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**Atmospheric
Chemistry
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Photochemical modeling of glyoxal at a rural site: observations and analysis from BEARPEX 2007

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Abstract. We present roughly one month of high time-resolution, direct, in situ measurements of gas-phase glyoxal acquired during the BEARPEX 2007 field campaign. The research site, located on a ponderosa pine plantation in the Sierra Nevada mountains, is strongly influenced by biogenic volatile organic compounds (BVOCs); thus this data adds to the few existing measurements of glyoxal in BVOC-dominated areas. The short lifetime of glyoxal of ∼1 h, the fact that glyoxal mixing ratios are much higher during high temperature periods, and the results of a photochemi-

cal model demonstrate that glyoxal is strongly influenced by BVOC precursors during high temperature periods.

A zero-dimensional box model using near-explicit chemistry from the Leeds Master Chemical Mechanism v3.1 was used to investigate the processes controlling glyoxal chemistry during BEARPEX 2007. The model showed that MBO is the most important glyoxal precursor (∼ 67 %), followed by isoprene (∼ 26 %) and methylchavicol (∼ 6 %), a precursor previously not commonly considered for glyoxal production. The model calculated a noon lifetime for glyoxal of ∼0.9 h, making glyoxal well suited as a local tracer of VOC oxidation in a forested rural environment; however, the modeled glyoxal mixing ratios over-predicted measured glyoxal by a factor 2 to 5. Loss of glyoxal to aerosol was not found

to be significant, likely as a result of the very dry conditions, and could not explain the over-prediction. Although several parameters, such as an approximation for advection, were found to improve the model measurement discrepancy, reduction in OH was by far the most effective. Reducing model OH concentrations to half the measured values decreased the glyoxal over-prediction from a factor of 2.4 to 1.1, as well as the overprediction of HO_2 from a factor of 1.64 to 1.14. Our analysis has shown that glyoxal is particularly sensitive to OH concentration compared to other BVOC oxidation products. This relationship arises from (i) the predominantly secondary- or higher-generation production of glyoxal from (mainly OH-driven, rather than O_3-driven) BVOC oxidation at this site and (ii) the relative importance of photolysis in glyoxal loss as compared to reaction with OH. We propose that glyoxal is a useful tracer for OH-driven BVOC oxidation chemistry.

1 Introduction

Ozone (O_3) and aerosols influence climate (Intergovernmental Panel on Climate Change, 2007) and have a direct impact on human health (Bates, 1993; Jakab et al., 1995) and the biosphere (Karnosky et al., 1996; Percy et al., 2002). It is well established that the formation of O_3 and secondary organic aerosol (SOA), which is an important component of ambient aerosol (Zhang et al., 2007), are both directly tied to the gas-phase oxidation of volatile organic compounds (VOCs), in particular in the VOC-HO_x-NO_x catalytic cycle ($HO_x \equiv OH + HO_2$, $NO_x \equiv NO + NO_2$) (Kroll and Seinfeld, 2008; Wood et al., 2010; Herndon et al., 2008). Substantial challenges remain, however, in modeling SOA (de Gouw et al., 2005; Volkamer et al., 2006; Goldstein and Galbally, 2007; Carlton et al., 2009; Hallquist et al., 2009) and O_3 away from urban centers (e.g., Trainer et al., 1987; Plummer et al., 1996). The challenges for O_3 are especially pronounced in rural, forested areas with high biogenic VOC emissions, e.g., terpenes, isoprene, and 2-methyl-3-buten-2-ol (MBO), which together constitute the majority of global non-methane VOC emissions (Guenther et al., 2000). The failure of models in rural vegetated regions, where BVOC and aldehyde reactivity dominates (Steiner et al., 2008) indicates that more attention needs to be paid to primary emissions of oxygenated VOC and the secondary production of oxygenates, of which α-dicarbonyls are a subset.

Glyoxal, the smallest (α-)dicarbonyl, has a lifetime of only a few hours with respect to photolysis and reaction with OH. Thus, glyoxal can be viewed as a local tracer of VOC oxidation chemistry, which is advantageous for comparisons between models and measurements. According to commonly used mechanisms available in the literature, such as the National Center for Atmospheric Research (NCAR) Master Mechanism, Leeds Master Chemical Mechanism

(MCM), and the Mainz Isoprene Mechanism 2 (Madronich and Calvert, 1990; Bloss et al., 2005a,b; Taraborrelli et al., 2009) daytime glyoxal production from BVOCs proceeds largely via reaction of OH, while reaction with ozone contributes relatively little, making glyoxal a promising tracer of OH–driven BVOC oxidation. Furthermore, these mechanisms treat glyoxal solely as a higher generation oxidation product of isoprene, MBO and terpenes. All stages of VOC oxidation can contribute to O_3 formation, and, for example for isoprene, more than one oxidation step is required to reduce the volatility of products to the extent that partitioning-driven SOA formation is expected (e.g., Claeys et al., 2004; Edney et al., 2005; Paulot et al., 2009). Thus, glyoxal measurements in rural, forested regions can provide a local tracer of VOC oxidation chemistry, and may be used to test our understanding of higher generation oxidation processes.

In addition to the challenges of modeling ozone in forested areas dominated by BVOCs, there recently has been much focus on the often large discrepancies between measured and modeled OH radical concentrations in areas dominated by BVOCs, especially isoprene (Tan et al., 2001; Thornton et al., 2002; Ren et al., 2008; Lelieveld et al., 2008; Hofzumahaus et al., 2009; Peeters et al., 2009; Paulot et al., 2009; Peeters and Muller, 2010; Archibald et al., 2010; Stavrakou et al., 2010; da Silva, 2010; Whalley et al., 2011). Models typically underpredict OH, sometimes by up to an order of magnitude (Lelieveld et al., 2008; Whalley et al., 2011), relative to observations. A model of atmosphere-forest exchange for the measurement site of the work described here under-predicts OH by a factor of six (Wolfe et al., 2011). As OH radicals are the major oxidizing species in the troposphere this disagreement has large implications for the ability of models to accurately reproduce BVOC oxidation and resulting O_3 and SOA formation. A recent intercomparison of the different techniques employed for measuring ambient OH showed slopes in the linear regressions of the daytime measurements of different instruments of 1.01–1.13 for experiments in the SAPHIR chamber and 1.06–1.69 for ambient measurements (Schlosser et al., 2009). This demonstrates that OH continues to prove difficult to measure under all conditions. Clearly, BVOC oxidation and hence production of BVOC oxidation products (OVOCs) depends critically on oxidant concentrations, with OH being of central importance. Thus, using OVOCs as tracers of BVOC oxidation can provide insight into how rapidly BVOC oxidation is occurring, and, if the OVOCs are produced primarily via reaction of OH with BVOCs, their formation will in turn reflect ambient OH concentrations.

In addition to its use as tracer of VOC oxidation chemistry, glyoxal also is of current interest due to its potential direct contribution to SOA formation (Carlton et al., 2007; Volkamer et al., 2007; Corrigan et al., 2008; Nozière et al., 2008; Galloway et al., 2009; Shapiro et al., 2009; Tan et al., 2009). In models of SOA formation that include glyoxal, it is often a substantial contributor (Carlton et al., 2007; Volkamer et al.,

2007; Fu et al., 2008; Ervens and Volkamer, 2010). It is thus important to validate glyoxal concentrations and chemistry in models by comparison with field-measurements. As model studies show that oxidation of BVOCs contributes the majority of glyoxal on a global scale (Fu et al., 2008; Myriokefalitakis et al., 2008; Stavrakou et al., 2009) a comparison with glyoxal measurements for biogenic regions is particularly important.

The site of the Biosphere Effects on AeRosols and Photochemistry EXperiment (BEARPEX) 2007 field campaign, near Blodgett Forest Research Station (BFRS) in the Sierra Nevada, California, is located in a region influenced by high BVOC emissions, in particular of MBO and isoprene as well as terpenes (Lamanna and Goldstein, 1999; Holzinger et al., 2005; Bouvier-Brown et al., 2009) with regular and well characterized meteorology. There have been a number of studies detailing the BVOCs observed at the site (Lamanna and Goldstein, 1999; Holzinger et al., 2005; Bouvier-Brown et al., 2009) making the location ideal for a detailed study of BVOC oxidation.

In this paper we present the first fast (<1 min), high sensitivity, direct in situ measurements of glyoxal, taken using the Madison Laser-Induced Phosphorescence (MAD-LIP) Instrument (Huisman et al., 2008). We present a description of this new type of data-set for glyoxal, which provides a new point of intercomparison for models in a region dominated by BVOCs. We also present an analysis that investigated the factors influencing glyoxal concentrations at the site and employ glyoxal as a local tracer of VOC oxidation chemistry at the site, in particular with respect to oxidant levels and the sensitivity of model glyoxal concentrations to OH.

2 Measurements site and methods

2.1 Site description

Glyoxal mixing ratios were measured during the BEARPEX 2007 campaign at a research site located on a ponderosa pine plantation in the Sierra Nevada mountains, ∼ 80 km east of Sacramento, CA (38°53′42.9″ N, 120°37′57.9″ W). The site, on Sierra Pacific Industries land, is at an elevation of 1315 m and is near the Blodgett Forest Research Station (BFRS) and has been described in detail previously (Goldstein et al., 2000). It experiences a Mediterranean climate which is typically hot and dry during the summer before transitioning to a cool, wet period starting in September. During the summer, daytime wind is consistently out of the west to southwest while nighttime wind is easterly to northeasterly. The cycling of polluted air from the Central Valley that arrives in late afternoon and clean air from upslope at night leads to regular diurnal patterns in many trace gases (e.g., Lamanna and Goldstein, 1999; Dillon et al., 2002; Murphy et al., 2007; Wolfe et al., 2009).

2.2 Madison LIP instrument

Glyoxal data were collected using the Madison LIP Instrument, which has been described in detail elsewhere (Huisman et al., 2008). Briefly, gas phase glyoxal was detected via laser-induced phosphorescence and gated photon counting using a white-type multipass cell. The inherent spectral and temporal resolution of the phosphorescence signal allowed a limit of detection (3σ) of 18 ppt$_v$ in 1 min during the BEARPEX 2007 deployment. For the BEARPEX 2007 deployment, the tower portion of the Madison LIP Instrument was initially situated near the south tower, which was 10 m south of the main scaffold tower, on which all measurements to which we compare our data were made except meteorology. The inlet consisted of either 7.6 m or 1 m of 1/2 in OD PTFE tube with no filters of any kind. Field tests showed no discernible inlet effects with respect to length of inlet (cf. Huisman et al., 2008) and more recent tests have provided additional evidence that the length and material of inlet have negligible effect on the glyoxal signal. While the instrument was near the tower, it used an inlet (7.6 m 1/2 in PTFE tube) at 3.7 m above ground level (a.g.l.) on the tower, where it remained from 24 August–18 September (day of year, DOY, 236 to DOY 261. After 18 September the instrument was placed on the tower, where it remained until the end of glyoxal measurements on 27 September, DOY 270, with a short (1 m) inlet at 12.0 m a.g.l. Tests carried out in the field show that the data from 3.7 m and 12 m a.g.l. were comparable during the daytime, though not necessarily identical (Huisman et al., 2008).

2.3 Other measurement techniques

A suite of measurements was available for BEARPEX 2007, including meteorological parameters, such as wind speed and direction, air temperature, humidity, and ozone concentration. Volatile organic compounds where measured using two gas chromatographs with quadrupole mass spectrometers (GC-MS). Speciated acyl peroxy nitrate (APN) measurements were obtained via a thermal dissociation–chemical ionization mass spectrometer. Laser-induced fluorescence instrumentation was used for measurements of OH, HO$_2$ and NO$_2$. Oxygenated organic aerosol (OOA) and hydrocarbon-like organic aerosol (HOA) were obtained using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer. Aerosol surface area was estimated using a scanning mobility particle sizer and observations of boundary layer height were obtained from temperature, humidity, and wind profiles obtained with a tethersonde during BEARPEX 2007. Details of the instrumentation and methods used to obtain these data can be found in Supplement Sect. 1.1.

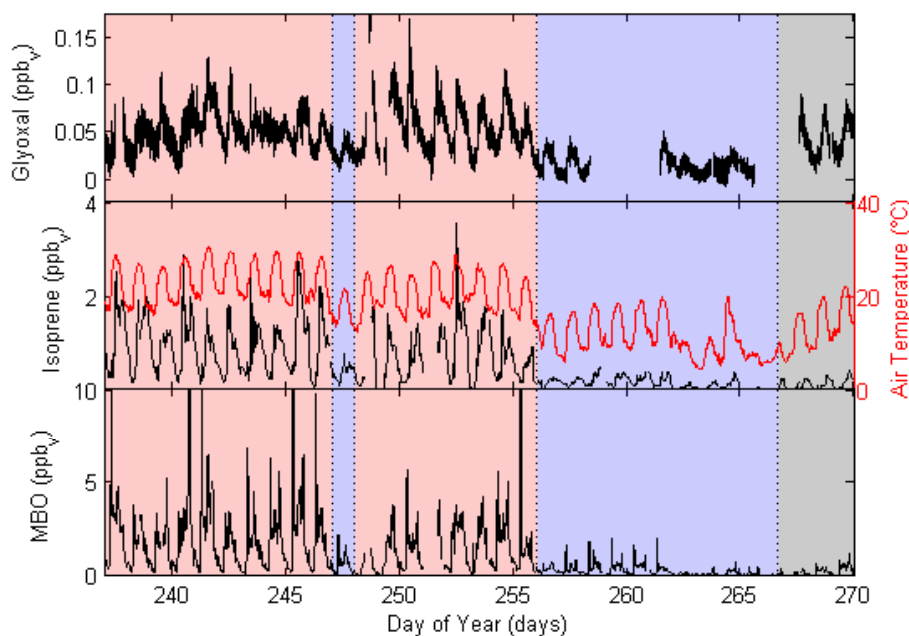**Fig. 1.** Overview of glyoxal measurements, separated by temperature period (red, blue, gray corresponding to hot, cold, and intermediate period). Isoprene and MBO, the most important glyoxal BVOC precursors, are included along with air temperature on the center axis on right.

3 Observations at BEARPEX 2007

3.1 General observations

There is only limited glyoxal data available in rural settings and to our knowledge we present the first such data obtained that has a high time resolution obtained with an instrument utilizing a direct, in situ detection method. The complete dataset for glyoxal is presented in Fig. 1 along with ambient temperature and the biogenic VOCs isoprene and MBO, which were the major precursors of glyoxal at the site. Meteorological conditions at BRFS were dry and hot for the majority of the period for which glyoxal data was collected. An abrupt change in weather occurred around DOY 256 (13 September), after which temperatures were substantially lower. The data were divided into a "hot", "cold" and "intermediate" period as defined in the following: the hot period, DOY 240–246 and 248–256, had an average high and low temperature of ~ 27, and $\sim 18\,°C$, respectively. The cold period, DOY 247, 256–257, 261–266, had an average high and low temperature of ~ 15, and $\sim 8\,°C$, respectively. No measurements were taken on DOY 258–261. The intermediate period, DOY 267–270, had an average high and low temperature of ~ 19, and $\sim 9\,°C$, respectively, closer to the cold than the hot period, but the data set was separated from the cold period because of substantially higher glyoxal mixing ratios. The cause of the higher glyoxal mixing ratios during the intermediate period remains unclear, as the average diurnal temperature and VOC profile of this period resembles that of the cold period. The raw data from the Madison LIP Instrument did not show an offset and instrument data logs indicated normal operation during this period, which followed the first rain falls of the season. The substantial change in temperature from hot to cold period provides a basis for studying the dependence of glyoxal concentrations on biogenic emissions, which are strongly tied to temperature (e.g., Guenther et al., 1991; Schade et al., 2000).

The complete dataset for glyoxal, which spans DOY 236–270, had strong diurnal trends with mean of $43.6\,ppt_v$ and median of $41.2\,ppt_v$ with 95 % bounds of the complete set of $4.6\,ppt_v$ to $121.7\,ppt_v$ (see Table 1). The measurement uncertainty was $\sim 20\,\%$. A previous measurement at this site by Spaulding et al. (2003) found glyoxal mixing ratios of $6–83\,ppt_v$ during 10 days in August and September 2000, with average mixing ratio $27 \pm 15\,ppt_v$ and a diurnal profile weaker than that observed here. The previous measurements, although occurring in a different year and with different mean temperatures than those reported here, are still within one standard deviation of our mean observations.

The BEARPEX 2007 campaign was located in a region with high BVOC emissions, in particular the glyoxal precursors isoprene and MBO. Thus a strong influence of BVOCs is expected on glyoxal at the site and comparison of the hot and cold period confirmed this (see Fig. 2): there is a large difference between hot and cold period in BVOC concentrations and OVOCs that only form from BVOCs, e.g., isoprene, MBO, MVK. Glyoxal shows a similar, but somewhat smaller difference, whereas the anthropogenic tracer propene showed
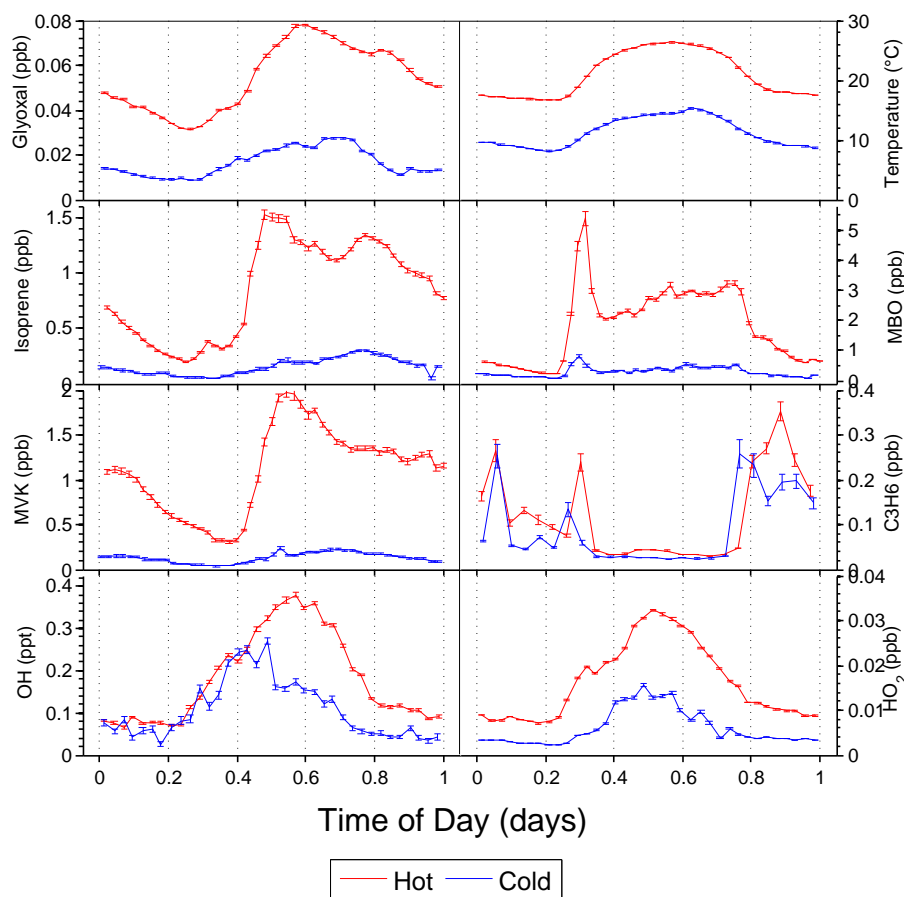
Fig. 2. Diurnal averages of glyoxal, temperature, example biogenic and anthropogenic species, and HO$_x$ separated into hot and cold period. Here the hot period spans 15 days. The cold period contains only data for which glyoxal was recorded. Error bars indicate the 1 standard deviation envelope as calculated based on the variability in the data from day to day and neglecting reported or calculated error from each measurement.

quite different behavior (see Fig. 2). Similarly, daytime concentrations of toluene at the site were essentially unchanged between the two periods, as were those of benzene and other anthropogenic precursors/tracers. Thus, the measurements qualitatively support that there was a strong biogenic influence on glyoxal at the site, and the results from the photochemical model described in Sect. 4.1 supports this.

The correlation of half-hourly glyoxal measurements to measurements of known glyoxal BVOC precursors and BVOC oxidation products were high, whereas correlations with known anthropogenic glyoxal precursors, such as toluene, benzene and acetylene were lower. During the hot period, the strongest correlation was observed with the BVOC oxidation products MPAN ($R^2 = 0.59$, $n = 362$ points), and MVK ($R^2 = 0.41$, $n = 671$), whereas correlations with anthropogenic tracers were substantially smaller (see Table S1). Hot (and cold) period glyoxal was very poorly correlated ($R^2 < 0.10$) with the total OA and OOA factors as measured by Aerosol Mass Spectrometer (AMS) (see Table S1). In addition to the poorer correlations of gly-

Table 1. Glyoxal dataset parameters by temperature period, all values in pptv.

Period	Mean	95 % bounds	
		Lower	Upper
Campaign	43.6	4.6	121.7
Hot	53.9	22.3	127.3
Cold	16.3	0.9	48.4
Intermediate	42.1	19.4	93.4

oxal with anthropogenic glyoxal precursors, the concentrations of these precursors were low, so that production rates from the BVOCs were much higher, as discussed in Sect. 4.1.

3.2 Deposition

The profile of glyoxal on many nights approximated a simple exponential decay, allowing an inference of the deposition
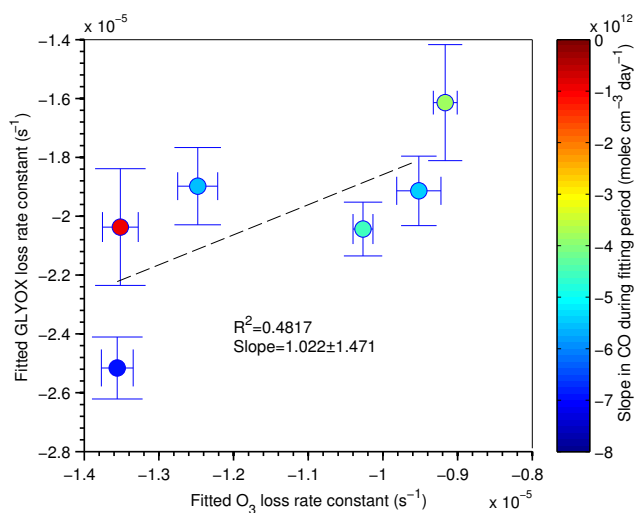
Fig. 3. Fitted deposition rates for glyoxal and O_3 from data taken at BEARPEX 2007. Color coding of points indicates the slope in CO, an indicator of the stability or dilution of the airmass.

rate by fitting in analogy to the method used by Sumner et al. (2001). Six nights were selected which could be fit well with a single-exponential decay in both glyoxal and O_3. The results of these fits are presented in Fig. 3, which also includes information on the slope of measured CO during the fitting period (0.8 to 0.2 d; 19.2 to 4.6 h), on a given night in the color of each point. It seems likely that those points exhibiting the least slope in CO indicate a consistent airmass, a requirement for using the decay to fit deposition. The average correlation coefficient between the inferred deposition rates of glyoxal and O_3, which were calculated independently, within each night was good ($R^2 = 0.68$), in agreement with the results of Sumner et al. (2001) for formaldehyde, but the overall correlation was relatively poor ($R^2 = 0.48$, $n = 6$ nights). Thus there was some degree of variability between the relative deposition rates of both glyoxal and O_3 on different nights, likely arising from the different processes which control the loss of each compound, such as reactions of O_3 with biogenic VOC (Fares et al., 2010) or loss of glyoxal to surfaces. We did not observe a relationship between RH and deposition rate of glyoxal, but this is not necessarily conclusive as we have only six points (corresponding to six nights).

The average of the fitted exponential loss rate in glyoxal was $-2.14 \times 10^{-5} \pm 2.7 \times 10^{-6}$ s^{-1}, which (assuming a nocturnal boundary layer of 70 m, Choi et al., 2010b) corresponded to a deposition velocity of approximately 0.15 cm s^{-1}, reasonably consistent with the value of Volkamer et al. (2007) of 0.3 cm s^{-1}. Equating the observed exponential decay to deposition in this manner assumes that there are no important production or loss processes, except for deposition. The photochemical model described in Sect. 4 required a deposition rate which was double that inferred here

to match the observed loss rate. This difference arises from the incorrect assumption in this analysis that no glyoxal is produced at night; in fact the average predicted nighttime production rate was approximately 10 % of the average noontime rate. The photochemical model described in Sect. 4 showed that deposition velocity of 0.3 cm s^{-1} was required to reproduce the observed loss rate, as according to the model there was slow nighttime glyoxal production.

4 Photochemical box model

We employed a photochemical model based on the reactions and kinetics in the Master Chemical Mechanism (MCM) v. 3.1 (Jenkin et al., 1997; Saunders et al., 2003) for comparison with observations to gain insight into the processes controlling glyoxal concentrations during BEARPEX 2007 and to evaluate the degree to which the MCM can be used to represent glyoxal in this rural setting. The model used the full MCM chemistry for the following species and their oxidation products: isoprene, MBO, α-pinene, β-pinene, acetylene (C_2H_2), benzene, and toluene. In addition to well-known biogenic precursors of glyoxal such as MBO and isoprene, we included methylchavicol, an oxygenated aromatic BVOC which was present in substantial concentrations (mean daily maximum of $\sim$0.3 ppb$_v$, with $\sim$0.6 ppb$_v$ as highest observed mixing ratio) during BEARPEX 2007 (Bouvier-Brown et al., 2009). Oxidation of methylchavicol by OH produces glycolaldehyde (see mechanism, Fig. S3) with a direct yield of 37 % (Lee et al., 2006). While methylchavicol does not yield as much glycolaldehyde as MBO, which has a corresponding direct yield of $\sim$ 65 % (Chan et al., 2009), it can produce additional glyoxal via higher-generation oxidation processes involving the aromatic system (see Fig. S3).

In all cases, the model was driven using half-hourly averaged observations of O_3, VOCs, campaign diurnally averaged NO_2, and temperature–period diurnally averaged OH (cf. Sect. 2 for measurement techniques and Sect. 3.1 definition of temperature periods). Different subsets of precursor VOCs were used to explore their influence and determine the main glyoxal VOC precursors. HO_2 and intermediates such as MVK were not driven to follow observations, providing comparisons of model and observations in addition to glyoxal. The model used the MCM in conjunction with standard HO_x-NO_x cycling with (a) adjustment of yields and production mechanism of glyoxal from isoprene and glycolaldehyde following Galloway et al. (2011), (b) adjustment of MPAN + OH rate constant following the recommendation of Orlando et al. (2002), (c) inclusion of dry deposition, (d) inclusion of loss of gas phase glyoxal to aerosol based on Volkamer et al. (2007), (e) diurnal dilution factor following Pérez et al. (2009), (f) inclusion of methylchavicol degradation chemistry. Details of the implementation are presented in Supplement Sect. 1.2. The model was allowed to "spin-up" to provide approximate starting concentrations for those
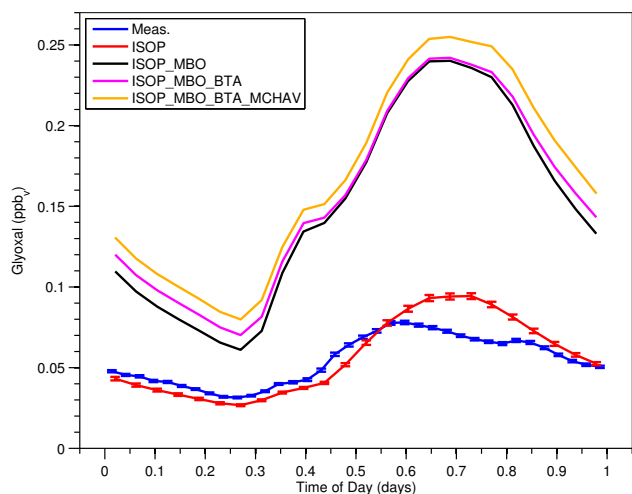
Fig. 4. Diurnally averaged model results from the hot period showing the incremental contributions of various VOC precursors. The model VOC precursor subsets correspond to: ISOP = isoprene; MBO = MBO; BTA = benzene, toluene, acetylene, and pinenes; MCHAV = methylchavicol. Error bars are omitted from upper traces for clarity, all are approximately equal in magnitude to those shown for that of ISOP. The form and magnitude of MBO alone is similar to that of ISOP + MBO.

species for which no measurements were available by looping over the same one hour period 25 times. After this equilibration, any species for which measurements were available were again set to match observation. This model was able to match glyoxal data taken by the Madison LIP Instrument in an identical operational configuration taken at the Caltech Environmental Chambers for experiments of isoprene and MBO oxidation (the dominant precursors of glyoxal at BFRS) under both NO rich and NO poor conditions (Galloway et al., 2011).

4.1 Base-case box model results

The optimized 0-D MCM-based box model described above was used to simulate BEARPEX 2007 conditions. The diurnally averaged model results for the hot period are shown together with the corresponding glyoxal measurement in Fig. 4. The model predicted the following apportionment of production of glyoxal from precursor VOCs (and their oxidation products) during the hot period when all precursors listed in Sect. 4 were included: 66.8 % MBO, 17.7 % higher-generation production from isoprene, 6.3 % direct isoprene, 5.5 % methylchavicol, and 3.7 % other (less than 1 % each). The anthropogenic VOCs benzene and toluene, as well as acetylene and the pinenes only contributed to a small degree. Although methylchavicol was a small source, contributing about 6 % of glyoxal, it was the third most important precursor VOC. Glycolaldehyde was the most important immediate precursor for glyoxal (~90 %), and ~75 %, ~17 %, ~6 %, of

glycolaldehyde arise from MBO, isoprene and methylchavicol oxidation, respectively. Altogether, these results corroborated the notion that the majority of hot period glyoxal production during BEARPEX 2007 was biogenic in nature, dominated by production from MBO and isoprene.

According to the model, glyoxal had a short (~ 0.9 h) daytime lifetime. The calculated average loss rate and equivalent lifetime in hours as a function of time of day for glyoxal are displayed in Fig. S5. The nighttime loss rate was dominated by reaction with OH and by deposition (cf. discussion of deposition in Sect. 3.2), while daytime loss rate was driven by photolysis, reaction with OH, and dilution with background air (Pérez et al., 2009), all contributing about equally at noon, and aerosol uptake contributing about half of each of the former. The short lifetime of glyoxal makes it ideally suited as a local tracer of VOC oxidation chemistry.

A striking feature of Fig. 4 is the degree of over-prediction of the model compared to the measurements, which is significantly outside of the measurement uncertainty of 20 %. In the following section we describe a sensitivity analysis of the parameters that were found to be most effective at influencing this over-prediction using only isoprene and MBO as glyoxal precursors. Using the full set of precursor VOCs, with a resulting 1005 species in the MCM was much more computationally demanding than using only MBO and isoprene (219 species in the MCM). In addition, MBO and isoprene contributed the majority of the over-prediction as they produced ca. 90 % of glyoxal.

4.2 Model sensitivity analysis

In this section we present an analysis of which model parameters were found to most strongly influence the model over-prediction of glyoxal. The following sinks and sources were investigated but found not to substantially contribute to the over-prediction:

- In order for low NO_x chemistry to lower glyoxal noticeably, unphysical (i.e. faster than gas kinetic) rate constants for the $RO_2 + HO_2$ reaction had to be employed. We did not alter the $HO_x + HO_x$ termination rate. In addition, the model employed here matched glyoxal production in low NO_x chamber studies of MBO and isoprene very well (Galloway et al., 2011).

- Decreasing glyoxal concentrations noticeably by increased mixing with background air via "vertical dilution" required a dilution rate constant much larger (~5x) than that used in other studies (Dillon et al., 2002; Pérez et al., 2009), which is unlikely to be correct.

- Increasing the daytime deposition velocity by an order of magnitude from the measured nighttime values in view of the recent work by Karl et al. (2010) had only a marginal (~ 10 %) effect.

– Reducing the glyoxal yield for the reaction of OH with glycolaldehyde clearly reduced glyoxal concentrations, however, a reduction to a yield of 0.045 (∼15 % nominal) was required to achieve agreement with average glyoxal measurements. In addition, the nominal yield of 0.29 in the model was calculated from chamber experiments of MBO oxidation which included glycolaldehyde measurements following BEARPEX 2007 with no observable change in instrument performance and hence should be optimized for this study. In other words, even if the measured glyoxal concentration is biased by some unknown systematic error, analysis of instrument performance strongly indicates that this should match between the field and chamber studies.

The sensitivity of model glyoxal to three parameters will be discussed in more detail: gas-to-aerosol partitioning, altered OH radical concentration, and a treatment of transport.

4.2.1 Gas-to-aerosol partitioning

Loss to aerosol has been proposed as an important sink of glyoxal in Mexico City (Volkamer et al., 2007). However, a number of factors were expected to make aerosol less important as a sink during BEARPEX 2007: the aerosol surface areas were about an order of magnitude lower (average aerosol surface areas of ∼ 100–200 $mm^2 m^{-3}$). It has been demonstrated that glyoxal uptake mainly depends on aerosol liquid water content (Volkamer et al., 2009), which is expected to be quite low for the dry conditions at BEARPEX 2007 (average daytime and nighttime relative humidity 24.2 ± 5.6 % and 45.7 ± 10.1 %, respectively). These facts imply that aerosol loss was not an important sink term for glyoxal during BEARPEX 2007. Additional insight into the role of aerosol as a sink for glyoxal was obtained by analyzing the difference between measured and modeled glyoxal as a function of observed aerosol surface area in model runs that did not include an aerosol loss term (see Fig. S2). If aerosol loss corresponded to an important sink of glyoxal, model-measurement agreement should degrade at high aerosol surface areas. However, this was not the case, in fact a small opposite trend was observed. As a result an increase in the aerosol sink term may improve the average glyoxal over-prediction but does so by overcorrecting during periods with higher aerosol load and hardly affecting the over-prediction during periods of low aerosol loads. This finding together with the low relative humidities make it unlikely that aerosol loss was one of the main contributors to the over-prediction. However, if glyoxal can be taken up into aerosol under the dry conditions during BEARPEX 2007, a higher value of γ would contribute to improving the average discrepancy between model and measurement.
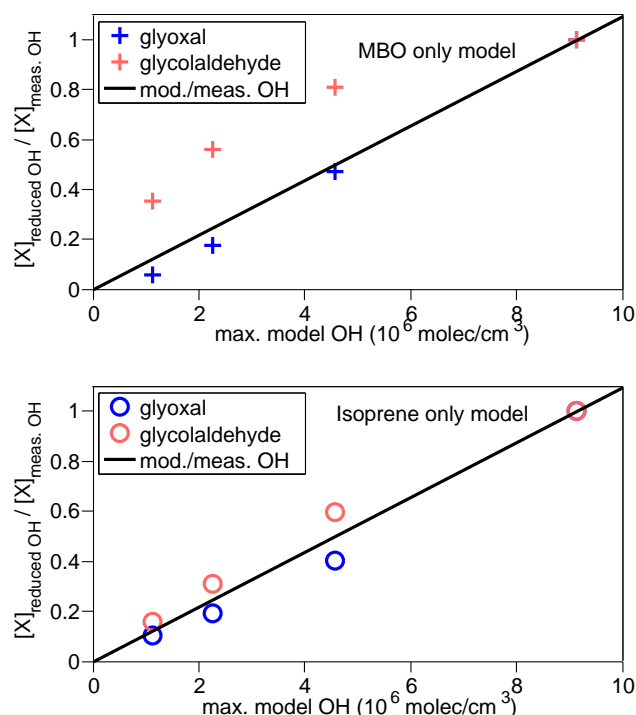

Fig. 5. The fractional reduction in glyoxal and glycolaldehyde concentration for models using either measured OH or reduced OH during the hot period. The top panel shows results using only MBO chemistry, and demonstrates that glyoxal is correlated to OH concentration while glycolaldehyde (a first generation product of MBO) shows less dependence on OH. In the bottom panel, the results of isoprene oxidation for the same changes in OH concentration are shown. Here, glyoxal and glycolaldehyde (both of which are mainly higher-generation products of isoprene oxidation) approximately follow changes in OH. The change in glyoxal is slightly more than 1:1 while that of glycolaldehyde is slightly less.

4.2.2 Reduced OH radical concentrations

Another means of reducing model glyoxal concentration is to alter the overall oxidation process via changes to OH radical abundance. The average reduction in glycolaldehyde and glyoxal upon reducing OH is shown in Fig. 5. In the top panel, which shows simulated MBO chemistry, glyoxal responded slightly more than linearly to reductions in OH while glycolaldehyde responded less strongly. In the bottom panel, which shows simulated isoprene chemistry, both glycolaldehyde and glyoxal responded approximately linearly to reductions in OH, with the response in glyoxal slightly stronger. Thus we demonstrate that glyoxal concentrations are very sensitive to OH levels; results of a model run using MBO and isoprene in which OH was reduced by a factor of two are presented in Fig. 6. Using half measured OH reduced the over-prediction of daytime glyoxal, defined as 0.35–0.8 d, or 8:30–19:00 h, from ∼ 140 % to ∼ 10 %, a reduction of glyoxal of slightly more than a factor of two. While this analysis
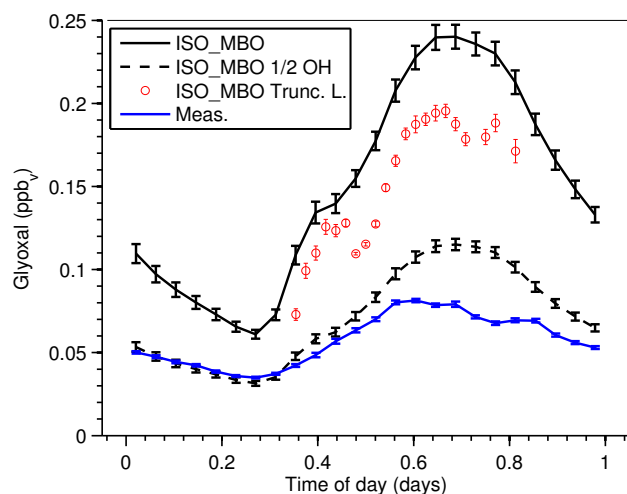
Fig. 6. Model results for OH sensitivity study. Simulations were performed using measured OH and 1/2 measured OH using combined isoprene and MBO chemistry. The Truncated Lagrangian model (daytime only) is shown for comparison. Error bars indicate the 1 standard deviation envelope as calculated based on the variability in the data and model outputs, not reported errors.

will focus on daytime chemistry, we note that nighttime production of glyoxal in the model is mediated almost entirely by OH, which may lead to changes in the deposition velocity needed in the model, but will not change the observed rate described in Sect. 3.2. The reduced OH improved the daytime model over-prediction of HO_2 from $\sim 64\%$ to $\sim 14\%$. Thus, reducing OH to slow overall photochemistry was very effective at improving model agreement with glyoxal and HO_2. A potential instrumental artifact which would influence this analysis is the possibility of a positive bias in HO_2 measurements due to interference by hydroxylalkyl peroxy radicals (Fuchs et al., 2011). As no specific information is available for the BFRS site in 2007 concerning this interference, no correction was attempted. However, it is possible that this affects our model-measurement comparison of HO_2 and hence care should be taken in using the model-measurement agreement of HO_2 as a metric for success in representing oxidation. The implied lower OH concentration refers to the OH concentration experienced over the lifetime of glyoxal and not necessarily the OH concentration at the measurement site. However, there is no reason to expect the OH concentrations to vary substantially in space over the distance relevant to the glyoxal lifetime.

It is worth discussing the merits of this sensitivity analysis, as the implications are important within the context of the disagreements between modeled and measured OH discussed in the introduction. The validity of a factor 2 reduction of the OH concentration in the model compared to the reported measurements appears questionable given the measurement absolute accuracy of 32 %, 2σ. Preliminary results

from a recent study by the PSU group during BEARPEX 2009 suggest that the measured daytime OH concentrations at this site could potentially be a factor of 2.5 lower than determined with the traditional measurement method used during BEARPEX 2007 (Brune et al., 2010). The results of our sensitivity analysis showed that reducing OH concentrations was one of the most effective means of reducing the glyoxal and HO_2 over-predictions and this adjustment, which is in general agreement with the preliminary findings of Brune et al. (2010), had a larger effect than any of the previously discussed parameters; at present, none of these other methods we employed to reduce glyoxal are corroborated in scientific literature.

LaFranchi et al. (2009) found that calculated steady-state concentrations of APNs were as much as two times measured values for the hot period of BEARPEX 2007, despite the fact that the steady-state model is expected to work well under these conditions. The authors attributed this to uncertainties in the chemistry of peroxy radicals, noting that a factor of three increase in the reaction rate of acyl peroxy radicals with RO_2 greatly improved model-measurement agreement. Reducing OH radical concentrations represents another potential solution, as this would decrease the production rate of acyl peroxy radicals.

4.2.3 Truncated-Lagrangian-transport model

Transport of glyoxal was not treated explicitly in the 0-D box model. This shortcoming can affect model glyoxal concentrations differently depending on whether the glyoxal precursors are emitted primarily locally, such as MBO, or primarily upwind of the measurement site, as is the case for isoprene. The 0-D model will overestimate glyoxal production for the former case and underestimate it for the latter: MBO is only emitted in a fairly limited spatial region upwind of the measurement site. Whereas in the box model afternoon air masses experienced MBO processing all day, in reality they only experienced MBO emissions with subsequent oxidation to glyoxal for a few hours. Major emissions of isoprene occur at a distance from the measurement site and isoprene is already substantially processed ($>50\%$) when it arrived at the site. Using the isoprene concentrations observed at the measurement site will under-predict the amount of oxidation products from isoprene, which can be seen in the MVK (and MACR) data shown in Fig. 7. As the daytime lifetime of glyoxal is ~ 1 h, the lack of inclusion of advection in the model is expected to have a limited effect, as transport of 3 h (the noon transport time to the measurement site from the zone where isoprene emissions give way to MBO emissions) will have lost most of the original glyoxal. As the 0-D model predicted too much glyoxal, we investigated what the largest possible reduction in over-prediction as a result of transport could be. In this approach we addressed the overestimate resulting from the locally emitted MBO and neglected the

underestimate resulting from isoprene. This represents an upper-limit of the effect of transport.

Using emission maps from Steiner et al. (2007) and measured wind speeds, we calculated the time that air at BFRS is influenced by MBO, for example ~ 3 h at mid-day. We constructed a truncated-Lagrangian model in which the Lagrangian model run was initialized when an air-mass with very low glyoxal and glycolaldehyde concentrations (1×10^5 moleculecm^{-3}) entered the MBO emitting area, where it experienced the chemical environment (OH, O$_3$, photolysis, etc.) measured at or calculated for the BEARPEX site. For example: the point at noon was estimated to need 3.12 h of transit time to reach the site from the edge of major MBO emissions, so the model concentration of glycolaldehyde was set very low at 8.88 h during each day of the simulation. In this case, air with little glyoxal and glycolaldehyde entered the box at time = 8.88 h. The air-mass then moved with the measured wind-speeds up to the measurement site, which it reached at noon, and the final value then represents the noon-time model value at the measurement site. Similar runs were performed for each half hour interval. The emission maps show that MBO emissions are fairly homogeneous throughout this region and thus we used the measured MBO concentrations, the most important glyoxal precursor for the entire transect. Site measurements were also used to constrain the other parameters, such as isoprene. As discussed above this is incorrect for isoprene, which has higher concentrations at the entry to the MBO emitting area than our model assumed, and hence would increase glyoxal concentration.

The effect of transport with this truncated Lagrangian model was tested using isoprene and MBO as precursors, which capture 90% of model glyoxal production in the hot period. The upslope wind-flow lasted from about 0.3 day to 0.8 day (7–19 h) on average; no data points are thus reported outside that time. The resultant set of half-hourly endpoints represent the daytime diurnal profile, with the influence of transport reduced or removed (assuming that air entered the MBO emission region with very low or zero concentration of these species). A dot is shown in Fig. 6, corresponding to the endpoints of each of these model runs. Glycolaldehyde was on average reduced to 86% of the original model level (not shown). This suggests that modeled concentrations of glycolaldehyde were only moderately too high due to the failure of the model to treat transport, and hence the 0-D model is not a bad approximation for modeling glycolaldehyde. The effect on glyoxal (which the model predicts is largely an oxidation product of glycolaldehyde) was more pronounced, as production of glyoxal from MBO requires two reactions with OH while glycolaldehyde production from MBO needs only one. MBO was the dominant precursor of glycolaldehyde and glyoxal in this simulation. As glyoxal is a secondary product its appearance had a lag compared to that of glycolaldehyde. Due to the limited model run time, this made the effect on glyoxal more pronounced than for glycolalde-
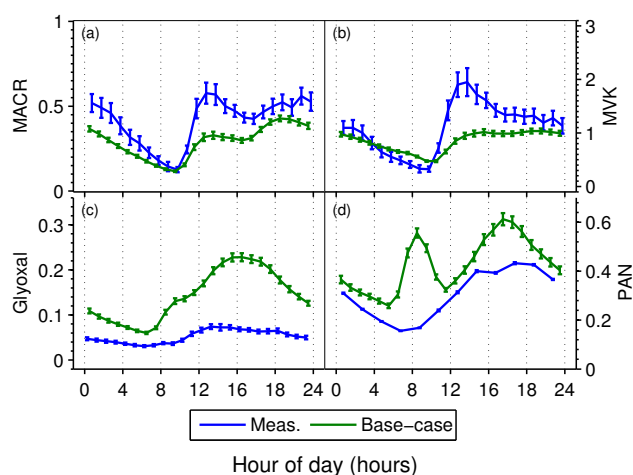

Fig. 7. Summary of model OVOCs and measurements as available, all in ppb. The model is broadly able to predict MVK and MACR, while it exceeds measurements of glyoxal substantially. The slight under-prediction of MVK and MACR is expected for the 0-D-box model as it underestimates the contribution of isoprene oxidation, which is largely emitted upwind of the measurement site. Error bars indicate the 1 standard deviation envelope as calculated based on the variability in the data, not reported errors.

hyde. However, the average reduction to 73% of the original glyoxal prediction was not sufficient to bring the model into agreement with measurement. For this reason, we conclude that transport alone is clearly not sufficient to explain the over-prediction in modeled glyoxal. In fact, the effect is likely to be smaller, as glyoxal from isoprene is underestimated.

4.3 Discussion

Analysis of the model results showed that the majority of glyoxal was formed by glycolaldehyde, which in turn was produced mainly from MBO, and to a lesser degree from isoprene and methylchavicol, which is in agreement with the fact that the glyoxal yield from MBO is substantially higher than from isoprene. The model included all main known precursors for glyoxal that were measured during BEARPEX 2007 and introduced methylchavicol as an additional one. The model substantially ($\sim$factor 2.5) over-predicted glyoxal at the measurement site. As MBO contributed ~ 70% of glyoxal, MBO oxidation also had to contribute the majority of the over-prediction. An upper-limit estimate of the effect of transport on MBO processing improved model-measurement disagreement but still had a substantial over-prediction ($\sim$factor 1.8). The slight improvement was a result of the short lifetime of glyoxal during BEARPEX 2007, which limited the effect of transport and supports the notion that glyoxal is a "local" tracer of VOC oxidation chemistry. The effect of transport is expected to be diminished in the model due to the underestimation of glyoxal from isoprene.

It is more likely that transport should increase glyoxal due to advection of precursors such as glycolaldehyde (from isoprene) which has approximately twice the lifetime of glyoxal. Other factors that could reduce the over-prediction are increased aerosol loss and a reduced yield of glyoxal from glycolaldehyde. The latter seems unlikely as the work done by Chan et al. (2009) used the Madison LIP instrument to parameterize glyoxal from glycolaldehyde. Since aerosol formation is proportional to liquid water content, the very dry conditions at BEARPEX eliminate aerosol as a significant sink. By far the most effective means to reduce the model over-prediction was reducing the OH concentration, which in addition was the only one supported by other evidence, i.e. the recent work by Brune et al. (2010). In addition, this was the only parameter that also resulted in a substantial improvement of modeled HO_2 concentrations. The high sensitivity of glyoxal to OH is interesting as one might expect OH levels to have little effect on glyoxal as it participates in both production and destruction of glyoxal. The high sensitivity in our model stemmed from three details of the underlying chemical mechanism and model: (1) the model was driven with measured BVOC concentrations, not emissions, and hence increased OH resulted directly in increased glycolaldehyde, (2) glyoxal is largely a higher-generation product of BVOC oxidation and thus increased OH increases production of the precursor glycolaldehyde and how fast it is converted to glyoxal, and (3) reaction with OH was not the dominant glyoxal loss channel. Clearly, a combination of adjustment of different parameters could be employed to further improve the model to measurement disagreement. However, such combinations without reduction in OH are not sufficient to reduce modelled glyoxal while, for example, maintaining the correct shape of the diurnal cycle.

5 Conclusions

We present the first high time resolution glyoxal data obtained with a direct, in situ detection method in a rural region dominated by BVOC emissions. Measurements of glyoxal during the BEARPEX 2007 campaign were used to examine the influence of BVOCs on glyoxal production and we conclude that during the hot period glyoxal production was dominated by BVOCs. This is supported by the fact that the site is in a region with much higher BVOC than anthropogenic VOC concentrations during high temperature periods combined with the fact that the daytime lifetime of glyoxal is substantially shorter than the transport time from the edge of this region. This is further supported by comparison between hot and cold period glyoxal concentrations. In addition, a photochemical model showed that most of hot period glyoxal production resulted from BVOCs, primarily MBO and isoprene with a small contribution from methylchavicol, a species that had not previously been taken into account for glyoxal production.
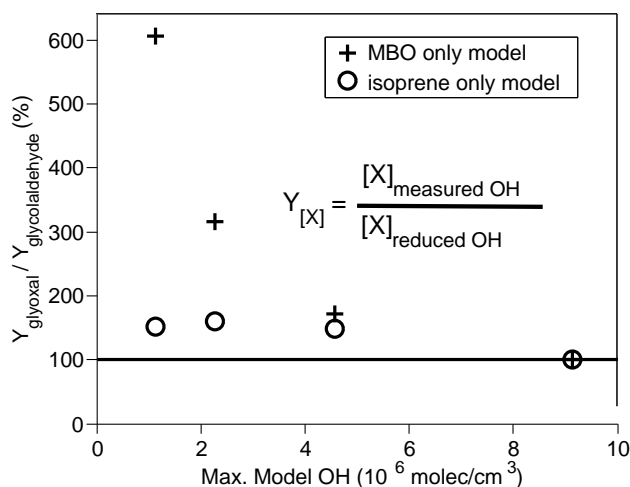

Fig. 8. The ratio of the response function Y of glyoxal for models using either measured OH or reduced OH to the response function Y of glycolaldehyde for the hot period. These results show that for MBO chemistry, glyoxal becomes increasingly more sensitive than glycolaldehyde to OH concentration as OH decreases. In isoprene chemistry, glyoxal is always more sensitive than glycolaldehyde (above 100 %) but the magnitude and the trend are less pronounced.

In contrast to the recent work on formaldehyde by Choi et al. (2010a), no evidence was found that glyoxal is produced via oxidation of unknown/missing BVOC emissions during the hot period. However, this does not imply that such BVOC emissions do not exist, as only some BVOCs produce glyoxal, whereas formaldehyde is a much more common oxidation product. In addition, the glyoxal observed during the intermediate period cannot be explained with the VOCs measured at BFRS and hence it could indicate an unknown precursor for glyoxal.

Globally, biogenic sources of glyoxal are predicted to exceed anthropogenic sources, so measurements in rural areas are important and we present the first detailed dataset of its kind. This data is also of interest to comparison with modeling studies of glyoxal despite the limitations of measurements at a single ground site as it presents an analysis of the processes controlling glyoxal concentrations in a biogenically influenced area. Thus, the work contributes to the broader understanding of the tropospheric chemistry of glyoxal.

The results of a photochemical model that was successfully tested using chamber studies of isoprene and MBO oxidation were compared to data taken during BEARPEX 2007 showing a substantial over-prediction despite the reduction of higher-generation yields of glyoxal from isoprene. An attempt to model the influence of MBO chemistry more realistically by making an upper-limit estimate of the effect of transport showed that this only contributed to a small degree to the over-prediction as did loss of glyoxal to aerosol.

A reduction of OH concentrations was determined to be by far the most effective way to reduce glyoxal model concentrations, and in addition was the only adjustment that has supporting evidence based on the recent work by Brune et al. (2010) and improved model HO_2 concentrations. This demonstrates that glyoxal can be a useful local tracer of OH–driven VOC oxidation chemistry, in particular given its short photochemical lifetime. For example, the relative sensitivity of glyoxal and glycolaldehyde to changes in OH is shown in Fig. 8, which demonstrates that glyoxal is more sensitive (i.e. has a greater reduction for reduced OH) than glycolaldehyde for both isoprene and MBO oxidation. The sensitivity is especially enhanced for the case of MBO, in which glycolaldehyde is a first generation product and glyoxal is a higher–generation product, but remains even for isoprene in which both are mainly higher–generation products. Our analysis has shown that glyoxal concentrations are more sensitive to OH than other BVOC oxidation products as it is predominantly a secondary product of mainly OH-driven BVOC oxidation, rather than O_3-driven chemistry, combined with the fact that photolysis is usually more important as a sink than reaction with OH. We propose that glyoxal is a useful tracer for OH-driven BVOC oxidation chemistry.

Supplementary material related to this article is available online at:
http://www.atmos-chem-phys.net/11/8883/2011/
acp-11-8883-2011-supplement.pdf.

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