S1 in the Supplement). During these stable periods the CE-DOAS and BBCEAS instruments changed the lengths of their sampling lines to attempt to observe any change in the measured concentration. The only effect observed from longer Teflon lines was an increased amount of NO_2 with longer sample lines caused by the reaction of O_3 with NO trapped at the surface of the tubing. In the second half of the experiment, attempts were made to observe glyoxal production in a dark, NO_x-free environment via reaction of OH with acetylene. The intention was to generate OH in the dark from the reaction of O_3 with 2,3-dimethyl-2-butene (tetramethylethylene, TME; ozonolysis OH yield of 0.90 –

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IUPAC recommendation). The chamber was left filled with 200 ppbv of O_3, acetylene (20 ppmv) was added and TME was to be injected into the chamber (with the chamber roof closed). However, before the TME could be injected, rapid glyoxal production ensued with the glyoxal concentration reaching 45 ppbv before the chamber was flushed clean (see Fig. S1 in the Supplement). The glyoxal is thought to have come from the reaction of O_3 with an impurity in the C_2H_2 (since several ppmv of C_2H_2 were added to the chamber an impurity with a relatively moderate yield of glyoxal would only have need to be 1 % of the C_2H_2 added). Several of these impurities were detected by FTIR including 60 ppbv of ethene and 160 ppbv of acetone. The ozonolysis of ethene produces OH and likely then reacted with acetylene, which produces glyoxal as well as regenerates OH.

3.2.6 Determination of precision and detection limits

Experiment 8b investigated the precision and detection limits of the various instruments by the injection of ~60 ppbv of glyoxal followed by an overnight flush of the chamber (4000 lpm flush rate) with all of the instruments measuring continuously in their normal operating set up until the following morning. A time series of the data is shown in Fig. S2 as part of the Supplement. Experiment E8b allowed for the acquisition of several hours of data in a clean chamber. From these baseline data (02:00 to 06:00 UTC) histograms were calculated for each of the instruments with available data. A Gaussian function was fitted to the histograms except in the case of the FT-IR, where the spread of data did not form a Gaussian distribution and instead a simple average and standard deviation were calculated.

From the Gaussian distribution the standard deviation and mean were calculated for each instrument (see Fig. 9 for glyoxal and Fig. 10 for methyl glyoxal, also using data from Exp. E8b). The limit of detection (LOD) is defined as follows:

$$\mathrm{LOD}_{\mathrm{exp}} = 3 \cdot \sigma_{\mathrm{Gaussian}}. \quad (7)$$

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Unless otherwise noted we refer to 1-sigma standard deviations for errors and 3-σ is used as the accepted definition of detection limit (Eq. 7). We employ 95 % confidence intervals in assessing differences between methods. LODs for each instrument are given in Table 4 and discussed in more detail in the next section.

4 Discussion

4.1 UV-vis vs. IR absorption cross-sections

The NCAR set of experiments compared 3 different calibration sources: (1) UV-vis absorption cross-section, (2) infrared absorption cross-section, and (3) PTR-ToF-MS activity related calibrations (from predicted reactivity of methyl glyoxal with H_3O^+). For glyoxal, the high-resolution UV-visible cross-section (Volkamer et al., 2005b) was adjusted to the instrument resolution of CE-DOAS by convolution with the instrument line-shape function (FWHM $\sim$0.5 nm, characterized by the Hg atomic emission line at 435 nm or Cd lamp line at 480 nm). The UV absorption line strengths have previously been compared directly to IR line strengths by observing an identical gas-mixture in both spectral ranges simultaneously (Volkamer et al., 2005b). The integrated glyoxal IR cross-sections near 2830 cm^{-1} (used to calibrate the EUPHORE FTIR) is 1.75×10^{-17} cm molecule^{-1} (base *e*, 2726–2922 cm^{-1}, see Profeta et al., 2011, more details for energy ranges). The integrated glyoxal IR cross-section near 1740 cm^{-1} (used to calibrate the NCAR FTIR) is 2.33×10^{-17} cm molecule^{-1}. This is 4.6 % higher than the values reported by Niki et al. (1985), 2.6 % higher than the integral IR cross-section reported by Volkamer et al. (2005), and 1.6 % lower than the IR cross-sections measured by Pacific Northwest National Laboratory (Profeta et al., 2011). The correlations for CE-DOAS and FT-IR (Table 3) from NCAR experiments agree within 2 ± 2 % at all temperatures (293–330 K). This excellent agreement demonstrates that the absolute cross-sections in either spectral range are well known. We conclude that the uncertainty in the UV and IR spectral parameters is consistent with the error budget

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of 3 % uncertainty for absorption cross-sections at the visible and IR spectral ranges (Volkamer et al., 2005b).

Measurements of methyl glyoxal in this study are calibrated using an integrated IR cross-section of 7.88×10^{-18} cm molecule^{-1} near 2830 cm^{-1} to calibrate the EUPHORE FTIR, and 2.58×10^{-17} cm molecule^{-1} near 1740 cm^{-1} to calibrate the NCAR FTIR. Direct comparison of the EUPHORE and NCAR IR spectra showed a factor of 0.78 difference, which was traced to a near identical correction factor that had previously been applied to the EUPHORE-IR spectrum (see Sect. 2.1.8). This factor comes from the use of an older cross-section (Raber, 1992) and cross-calibration with the W-DOAS system. We note that the NCAR IR cross-section spectrum is 4 % lower than the IR cross-section measured at Pacific Northwest National Laboratory (PNNL) (Profeta et al., 2011), and further agrees well with other studies (Raber, 1992; Talukdar et al., 2011). After re-normalization (eliminating the factor 0.78) the EUPHORE IR spectrum agrees well with the other IR spectra (Profeta et al., 2011; Talukdar et al., 2011). Further, the NCAR experiments provide a first temperature dependent cross-calibration of the vis- and IR spectral ranges for methyl glyoxal. The correlations for NCAR experiments find no evidence for a temperature effect, and slopes are unity with 1 % error. The vis spectrum by Meller et al. (1991) results in a near identical calibration for CE-DOAS as the above integral IR cross section for the NCAR FTIR. Finally, ion-molecule rate constant calculations for the reaction of methyl glyoxal with H_3O^+ result in slopes between PTR-ToF-MS and CE-DOAS of 0.95 ± 0.03; this is essentially unity at the 95 % confidence level. Six independent sources of calibration are therefore consistent within 5 %, which we interpret as an upper limit for the uncertainty in the vis- and IR cross sections of methyl glyoxal, and as the uncertainty in the ion-molecule rate constant (rate = 1.47×10^{-9} cm^3 s^{-1}). Based on the comprehensive evidence we recommend the following integrated IR cross-section values for use in future studies: 3.0×10^{-17} cm molecule^{-1} near 1740 cm^{-1}; 9.9 x10^{-18} cm molecule^{-1} near 2830 cm^{-1}.

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4.2 Precision, accuracy, and limit of detection

The methods underlying determination of detection limits for instruments compared in this study differ, and hence values reported for limit of detection, LOD, in the literature are not easily comparable. The simultaneous observation of the same air mass provides an opportunity to calculate LOD using a consistent definition, i.e., LOD = $3 \cdot 1\text{-}\sigma$ variability + background. Here "variability" is assessed during a period when the sensor signal is expected to be constant. This definition represents the only way to define LOD for single-channel instruments (e.g. fluorescence, chemiluminescence, phosphorescence, and voltammetry), and is widely used in analytical chemistry (IUPAC, 2006). It also is closely related to the fit-error from spectral fitting of multi-channel detectors. These multi-channel sensors, however, can leverage additional information (channels, through spectral fitting) to define LOD, for example, accounting for systematic residual structures that may remain after all known absorbers have been accounted for. Such structures – if present – inform on the potential for systematic bias due to spectral cross-correlation (see Sect. 4 in Thalman and Volkamer, 2010). Any deviation from pure white-noise residuals can be accessed from multi-channel sensors, and provides additional information to assess LOD from a perspective of "accuracy". These different definitions can lead to a factor of 6 difference between notations for LOD numbers reported in the literature (Stutz and Platt, 1996; Thalman and Volkamer, 2010).

We used Eq. (7) to calculate experimental LODs using the 1-σ variability of data from the overnight dilution experiment on 5–6 July 2011 (E8b; see Fig. S2 in the Supplement). These experimental LODs are listed together with LOD values submitted with their measurement data by the operators of the various instruments. We find excellent agreement between the experimental LODs determined here and the reported LODs, once a common definition is applied. As seen in Figs. 9 and 10, the distributions are Gaussian (except for FTIR) and yielded LODs lower than or similar to the values reported for each instrument (see Table 4). All instruments performed within their specifications.

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For the Mad-LIP instrument problems caused by the initially low flows prevented noticing that the multi-pass optics in the LIP cell were degraded. Testing after the field campaign confirmed that mirror degradation had a two-fold effect in that the background scatter was increased and the effective laser-power reduced. Both factors reduce the LOD explaining the difference between the LOD reported in Henry et al. (2012) and the value in Table 4. The variability of the slope of the LIP instrument is attributed to alignment variations of the multi-pass cell. Changes in alignment affect the net laser power in the detection volume and are hard to account for. Such alignment changes resulted from the instrument maintenance performed during the intercomparison as part of the diagnostics of the flow problems and the low detection limit. Based on the results of this intercomparison a new version of Mad-LIP is using a single-cell detection axis with comparable detection efficiency but much greater stability (as demonstrated for LIF measurement of formaldehyde (Keutsch and Wolfe, 2014)).

Assessing the accuracy of an instrument is not possible without comparison to other instruments. Accuracy represents the measurement uncertainty at high signal to noise (see Ryerson et al. (2013), Thalman and Volkamer, 2010). We assess it from the variability in slopes relative to CE-DOAS, using only data from experiments where the maximum concentration is at least 10 times larger than the 1-σ variability deduced from the overnight dilution experiment (LOQ, limit of quantification). We note that all instruments during EUPHORE experiments were either calibrated directly or indirectly from the same UV-visible cross-section (Volkamer et al., 2005b). This calibration is directly accomplished by fitting the convoluted literature cross-sections for W-DOAS, CE-DOAS and BBCEAS. Calibration is less direct for FTIR (cross-section calibrated to the W-DOAS, SPME calibrated to the FTIR). Mad-LIP is calibrated by flowing a calibration gas through a ring-down cell monitoring the 440 nm absorption feature, and into the LIP instrument; UV-visible absorption by the ring-down cell is calibrated from the glyoxal or methyl glyoxal UV-visible cross-section. By relating all instruments to a common source of calibration information the experiments at EUPHORE eliminate potential for calibration bias, and isolate other (unknown) factors that may limit accuracy.

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The observed variability in slopes between experiments is usually larger than the uncertainty in the cross-section (see Sect. 4.1.). The 95 % confidence intervals of slopes are listed in Table 4 for all instruments (relative to CE-DOAS) as a measure of accuracy at high signal-to-noise. This was done by averaging these slopes relative to CE-DOAS for each instrument and assessing the confidence interval of this sample of slopes (thus omitting experiments where the correlation does not include a maximum value of at least 10 × the 1-sigma detection limit). It is generally smallest (4–7 %) for instruments which benefit from direct calibration, and larger for Mad-LIP (glyoxal: average slope = 1.06 ± 0.53; methyl glyoxal: average slope = 1.80 ± 0.58), and SPME (glyoxal: average slope = 1.14 ± 0.53; methyl glyoxal: average slope = 0.75 ± 0.18) and PTR-ToF-MS (1.23, only one measurement).

We chose CE-DOAS to assess relative differences to other instruments for the following reasons: (1) the instrument participated in both campaigns, (2) had excellent data coverage, and (3) high time resolution. Use of CE-DOAS yields the maximum number of data points to calculate correlations between different instruments at EUPHORE. Further, (4) CE-DOAS demonstrated the lowest LOD for both glyoxal and methyl glyoxal among all available instruments (see Table 4); (5) CE-DOAS benefits from inherent path length calibration through O_4 at very high signal-to-noise to demonstrate control over cavity alignment with very little error (2 %). Both CE-DOAS and BBCEAS fit most of these criteria but ultimately CE-DOAS was chosen as the reference technique to tie the two separate measurement exercises together. The comprehensive coverage and consistent performance from CE-DOAS in context with the other instruments that we compared at both chamber facilities provides strong evidence to suggest CE-DOAS is precise, and accurate. The Supplement contains a discussion of potential sources for systematic bias with CE-DOAS measurements. The resulting error of 3.5 % is dominated by the uncertainty in the absorption cross-sections, and further information is provided in the Supplement, and Fig. S4 in the Supplement.

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4.3 Interference from biacetyl and O_3

Biacetyl is formed simultaneously with glyoxal and methyl glyoxal in a complex array of other ring opening and retaining products in the photo-oxidation of *o*-xylene. We did not observe any measurable interference in detection of glyoxal and methyl glyoxal from biacetyl up to ~2 ppbv (estimated from model simulation of the chamber reaction and known yields) during Experiment E3. Most instrument slopes agreed within 10 % for glyoxal, and differences of ~20 % for Mad-LIP cannot be explained by biacetyl signals, which would result in larger than unity slopes. BBCEAS, CE-DOAS and W-DOAS are expected to be insensitive to interference from biacetyl, due to its relatively unstructured absorption cross-section (see Fig. S4 in the Supplement) and the fact that the selectivity of retrievals arises from differential absorption structures (prominent for glyoxal). Similarly, sensitivity for biacetyl by Mad-LIP had been tested previously and the lack of sensitivity (no phosphorescence) due to quenching by oxygen is consistent with findings in this study (Henry et al., 2012).

The hypothesis for this experiment was that the structure of the biacetyl absorption cross-section (Fig. S3 in the Supplement) could cause interferences for other α-dicarbonyls. For methyl glyoxal, BBCEAS and SPME during Exp. E3 were 8 and 13 % respectively lower than CE-DOAS, while FTIR and Mad-LIP showed slopes that were 30 % and 70 % higher. For FTIR, this positive bias appears to be twice as high as during Experiment E2, the only other methyl glyoxal comparison available. We note that methyl glyoxal concentrations of 8 and 12 ppbv for FTIR and Mad-LIP (see Fig. 7), respectively, during Exp. E3 are only 2–3 times above the FTIR detection limit. Thus the difference of 15 % compared to Exp. E2 can probably (at least) partially explained by systematic bias of FTIR near the detection limit as well as the complex mixture in the chamber for photo-oxidation experiments including the incomplete subtraction of water bands in the FTIR. SOA formation is unlikely to affect the optical measurements; scattering is inefficient at IR wavelengths, and a filter removes SOA in the CE-DOAS sampling line. The positive difference in slope observed for Mad-LIP currently remains

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unexplained. Previous cross-sensitivity tests did not show a measurable sensitivity of methyl glyoxal signals towards biacetyl (Henry et al., 2012). We note that Experiments E6 and E7 revealed similar or larger bias in slopes for Mad-LIP methyl glyoxal, but no biacetyl was present during Exp. E7. Hence, the differences for Mad-LIP methyl glyoxal are likely due to other reasons, and cross interference from biacetyl is difficult to judge from this dataset.

The SPME results did not show a clear trend of a bias of glyoxal and methyl glyoxal, and were found highly variable during this comparison exercise. The SPME sampling carried out during the intercomparison exercise suffered from manual manipulation and possible contamination in the period after sampling from the chamber and desorption in the GC. This effect could be more evident when measuring lower concentrations. After the campaign an automated system has been implemented to eliminate manual manipulation and has enabled the improvement of the SPME system (Borrás et al., 2014).

The only effect of flowing O_3 observed in experiment E5 was the conversion of some of the NO trapped on/in the Teflon into NO_2 that varied with the length of the inlet line. No other effect on the methyl glyoxal or glyoxal signals were observed due to O_3. It should be noted that various groups had observed that O_3 flowing in Teflon (PFA) tubing can be a source for glyoxal (observed by CU-Boulder and UW-Madison for some limited sets of tubing). However, the effect of O_3 is usually only visible at very small glyoxal concentrations (<20 pptv). A more comprehensive and systematic study on the role of O_3 at very low glyoxal concentrations warrants future research.

4.4 Interference from NO_2

Elevated NO_2 concentrations did show an effect on the concentrations of glyoxal and methyl glyoxal determined by the cavity-based instruments (CE-DOAS and BBCEAS, but not for Mad-LIP glyoxal). We quantify the bias due to NO_2 as ca. 1 pptv glyoxal/ppbv NO_2 (Fig. 4) and 5 pptv methyl glyoxal/ppbv NO_2 (Fig. 6), though the effect does not have a clear trend (see Fig. S5 in the Supplement) and is generally smaller than the

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uncertainty in the measurements. The primary effects of high NO_2 (> 10 ppbv) are due to NO_2 light extinction. This limits the attainable effective absorption path lengths, and removes photons, thus further increasing photon shot noise as well as the effects of the differential absorption structure. All of these effects lead to increasing uncertainty for measured glyoxal and methyl glyoxal. For the CE-DOAS (R = 0.999972) 200 ppbv of NO_2 changes the sample path length from 15 to 3.5 km and the light throughput is reduced by a factor 4. The combined effect is a decrease of a factor of 16 in sensitivity. For BBCEAS the effects are similar, but the reduction in path length is from 5–2.3 km (a factor of 2). At the highest level of NO_2 (~ 200 ppbv) the absorption due to NO_2 is more than 500 times greater than that due to 0.3 ppbv of glyoxal and more than 300 times greater than for 6 ppbv of methyl glyoxal. The largest effect of the NO_2 is differential absorption structure of the NO_2 is to create residual structures (both in absorption and as the wavelength dependent path length begins to follow the structure of the NO_2 extinction) that make DOAS retrievals difficult for all of the visible light absorption techniques (W-DOAS, CE-DOAS and BBCEAS) as well creating a highly structured absorption path length in the cavity based instruments (CE-DOAS and BBCEAS). For instance, the variation in the absorption path length for CE-DOAS is 35 % over the space of 3 nm with 200 ppbv of NO_2 in the instrument. Despite this difference in the differential absorption, the very small biases in glyoxal and methyl glyoxal due to NO_2 is indeed surprising, and encouraging. The Mad-LIP glyoxal measurements are unaffected by large amounts of NO_2. The FTIR showed a slight increase in the methyl glyoxal signal relative to the SF_6 tracer (Fig. 6). The W-DOAS instrument may be similarly affected by large fitting residuals due to NO_2, but the range of glyoxal used in the experiment was below the detection limit for the instrument, as was the FTIR for the glyoxal experiment and the Mad-LIP was off-line for the methyl glyoxal experiment. For the SPME the reported concentrations varied too widely to evaluate the interference.

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4.5 Relevance for α-dicarbonyl measurements in the atmosphere

Our results show that advances with measurement techniques in recent years are suitable to attempt the detection of glyoxal at ambient mixing ratios in urban, semi-polluted, biogenic, arctic and marine environments. In most urban environments the glyoxal detection by in situ UV-vis absorption techniques is feasible, i.e., there is no fundamental limitation due to typical ambient NO_2 concentrations. However, care must be taken with accurately characterizing the effect of NO_2 on the effective absorption paths, and the representation of overlapping absorption features during retrievals. Several optical techniques now facilitate the fast (few Hz) in situ detection of glyoxal. Such time resolution is suitable to conduct measurements from mobile platforms such as aircraft, or for micro-meteorological flux calculations. The first Eddy Covariance Flux measurements of glyoxal have recently been demonstrated by CE-DOAS over the remote ocean (Coburn et al., 2014).

Measurements of methyl glyoxal in the atmosphere are complicated by a short atmospheric lifetime ($\sim$ 0.5–1 h). As a result, ambient mixing ratios are comparable and often lower than those of glyoxal. Detection by optical absorption techniques at UV-vis wavelengths has limited sensitivity since the absorption cross-section of methyl glyoxal is $\sim$ 10 times lower compared to glyoxal; at IR wavelength the combination of low cross-sections and spectral overlap with other species complicates measurements of low ambient concentrations. Detection by phosphorescence is complicated by significant interferences from glyoxal that renders calibration factors too strong a function of environmental conditions to facilitate a meaningful quantification of methyl glyoxal in the presence of glyoxal. Detection by PTR-ToF-MS has the issue of coincidental masses from reaction intermediates and the fragmentation of larger compounds upon protonation in the mass spectrometer. There still remains a need to develop highly time-resolved on-line measurements of methyl glyoxal at ambient mixing ratio levels.

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5 Conclusions

During two separate inter-comparison campaigns nine instruments that measured α-dicarbonyls were compared (3 at NCAR, 7 at EUPHORE; CE-DOAS participated in both campaigns). The nine instruments used three independent sources of calibration (see Sect. 4.1), and additional comparisons with calibrations of literature cross-section data were conducted. Systematic bias between techniques was eliminated by observing the same air volume, and calibration bias was minimized as far as possible by relating the calibrations of most instruments at EUPHORE (except the PTR-ToF-MS for methyl glyoxal) to the UV-vis absorption cross-sections. We conclude:

1. The absorption cross-section spectra for glyoxal and methyl glyoxal at Vis and IR wavelengths are robust. Simultaneous measurements at vis and IR wavelengths agree within 2 ± 3 % for glyoxal, and within 1 ± 4 % for methyl glyoxal. No evidence is found for a temperature effect over the range from 293 K to 330 K in either glyoxal or methyl glyoxal cross-sections. Further, the NCAR PTR-ToF-MS calibration based on a theoretical calculation of the proton affinity of methyl glyoxal agrees with visible and IR calibrations within 5 %.

2. Seven instruments at EUPHORE used a common source for calibration from the same UV-visible spectrum for glyoxal (Volkamer et al., 2005b) and methyl glyoxal (Meller et al., 1991). We find excellent linearity between all instruments under idealized conditions (pure glyoxal or methyl glyoxal, $R^2 > 0.96$), and in complex gas mixtures characteristic of dry photochemical smog systems (o-xylene/NO_x and isoprene/NO_x, $R^2 > 0.95$; $R^2 \sim 0.65$ for offline SPME measurements of methyl glyoxal). The correlations are slightly more variable in humid ambient air mixtures (RH > 45 %) for methyl glyoxal ($0.58 < R^2 < 0.68$) than for glyoxal ($0.79 < R^2 < 0.99$).

3. The intercepts of correlations were largely found to be insignificant (below experimentally determined detection limits), and slopes varied by less than 5 % for NO_2.

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For glyoxal and methyl glyoxal the slopes varied by 12 % and 17 % (3-sigma), respectively, between inherently calibrated instruments (i.e., direct calibration from the absorption cross-section). A larger variability is found among techniques that employ external calibration sources (75–90 %, 3-sigma), and/or offline analysis (SPME); we identify ~ 80 % high-bias in Mad-LIP methyl glyoxal (see Sects. 2.1.6 and 4.2). Instrument specific differences are 4–20 times larger than the uncertainty in the cross-sections. We conclude that the accuracy of calibration procedures can introduce systematic bias as large as a factor of 2 for both glyoxal and methyl glyoxal.

4. Differences in reports about precision and detection limits (LOD) in the literature are evaluated, and can lead to differences in perceived instrument sensitivities as large as a factor of 4–5 (Table 4). The accuracy of instruments is found to vary between 3.5 % and up to a factor of 2, depending on the instrument and species.

5. No evidence for systematic bias in α-dicarbonyl quantification is found upon addition of NO_2, water vapour (H_2O), O_3, or biacetyl under atmospherically relevant concentrations. At the moderate relative humidity conditions investigated here (45 % to 58 % RH) no evidence is found that glyoxal or methyl glyoxal is removed by aerosol filters placed into sampling lines if these filters are changed routinely based on the good agreement of CE-DOAS (filtered) and BBCEAS (unfiltered).

There is a need to develop fast on-line measurement techniques capable of detecting selectively methyl glyoxal at low ambient concentrations. Future studies should further investigate in detail the effect of O_3 and H_2O at very low concentrations of α-dicarbonyls (< 20 pptv) and high relative humidity (> 80 % RH), when losses/formation of α-dicarbonyls in sampling lines or to/from aerosol filters are likely to be more relevant. Further, measurements in the visible spectral range (420 to 470 nm) would benefit from better knowledge about molecular spectroscopic parameters of H_2O, which in particular at high RH can limit the attainable detection sensitivity.

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Table 1. Instrumentation and measured species at NCAR and EUPHORE.

Instrument[a]	Participant[b]	Location	Measured Species[c]	Measured quantity	Sample location
CE-DOAS	CU	NCAR	G,M, N	[d]	Outside
NCAR FTIR	NCAR	NCAR	G, M, N	[d]	Inside
PTR-ToF-MS	NCAR	NCAR	M	[e]	Outside
CE-DOAS	CU	EUPHORE	G, M, N	[d]	Outside Edge
BBCEAS	Leic	EUPHORE	G, M, N	[d]	Center
PTR-ToF-MS	Leic	EUPHORE	M	[e]	Outside Edge
Mad-LIP	UW	EUPHORE	G, M	[d]	Outside Edge
W-DOAS	CEAM	EUPHORE	G, M, N	[d]	Inside
EUPHORE FTIR	CEAM	EUPHORE	G, M	[d]	Inside
SPME/GC-FID	CEAM	EUPHORE	G, M	[e]	Outside Edge

[a] Abbreviations given in the text.
[b] Participants (CU – University of Colorado Boulder, USA; NCAR – National Center for Atmospheric Research, Boulder, CO, USA; Leic – University of Leicester, UK; CEAM – CEAM, Spain).
[c] G – glyoxal (GLY), M – methyl glyoxal (MGLY), N – NO_2.
[d] Concentration (molecule cm^{-3}).
[e] Volume mixing ratio referenced to temperature and pressure of the chamber as measured in the chamber.

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Table 2. Overview and description of experiments at NCAR(N) and EUPHORE(E).

Exp #	Date	Experiment Name	Description
N1	14 Jan 2011	Hydroxyacetone (HACET) + Cl	Methyl glyoxal comparison at 295 K
N2	14 Jan 2011	C_2H_2 + Cl	Glyoxal comparison at 295 K
N3	14 Jan 2011	C_2H_2 + OH	Glyoxal comparison at 295 K
N4	2 Feb 2011	HACET + Cl	Methyl glyoxal comparison at 295 K
N5	4 Feb 2011	HACET + Cl	Methyl glyoxal comparison at 295 K
N6	9 Mar 2012	C_2H_2 + Cl	Glyoxal comparison at 295 K
N7	9 Mar 2012	HACET + Cl	Methyl glyoxal comparison at 295 K
N8	22 Mar 2012	HACET + Cl	Methyl glyoxal comparison at 320 K
N9	22 Mar 2012	C_2H_2 + Cl	Glyoxal comparison at 320 K
E1[a]	24 Jun 11	Glyoxal Inter-comparison	Injection of 40 pbbv of glyoxal followed by dilution to 10's of pptv
E2[a]	27 Jun 2011	Methyl Glyoxal Inter-comparison	Injection of 20 ppbv of methyl glyoxal followed by sequential dilution to 100 pptv
E3[b]	28 Jun 2011	*o*-xylene oxidation	photo-oxidation of *o*-xylene
E4[b]	29 Jun 2011	Isoprene, High NO_x	In-situ generation of products of isoprene oxidation under high-NO_x conditions. OH production by photolysis of injected HONO.
E5[b]	30 Jun 2011	O_3 (A); O_3 + C_2H_2 (B)	(A) Chamber (Teflon) plus ozone and line residence times; (B) In-situ generation of glyoxal from the reaction of OH + acetylene (OH from TME + O_3) in the presence of ozone in the dark
E6[b]	1 Jul 2011	Ambient Air	Ambient Air filling the chamber followed by addition of NO_x and Isoprene (80 µL)
E7[b]	4 Jul 2011	Isoprene, NO_x Control	Repeat of E4 with NO_x control working and lower initial isoprene to keep at lower NO_x levels in the chamber
E8a[a]	5 Jul 2011	Glyoxal Inter-comparison	Repeat of Exp 1
E8b[a]	5–6 Jul 2011	Glyoxal overnight dilution	Injection of 55 ppbv glyoxal and dilution overnight
E9[a]	6 Jul 2011	NO_2 interference with glyoxal	Addition of 10–200 ppbv of NO_2 on top of ~ 300 pptv glyoxal
E10[a]	6 Jul 2011	NO_2 interference with Methyl Glyoxal	Repeat of E9 with the addition of 10–200 ppbv of NO_2 on top of ~ 5 ppbv methyl glyoxal

[a] Experiments with injection of glyoxal or methyl glyoxal.
[b] Experiments with in-situ production of glyoxal/methyl glyoxal.

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Table 3. Correlation data for instruments vs. CE-DOAS for individual experiments.

Exp #	Species	Instrument	# pts	Slope	Intercept (ppbv)	R^2	Avg t (min)
Pure compound experiments							
NCAR[a]	GLY	FT-IR	19	1.02(2)	$5(4) \times 10^{11}$[b]	0.996	4
NCAR[a]	MGLY	FT-IR	25	1.00(1)	$1.2(7) \times 10^{12}$[b]	0.996	4
N7	MGLY	PTR-ToF-MS	5	0.95(3)	$8.5(10) \times 10^{12}$[b]	0.997	4
NCAR[a]	NO_2	FT-IR	80	1.06(2)	$-2(4) \times 10^{12}$[b]	0.98	4
E1	GLY	BBCEAS	492	0.970(2)	−0.005(2)	0.9997	1
E1	GLY	Mad-LIP	338	0.82(1)	−0.003(1)	0.9998	1
E1	GLY	W-DOAS	284	0.917(3)	−0.06(1)	0.9998	1.5
E1	GLY	FT-IR	13	0.98(3)	0.1(7)	0.999	10
E1	GLY	SPME	15	0.95(10)	−0.01(1)	0.996	5
E1	GLY	CE-DOASb[e]	492	0.98(1)	0.17(10)	0.998	1
E8a	GLY	BBCEAS	546	0.967(5)	−0.012(2)	0.9998	1
E8a	GLY	Mad-LIP	528	1.11(2)	−0.002(3)	0.998	1
E8a	GLY	W-DOAS	239	0.916(7)	−0.07(2)	0.998	1.5
E8a	GLY	FT-IR[c]	53[c]	0.99(2)[c]	−0.2(1)[c]	0.992	10
E8a	GLY	SPME	14	0.85(8)	0.00(1)	0.998	10
E8a low[d]	GLY	BBCEAS	316	1.009(9)	−0.021(3)	0.9994	1
E8a low[d]	GLY	Mad-LIP	239	1.17(2)	−0.006(4)	0.997	1
E8a low[d]	GLY	W-DOAS	144	0.68(5)	−0.03(2)	0.87	1.5
E2	MGLY	BBCEAS	503	1.010(3)	0.36(2)	0.9987	1
E2	MGLY	Mad-LIP	503	1.43(2)	−0.08(3)	0.997	1
E2	MGLY	FT-IR	55[c]	1.174(13)[c]	0.65(13)[c]	0.996	10
E2	MGLY	PTR-ToF-MS	375	1.231(5)	−1.05(2)	0.96	10
E2	MGLY	W-DOAS	228	0.97(3)	−0.2	0.96	1.5

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Table 3. Continued.

Exp #	Species	Instrument	# pts	Slope	Intercept (ppbv)	R^2	Avg t (min)
Mixed compound experiments							
E3	GLY	BBCEAS	348	0.988(3)	−0.012(2)	0.999	1
E3	GLY	Mad-LIP	211	0.83(1)	−0.034(2)	0.998	1
E3	GLY	W-DOAS	240	0.88(2)	−0.22(8)	0.97	1.5
E3	GLY	FT-IR[c]	58[c]	1.5(1)[c]	0.95(10)[c]	0.88[c]	10
E3	GLY	SPME	10	1.1(2)	0.08(2)	0.98	5
E3	MGLY	BBCEAS	316	0.92(2)	0.17(2)	0.97	1
E3	MGLY	Mad-LIP	240	1.66(3)	0.13(4)	0.95	1
E3	MGLY	FT-IR	58	1.3(1)	0.3(1)	0.99	10
E3	MGLY	SPME	10	0.86(13)	0.5(1)	0.65	5
E3	NO_2	BBCEAS	345	1.0087(8)	0.046(3)	0.998	1
E3	NO_2	W-DOAS	240	0.95(1)	0.14(2)	0.994	1.5
E5	GLY	BBCEAS	567	1.023(4)	−0.053(2)	0.99995	1
E5	GLY	Mad-LIP	241	[f]	[f]	[f]	1
E5	GLY	FT-IR	79	1.07(1)	−0.4(1)	0.998	10
E6	NO_2	BBCEAS	505	0.98(2)	0.02(2)	0.995	1
E6	GLY	BBCEAS	505	0.95(1)	−0.19(4)	0.987	1
E6	GLY	Mad-LIP	308	1.09(2)	−0.005(5)	0.97	1.5
E6	GLY	SPME	14	1.5(2)	0.04(5)	0.79	5
E6	MGLY	BBCEAS	505	0.68(3)	0.17(5)	0.68	1
E6	MGLY	Mad-LIP	308	1.90(6)	−0.1(1)	0.58	1.5
E6	MGLY	SPME	14	0.7(2)	0.2(2)	0.69	5
E7	NO_2	BBCEAS	553	0.985(4)	−0.27(1)	0.999	1
E7	GLY	BBCEAS	553	0.927(3)	−0.034(3)	0.999	1
E7	GLY	Mad-LIP	326	1.47(2)	−0.033(6)	0.993	1.5
E7	GLY	FT-IR[c]	111[c]	2.5(1)[c]	−0.2(1)[c]	0.93[c]	10
E7	GLY	SPME	10	1.3(1)	0.04(4)	0.95	5
E7	MGLY	BBCEAS	553	0.92(1)	−0.20(4)	0.987	1
E7	MGLY	Mad-LIP	326	2.21(4)	0.6(1)	0.98	1.5
E7	MGLY	FT-IR[c]	111[c]	0.68(4)[c]	−0.6(2)[c]	0.84[c]	10
E7	MGLY	SPME	14	0.7(1)	1.3(5)	0.65	5

Number in is the 1-σ uncertainty of the last digit of the number.
[a] NCAR experiment data is pooled over experiments listed in Table 2 (for GLY and MGLY) or for all oxidation experiments in 2011 and 2012 (30 + experiments at 3 different chamber temperatures).
[b] Intercepts in molecules cm^{-3} due to the constant volume of the chamber and the changing pressure and temperature over the course of more than 30 different experiments (as described in note a).
[c] Experiment near detection limit.
[d] Only concentrations below 2 ppbv fitted for instruments with applicable detection limits.
[e] Results from fit of the weak glyoxal bands (see Sect. 2.1.3).
[f] Result is non-linear, Fig. S1 in Supplement.

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Table 4. Detection limits of all instruments at NCAR and EUPHORE.

Instrument[b]	Precision (ppbv) GLY LOD_{report}[c]/LOD_{exp}[d]	MGLY LOD_{report}[c]/LOD_{exp}[d]	Accuracy (%)[a] GLY	MGLY	Time (min.)
CE-DOAS	0.015/0.012	0.15/0.27	–	–	1
NCAR FT-IR	50/**–**	92/–	–	–	4
NCAR PTR-ToF-MS[d]	–	–/1.2	–	–	0.167
CE-DOAS	0.015/0.012	0.21/0.27	–	–	1
BBCEAS	0.75/0.045	1.0/0.6	7	10[e]	1
PTR-ToF-MS	–	0.53/**5.3**	–	–	1
Mad-LIP	0.06/0.038	1.2/0.9	53	80[e]	1
W-DOAS	0.4/0.3	6.0/–	4	–	1.5
EUPHORE FTIR	2.5/1.1	2.7/–	150	70	10
SPME with GC-FID detection	0.1/–	0.15/–	50	20	10

[a] Accuracy evaluated as the 95 % C.I. of the fitted slopes.
[b] Abbreviations given in the text.
[c] Reported Detection Limits 3σ.
[d] LOD measured during Exp 8b from Histograms in Figs. 9 and 10 for EUPHORE experiments and as the LOD in the instruments for other background data for NCAR (LOD = 3σ, ppbv, see Sect. 4.2).
[e] Omits Exp. E6 due to the lack of variability in the MGLY concentration (see Fig. 8c).

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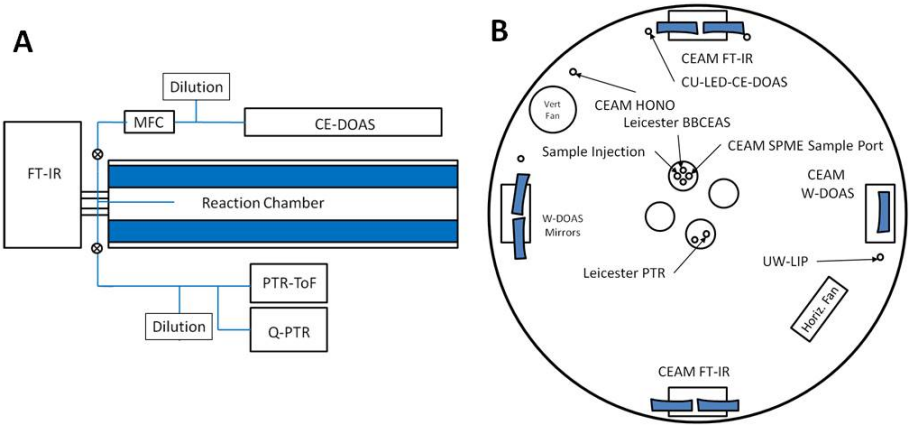

Figure 1. Layout of instruments at NCAR **(a)** and EUPHORE **(b)**. In **(b)** small circles indicate sampling ports; the EUPHORE FTIR, W-DOAS and NCAR-FTIR light paths cross the entire chamber, while other instruments draw air from the chamber for analysis below/outside the chamber.

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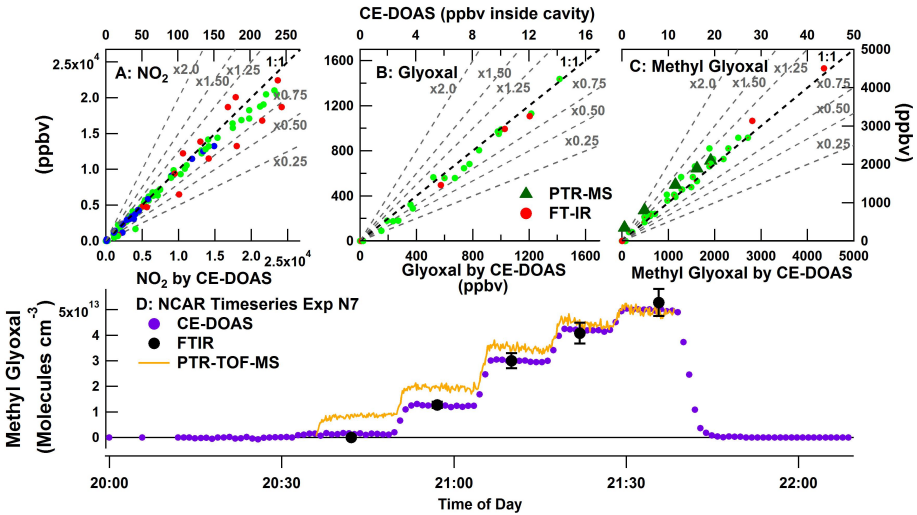

Figure 2. Correlation of FT-IR and PTR-ToF-MS relative to CE-DOAS for Experiments N1–N9 at NCAR (NO_2 includes additional experiments, see text). Data from individual experiments have been pooled at different temperatures. **(a–c)** FT-IR (dots), PTR-ToF-MS (triangles), three temperatures (blue – 260 K, green – 293 K, red – 330 K). **(d)** Shows a time series for experiment N7 to produce methyl glyoxal. Units of fit intercepts in **(a–c)** (molecules cm^{-3}) have been converted to volume mixing ratios using the chamber temperature and pressure measured inside the chamber.

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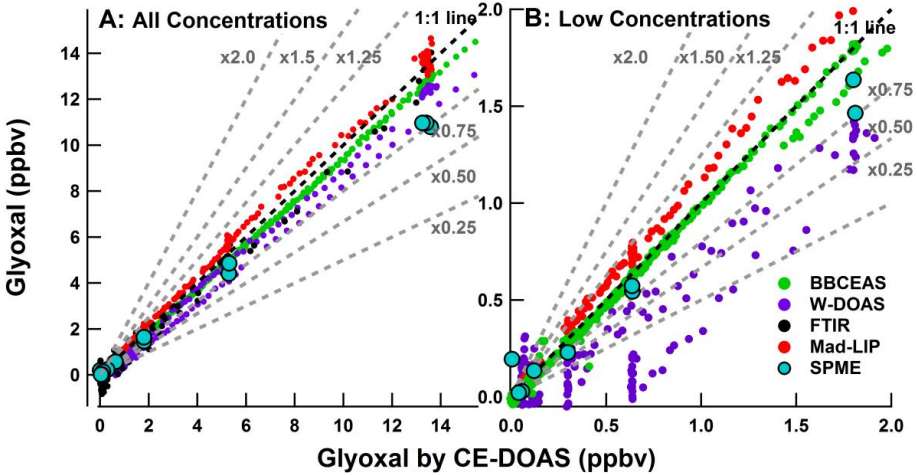

Figure 3. Correlations for the glyoxal comparison experiment E8a (see Fig. S2 in the Supplement for a time series of these points). **(a)** Shows the full concentration range; **(b)** shows concentrations below 2 ppbv. Data are only shown from instruments where the maximum concentration exceeds the LOQ (see Sect. 4.2).

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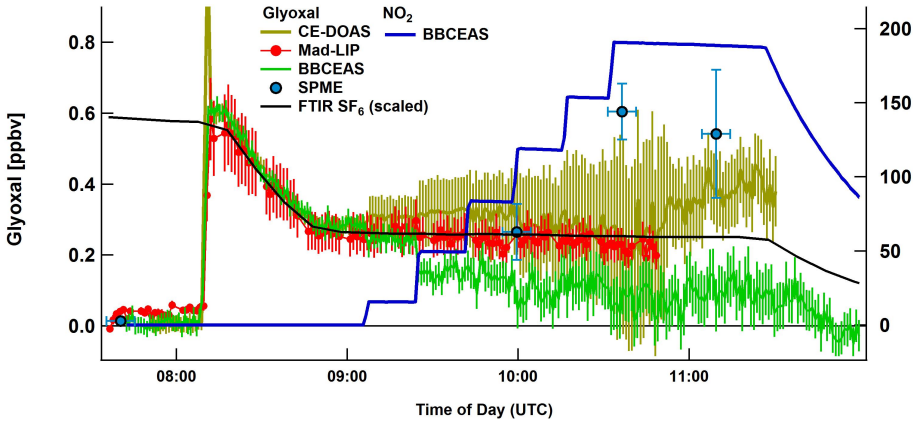

Figure 4. Sensitivity of glyoxal to high levels of NO_2 (Experiment E9). Chamber dilution has been scaled relative to concentrations at 0815 from the decay of the SF_6 tracer. See text for details.

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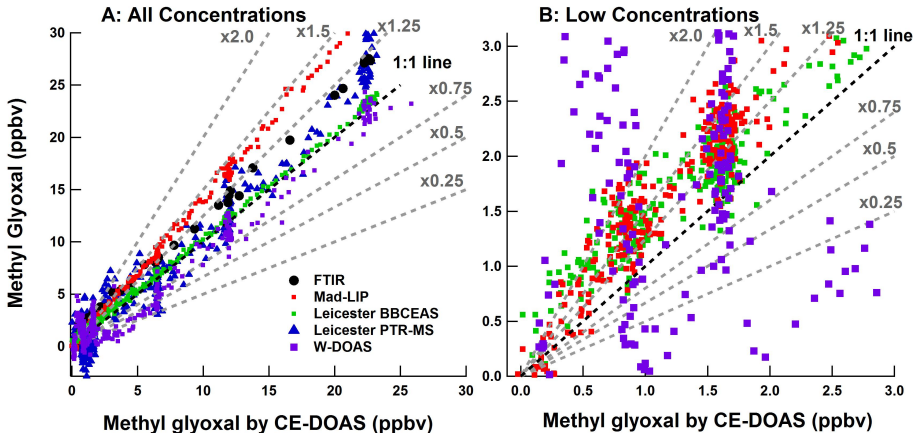

Figure 5. Correlation plots for methyl glyoxal comparison Experiment E2. **(a)** Shows the full range of measured concentrations, while **(b)** shows only concentrations below 3 ppbv. Only data is shown from instruments where the maximum concentration exceeds the LOQ (see Sect. 4.2).

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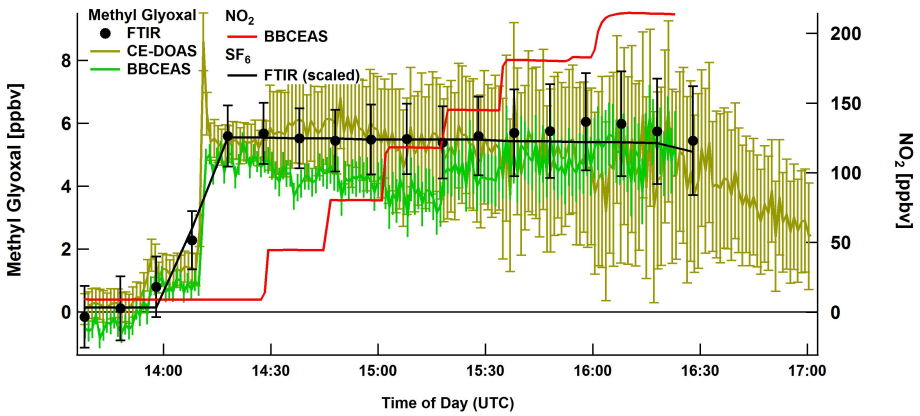

Figure 6. Sensitivity of methyl glyoxal to high levels of NO_2 from experiment E10. Chamber dilution has been scaled relative to concentrations at 14 : 10 from the decay of the SF_6 tracer. See text for details.

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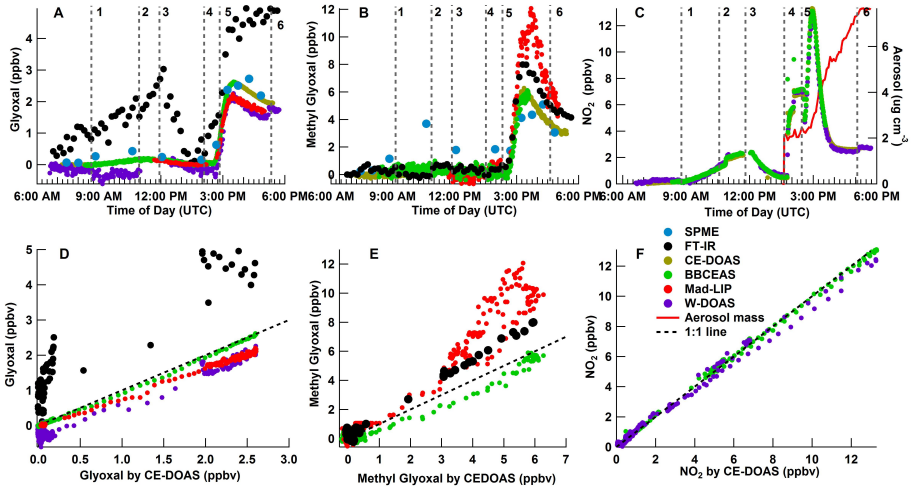

Figure 7. Dry photo-oxidation of *o*-xylene during Experiment E3. **(a–c)** Show the time traces of glyoxal, methyl glyoxal and NO_2, respectively. **(d–f)** Show the correlation plots of the respective compounds. E3 began in the morning with a clean, flushed chamber. The chamber roof was opened (1) while clean and the build-up of NO_2 and other contaminates was observed and then closed (2) and flushed clean (3). In the afternoon, HONO was added to the chamber (4) and with it some NO_2, then the chamber roof was opened (5) to initiate the photo-chemistry and closed to finish the experiment (6).

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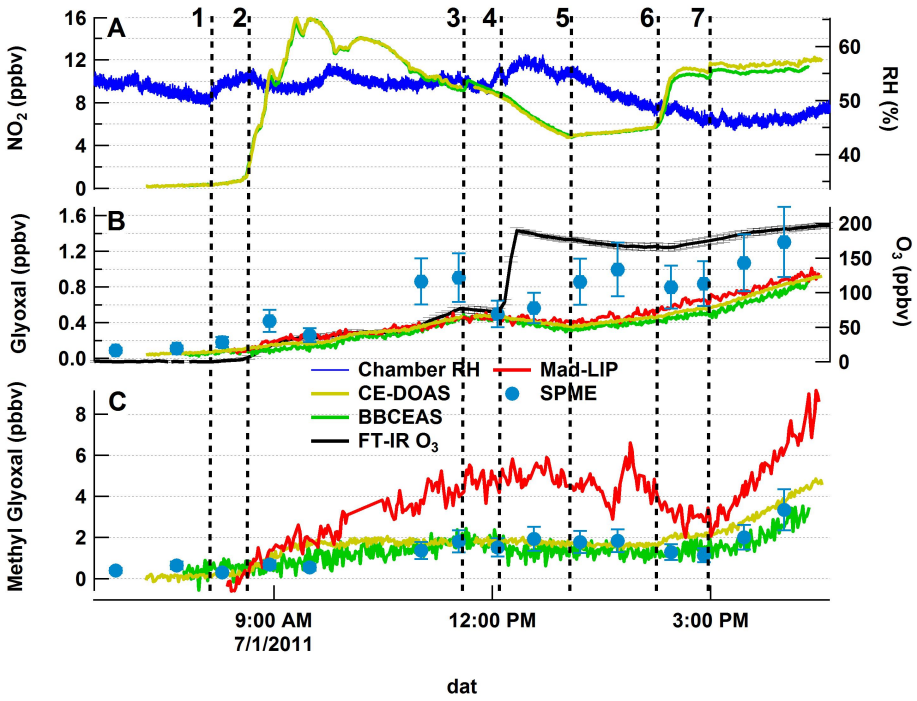

Figure 8. Ambient air experiment E6. **(a)** shows the NO_2 and relative humidity, **(b)** glyoxal and ozone, and **(c)** methyl glyoxal. The chamber operations for the day were as follows: (1) chamber roof open, (2) ambient air introduction, (3) chamber roof closed, (4) O_3 injection, (5) chamber roof open, (6) NO_x control on (HONO injection), (7) isoprene injection.

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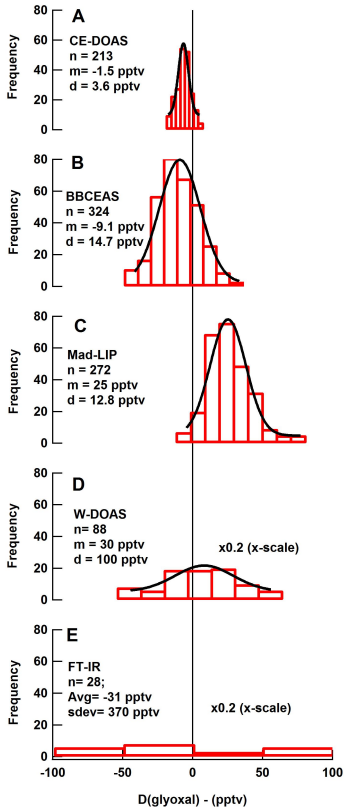

Figure 9. Histograms of glyoxal baseline variability during experiment E8b, 5 July 2011 from 02:00–06:00 UTC. The instruments sampled from a clean chamber. The number of points in the distribution (n), the mean (m) and 1-σ standard deviation (d) are listed on each graph, and experimentally determined limits of detection as quoted in Table 4 were calculated as $LOD_{exp} = 3 \cdot d$. The time series of the data used to produce the histograms is shown in Fig. S2 in the Supplement.

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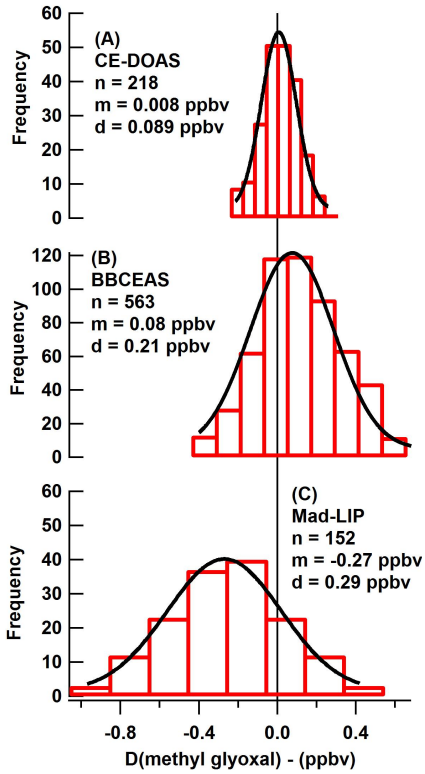

Figure 10. Histograms of methyl glyoxal baseline variability in experiment E8b. The number of points in the distribution (n), the mean (m) in ppbv and 1 standard deviation (d) of the distribution are listed in each panel (**a**: CE-DOAS; **b**: BBCEAS; **c**: Mad-LIP). Histogram distributions are used to calculate experimentally determined limits of detection as $LOD_{exp} = 3 \cdot d$.

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