

We thank Referee #1 for his/her comments on our paper, which helped us to improve the quality of the paper. Below, we answer the reviewer's question point by point.

General comments

This paper reported the development of an incoherent broadband cavity enhanced absorption spectrometer for simultaneous measurement of NO₂, glyoxal (GLY) and methylglyoxal (MGLY). A NO₂ photolytic convertor (NPC) was used to minimize the interference of high concentration NO₂ to GLY. The photolysis of NO₂ can lead to the formation of O₃. My major comment is that if the photolysis of ambient air can potentially generate artificial GLY or MGLY, especially in VOCs rich environments.

Reply:

Given the size of the photolysis cell (i.e., a cylinder with 60 mm length and 13.4 mm inner diameter) and the sampling flow rate of 2 L/min, the residence time of the sampled air in the cell is about 0.25 s. In such a short period, the production of GLY and MGLY in the cell is negligible which can be verified by model simulations. The model includes the full MCM chemistry (version 3.3.1, <http://mcm.leeds.ac.uk/MCM/>) for all NMHCs and their oxidation products. The initial concentrations of OH, HO₂, O₃, NO, HONO, CO, CH₄, C₂-C₁₂ NMHCs are set to the average values obtained during a field observation campaign in 2018 in Yangtze River Delta, China (Table S1). The total OH reactivity due to NMHCs is about 3.1 s⁻¹. The relative humidity, temperature, and pressure are constrained by the campaign averages, i.e., 60%, 300 K, 1007.65 hPa, respectively. The photolysis frequencies are constrained by values calculated from the spectral actinic flux inside the cell (Fig. S1). The spectral actinic flux is estimated by the LED emission spectrum and by the concentration change of NO, NO₂, and O₃ when NO₂ standard (100 ppb) is running through the system. The initial values of NO₂, GLY, MGLY are set to 60 ppb, 100 ppt, and 100 ppt, respectively. Fig. S2 shows the calculated concentrations of NO₂, O₃, GLY, and MGLY for the period of 0.25 s residence time. While the NO₂ concentration drops from 60 ppb to 15 ppb leading to an increase of O₃ concentration by approximately 45 ppb, the change of GLY and MGLY concentrations is only around 1%. As shown in Fig. S3, the production rate of GLY and MGLY increases to around 5 ppb h⁻¹ which could only result in maximumly 0.34 ppt increase of GLY and MGLY. Even if we increase the initial NMHCs concentration in the model by a factor of 10, the maximum production of GLY and MGLY within 250 ms is less than 2 ppt which is only 2% of their initial concentration (Fig. S4). Since the NMHCs concentration in the model represents typical atmospheric condition influenced by urban air pollution, our model simulation clearly shows that the NPC can be used in the field observations for removing NO₂ without additional production of GLY and MGLY.

The above discussions are added in the Supplement.

Specific comments

1, page 2, line 17. A careful survey of GLY instruments is encouraged. A short discussion about recent IBBCEAS systems used for GLY measurements and their detection limits is better than only a sentence of other gas's applications.

Reply:

The following texts are added on page 2, line 24 in the revised manuscript.

“Washenfelder et al. were the first to use this technology to measure GLY. The precision (1σ) of their system is 29 ppt for a 1 min sampling time (Washenfelder et al., 2008). Under the same time resolution, Thalman and Volkamer reduced the detection limit (2σ) to 19 ppt for their LED-CE-DOAS (Thalman and Volkamer, 2010). The above two systems have been successfully applied to GLY measurements in field observations (Washenfelder et al., 2011; Coburn et al., 2014). From aspects of miniaturization and improving time resolution, Min et al. optimized Washenfelder et al.'s IBBCEAS for aircraft GLY measurements. The measurement precision (2σ) is 34 ppt in 5 s (Min et al., 2016). The IBBCEAS developed by Fang et al. has a precision of 28 ppt for GLY at 1 min averaging time. By applying Kalman filter to the retrieved concentrations, their measurement precision was improved to 8 ppt in 21 s (Fang et al., 2017). ”

2, page 2, line 28. I note a paper recently accepted for publication in AMT that also tried to fix the problem of NO₂ interference to GLY, which should be included in the introduction.

Liang, S., Qin, M., Xie, P., Duan, J., Fang, W., He, Y., Xu, J., Tang, K., Meng, F., Ye, K., Liu, J., and Liu, W.: Development of an incoherent broadband cavity-enhanced absorption spectrometer for measurements of ambient glyoxal and NO₂ in a polluted urban environment, *Atmos. Meas. Tech. Discuss.*, <https://doi.org/10.5194/amt-2018-430>, in review, 2018.

Reply:

The following texts are added in page 2, line 28 in the revised manuscript.

“Liang et al. thought that the interference was caused by the accuracy of the convoluted NO₂ absorption cross section and tried to solve this problem by measuring NO₂ cross section with their own spectrometer (Liang et al., 2019). In this case, the accuracy of the retrieved NO₂ and GLY concentrations will be dependent on the accuracy of the NO₂ cross section they measured. ”

3, page 5. How to determine the absolute GLY concentration in this work is still not clear, by measuring the pressure or flow rate?

Reply:

The absolute concentration of GLY is determined by fitting the reference spectra of NO₂, GLY, MGLY, etc. to the measured absorption coefficient, according to equations 1 and 2 in Page 5. We also measure the pressure and the temperature in the cavity of the IBBCEAS, so that the absolute concentration can be converted to mixing ratio. In this work, the absolute concentration of GLY in the NO₂ photolytic converter is determined by the IBBCEAS system. For checking the influence of NPC on the GLY

sampling efficiency, we only need to look at the relative change of the measured GLY concentration.

4, page 7, line 19. The relative change of 1-R is more meaningful than R.

Reply:

We revise the text according to your suggestion.

5, page 11, sec. 4.2. Please include the fitting residual information and give some discussion about the “unknown reasons”. Did the authors shift or stretch the reference spectrum?

Reply:

We did apply shift and stretch on the reference spectra. The shift was limited within -1 nm to 1 nm and the stretch was limited within 0.9 to 1.1. The following texts are added in Sect. 4.2.

“...The fitting residual increased from 4×10^{-10} to 2×10^{-9} as the NO_2 concentration increased.... The uncertainty of simulation results is mainly caused by two reasons. (1) Random numbers could be not good enough to represent the actual noise of the whole system. Since the intensity of LED and the reflectivity of mirrors are not evenly distributed with the wavelength, the corresponding signal-to-noise ratios (SNR) are also different at different wavelength. As for our system, the SNR within 450-468 nm are higher than that at other wavelengths. If we only reduced the random number by 5 times within 450-468 nm and did not change that at other wavelengths, the fluctuation of the fitted GLY concentration was also reduced by 5 times. (2) The impact of Rayleigh scattering and Mie scattering are not explicitly considered during the simulation. In this case, whether polynomial should be added in the spectral fitting or not would be a problem. The retrieved GLY concentration by using a fifth-order polynomial was 20% higher than that without including polynomial. Therefore....”

6, page 12, sec. 4.4. Please include the comparisons with other IBBCEAS systems. The sensitivity of Min et al.'s was $1.5 \times 10^{-10} \text{ cm}^{-1}$, and the authors' was $8.4 \times 10^{-11} \text{ cm}^{-1}$ (with 100 s integration time, line 18 in the text). Table 2 is not clear (5s, 100s). The corresponding time for each detection limit needs to be clearly stated. Furthermore, please carefully check if the data used in Table 2 are correct.

Reply:

The second paragraph in Sect. 4.4 is rewritten in the revised manuscript.

According to figure 8 in Min et al. (2016), we estimated the Allan deviation of their system for a 100 s acquisition time as $1.5 \times 10^{-10} \text{ cm}^{-1}$ (2σ). With respect to its GLY detect limitation, it was given in as 5 s average in Min et al.'s paper. We carefully checked the data used in Table 2 and made necessary revisions.

7, page 23, Fig. 4, please check the convolution of MGL reference is correct. There is an obvious shift, and the peaks are vanished.

Reply:

Thank you for pointing out this mistake. We tested two high resolution cross sections

of MGLY at the very beginning of our experiments, one is from Meller et al. (1991) and the other is from Staffelbach et al. (1995). In the manuscript, we mistook convolution results based on Staffelbach's spectrum instead of that based on Meller's spectrum. We revised Fig. 4 accordingly and checked the whole manuscript to ensure that the correct cross section is used in every part involving MGLY spectral fitting.

8, page 27, Fig. 8(a). The symbols are not clearly indicated.

Reply:

Revised accordingly in the manuscript.

Reference

- Meller, R., Raber, W., Crowley, J. N., Jenkin, M. E., and Moortgat, G. K.: THE UV-VISIBLE ABSORPTION-SPECTRUM OF METHYLGLYOXAL, *Journal of Photochemistry and Photobiology a-Chemistry*, 62, 163-171, 1991.
- Min, K. E., Washenfelder, R. A., Dubé, W. P., Langford, A. O., Edwards, P. M., Zarzana, K. J., Stutz, J., Lu, K., Rohrer, F., Zhang, Y., and Brown, S. S.: A broadband cavity enhanced absorption spectrometer for aircraft measurements of glyoxal, methylglyoxal, nitrous acid, nitrogen dioxide, and water vapor, *Atmos Meas Tech*, 9, 423-440, 2016.
- Staffelbach, T. A., Orlando, J. J., Tyndall, G. S., and Calvert, J. G.: THE UV-VISIBLE ABSORPTION-SPECTRUM AND PHOTOLYSIS QUANTUM YIELDS OF METHYLGLYOXAL, *J Geophys Res-Atmos*, 100, 14189-14198, 1995.

Table S1. Initial concentration of species included in the model simulation.

Species	Concentration	Species	Concentration
OH	107 cm-3	NO	0.60 ppb
HO2	109 cm-3	HONO	0.45 ppb
CH4	1.9 ppm	CO	0.33 ppm
O3	70.00 ppb	SO2	1.33 ppb
NO2	60 ppb	MGLY	100.0 ppt
GLY	100.0 ppt	TOLUENE	0.515 ppb
C2H2	1.000 ppb	NC8H18	0.034 ppb
CBUT2ENE	0.050 ppb	EBENZ	0.140 ppb
C2H4	0.900 ppb	MXYL	0.045 ppb
C2H6	2.130 ppb	NC9H20	0.019 ppb
IC4H10	0.380 ppb	OXYL	0.076 ppb
IC5H12	0.330 ppb	STYRENE	0.017 ppb
NC4H10	0.650 ppb	IPBENZ	0.012 ppb
NC5H12	0.240 ppb	PBENZ	0.014 ppb
PENT1ENE	0.004 ppb	METHTOL	0.016 ppb
TPENT2ENE	0.002 ppb	PETHTOL	0.015 ppb
C5H8	0.233 ppb	NC10H22	0.017 ppb
CPENT2ENE	0.003 ppb	TM135B	0.014 ppb
M22C4	0.019 ppb	OETHTOL	0.036 ppb
M23C4	0.020 ppb	TM123B	0.014 ppb
M2PE	0.100 ppb	PXYL	0.045 ppb
M3PE	0.076 ppb	NC11H24	0.019 ppb
HEX1ENE	0.009 ppb	C3H8	2.010 ppb
NC6H14	0.130 ppb	C3H6	0.120 ppb
M2HEX	0.030 ppb	C4H6	0.005 ppb
CHEX	0.044 ppb	TM124B	0.016 ppb
M3HEX	0.041 ppb	TBUT2ENE	0.002 ppb
BENZENE	0.364 ppb	BUT1ENE	0.040 ppb
NC7H16	0.055 ppb		

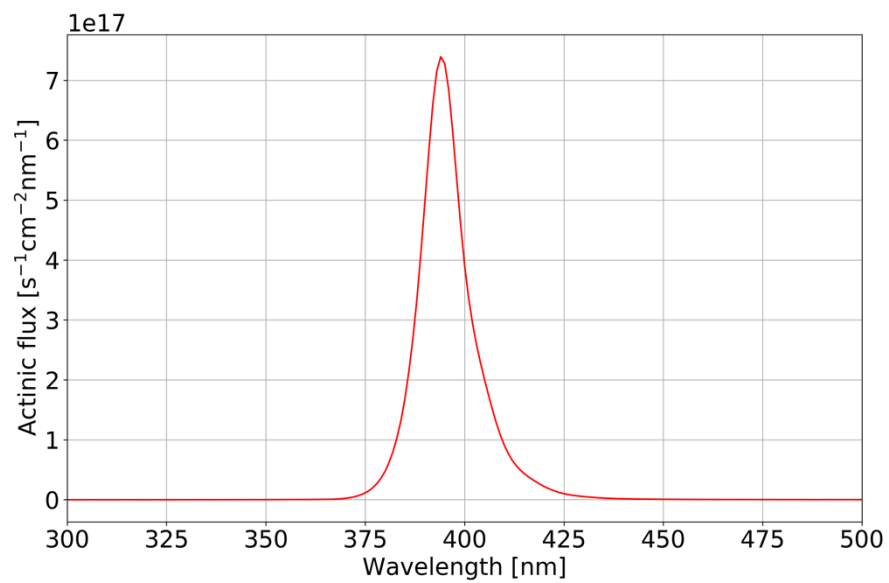


Figure S1. Spectral actinic flux inside the photolysis cell of the NO_2 convertor.

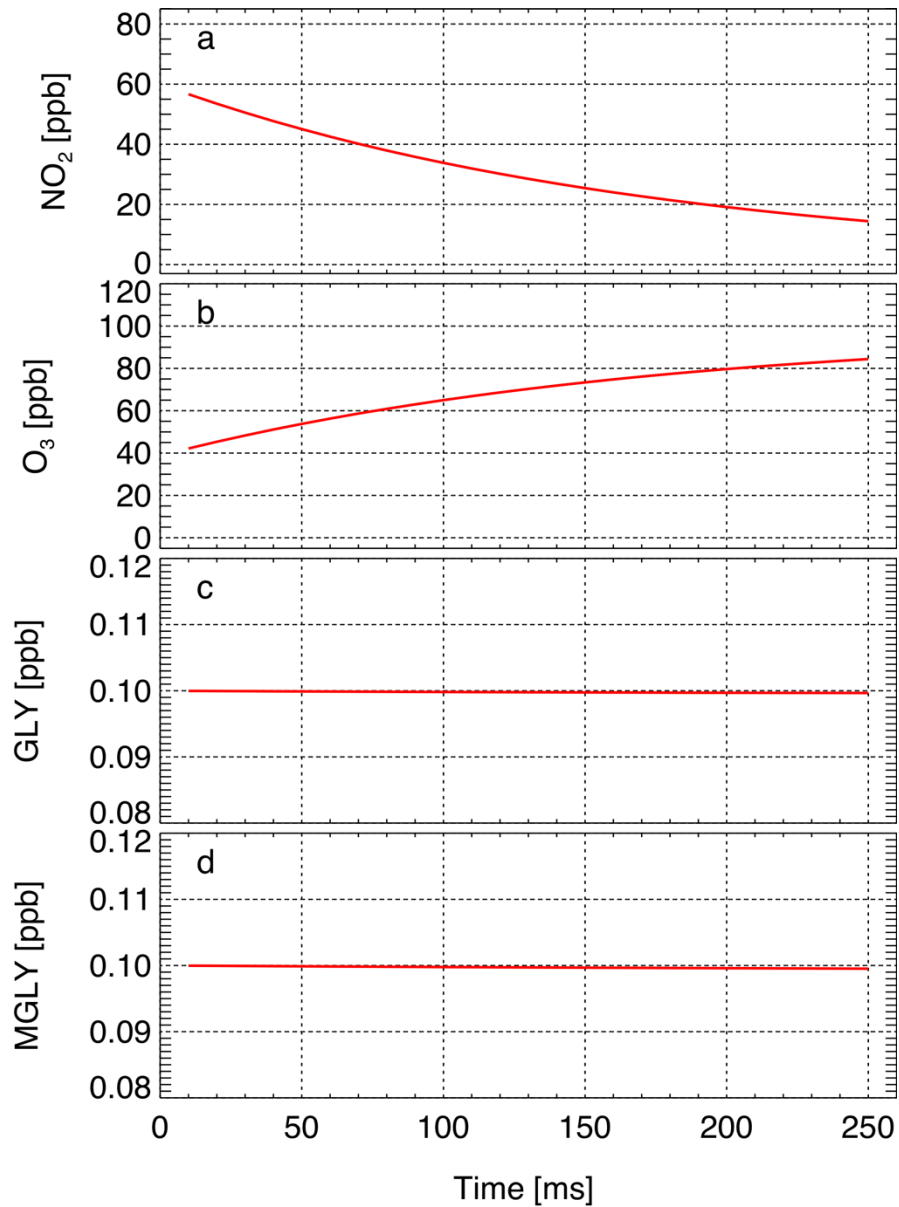


Figure S2. Model calculated concentrations of NO₂ (a), O₃ (b), GLY (c), and MGLY (d) in the photolysis cell of the NO₂ convertor. Note that the concentrations at 250 ms represent the condition of the sampled air exits the cell, since the residence time in the cell is about 250 ms.

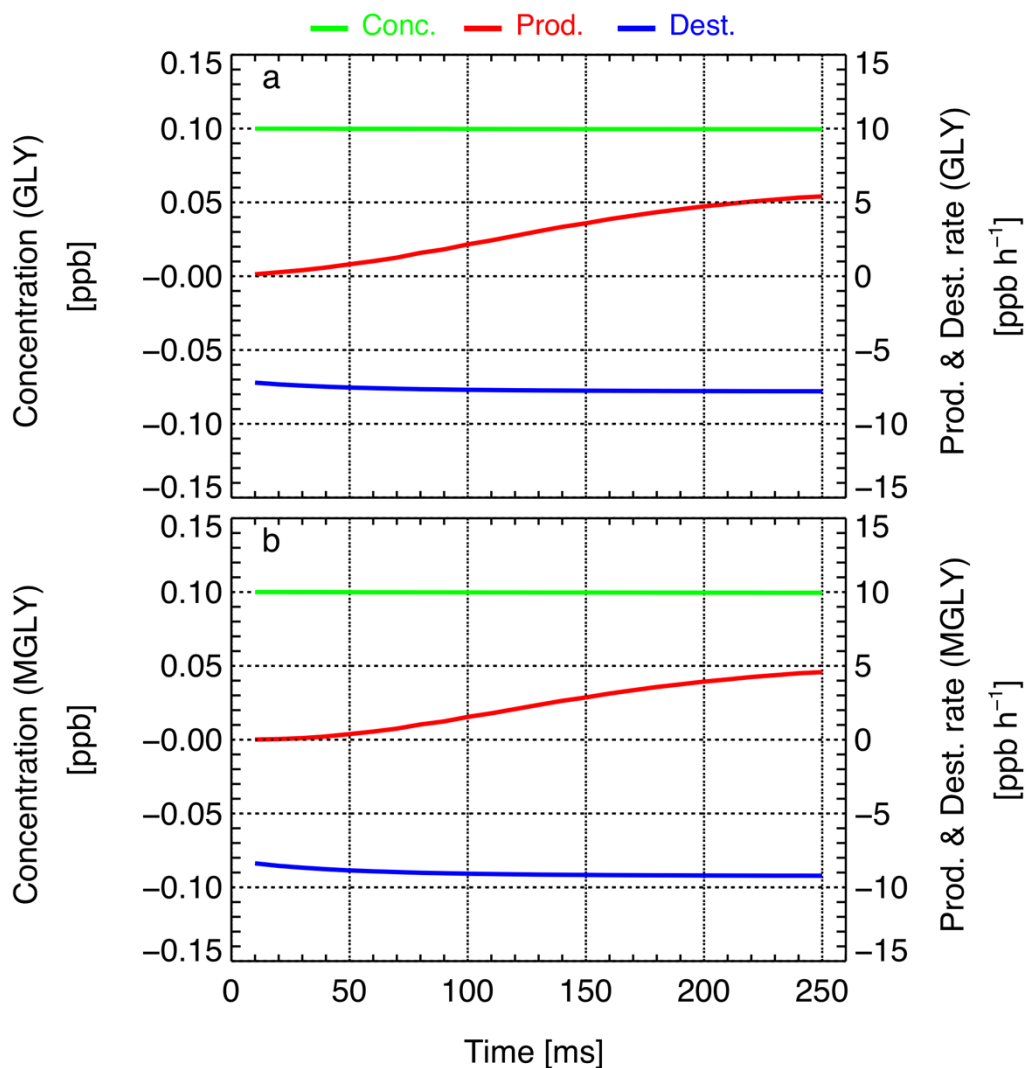


Figure S3. Model calculated concentrations (green), production rates (red), and destruction rates (blue) of GLY (a) and MGLY (b) in the photolysis cell of the NO₂ convertor. Note that the concentrations at 250 ms represent the condition of the sampled air exits the cell, since the residence time in the cell is about 250 ms.

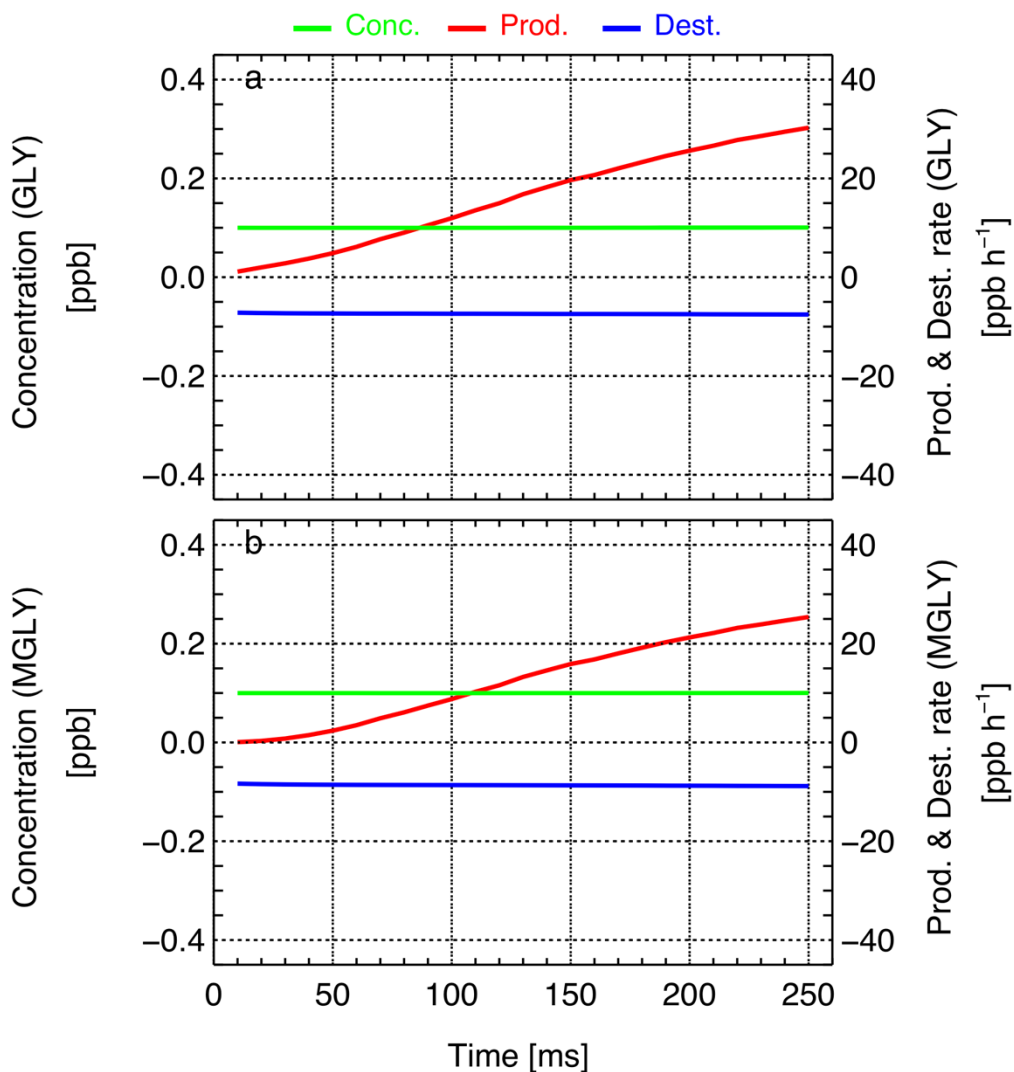


Figure S4. Model calculated concentration (green), production rate (red), and destruction rate (blue) of GLY (a) and MGLY (b) in the photolysis cell of the NO₂ converter. The initial concentrations of NMHCs in the model are set to 10 times of the values listed in Table 1. Note that the concentrations at 250 ms represent the condition of the sampled air exits the cell, since the residence time in the cell is about 250 ms.