

Responses to Referee # 1:

We thank the reviewers for the consideration and the constructive comments. The manuscript is revised based on the suggestions made and detailed responses to the reviewers are addressed as follows.

The authors present a detailed study of the aqueous-phase oxidation of methyl ethyl ketone (MEK). Their most significant finding is that this species may be a precursor for methylglyoxal in the aqueous phase. The experiments were carefully performed and a detailed modeling analysis was used to determine the reaction mechanism and rate constants. The paper is suitable for publication in ACP after a few minor points are addressed.

1) My main concern about this paper is that I would like to see a discussion of the relative importance of this source of methylglyoxal as compared to uptake from the gas phase. The Henry's Law constant of MEK is very low, 2-3 orders of magnitude lower than that of methylglyoxal itself. Considering mass transfer limitations, how significant of a source of methylglyoxal, and by extension, aqueous SOA, is this pathway?

#### Author`s comment

In Table 1 the Henry constants of MEK and methylglyoxal as well as measured concentrations in the gas, particle and aqueous phase are summarised.

Table 1: Henry constant and concentrations of MEK and methylglyoxal in gas-, particle- and aqueous phase.

	Henry constant [M atm <sup>-1</sup> ]	Concentration gas phase [ppb]	Concentration particle phase [µg m <sup>-3</sup> ]	Concentration aqueous phase [µmol L <sup>-1</sup> ]
MEK	7.7 – 50 <sup>abcdefg</sup>	0.02 – 15 <sup>bijklmn</sup>	0 – 0.1 <sup>i</sup>	0 – 0.65(CW) <sup>tu</sup> ; < 0.0005(OBW) and 0.00228 (SML) <sup>v</sup>
Methyl- glyoxal	3.7 × 10 <sup>3 h</sup> 3.2 × 10 <sup>4 d</sup>	≤0.05 – 0.09 <sup>o</sup> 0.03 – 270.6 <sup>pqrs</sup>	0 – 0.075 <sup>p</sup>	0.3 – 18(CW) <sup>ou</sup>

CW cloud water, OBW ocean bulk water, SML surface microlayer

*a Buttery et al., 1969; b Snider and Dawson, 1985; c Ashworth et al., 1988; d Zhou and Mopper, 1990; e Morillon et al., 1999; f Karl et al., 2002; g Schütze and Herrmann 2004; h Betterton and Hoffmann, 1988; i Grosjean et al., 1982, 1983, 2002; j Riemer et al., 1998; k Singh et al., 2004; l Goldan et al., 1995; m Müller et al., 2005; n Feng et al., 2004; o Munger et al., 1995; p Kawamura et al., 2013; q Ortiz et al., 2006; r Matsunaga et al., 2004; s Ieda et al., 2006; t Grosjean and Wright, 1983; u van Pinxteren et al., 2005; v Zhou and Mopper, 1997; w Collett et al., 1990*

As it can be seen, MEK has a lower Henry constant with 50 M atm<sup>-1</sup> as the maximum available value (Schütze and Herrmann, 2004) compared to methylglyoxal ( $K_H = 3.7 \times 10^3$  M atm<sup>-1</sup>, Betterton and Hoffmann, 1988) leading to the conclusion that the transfer from the gas in the aqueous phase is, according to the Henry constant, more important for methylglyoxal than for

MEK. Noticeably, van Pinxteren et al. (2005) found higher concentrations of MEK in cloud water as it was expected according to the Henry constant. Thus, phase transfer could be more important than it is known at this moment. Besides its transfer from the gas phase, the formation of MEK in the aqueous phase of clouds and hygroscopic particles should be considered as an additional source for aqueous MEK as well. The so-formed aqueous MEK will react to form methylglyoxal with a molar yield of 9.5%.

Methylglyoxal present in the aqueous phase originates from i) uptake from the gas phase and ii) aqueous-phase reactions. The uptake of methylglyoxal from the gas phase in the aqueous phase is not fully understood. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under various relative humidities. It was found that the uptake was not relevant for methylglyoxal even under high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of  $\gamma = 7.6 \times 10^{-3}$  on an acidic solution. They found an irreversible uptake, which decreases with increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets  $\gamma = 2.9 \times 10^{-3}$ , which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be  $\gamma = 1.47 - 2.92 \times 10^{-5}$ . Overall,  $\gamma$  was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) highlighting the discrepancies between the different literature studies.

As the uptake as well as the formation mechanisms of methylglyoxal are not fully understood, it cannot be excluded that the oxidation of MEK represents an important reaction channel for methylglyoxal formation.

Based on the Referee's comment the following paragraph was added to the manuscript:

Page 31907 Line 1 "*4. Atmospheric relevance*

*The sources of methylglyoxal in the aqueous phase are thus far not fully elucidated. Methylglyoxal can originate in the atmospheric aqueous phase through i) uptake from the gas phase, and/or ii) formation in the aqueous phase. The importance of the uptake from the gas into the aqueous phase is discussed in the literature but large discrepancies can be found. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under varying relative humidity. It was found that the uptake was not relevant for methylglyoxal even under high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of  $\gamma = 7.6 \times 10^{-3}$  on an acidic solution. They found an irreversible uptake, which decreases with*

increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets  $\gamma = 2.9 \times 10^{-3}$ , which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be  $\gamma = 1.47 - 2.92 \times 10^{-5}$ . Overall,  $\gamma$  was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) showing the discrepancies between the different studies available in literature.

The in-situ formation of methylglyoxal in the aqueous phase could be an important source as well (Blando and Turpin, 2000; Sempere and Kawamura 1994). Within the present study, MEK was found as a new precursor compound for methylglyoxal in the aqueous phase yielding methylglyoxal with a molar yield of 9.5%. Although the Henry constant of MEK (up to  $K_H = 50 \text{ M atm}^{-1}$ , Schütze and Herrmann, 2004) is lower compared to methylglyoxal ( $K_H = 3.7 \times 10^3 \text{ M atm}^{-1}$ , Betterton and Hoffmann, 1988), van Pinxteren et al. (2005) found higher concentrations in cloud water as it was expected. Thus, the phase transfer of MEK from the gas in the aqueous phase could be more important as currently derived from the available Henry constants. Besides the phase transfer, the in-situ formation of MEK in aqueous phase formation might also represents an important source.

As, the oxidation of MEK yielding methylglyoxal has not been studied much before, it should be considered as a formation process of methylglyoxal.”

Minor comments:

1) Methylglyoxal is conventionally one word in English, please change throughout.

Author`s comment

The authors agree with the reviewers comment. The term “methyl glyoxal” was changed to “methylglyoxal” throughout the manuscript.

2) Was there any gas phase in the reactor? Was it in equilibrium with the aqueous phase?

Author`s comment

The bulk reactor was filled with 300 mL of the aqueous solution at the beginning of the experiment containing the precursor compound and H<sub>2</sub>O<sub>2</sub>. Over the course of the experiment samples were taken in steps of 15 minutes (and for some cases 1 hour). Thus, the gas phase increased during the experiment. To take samples, the bulk reactor was opened. Even that the

opening time was kept as small as possible the gas phase of the bulk reactor might be mixed with the laboratory air changing the chemical composition. Nevertheless, the Henry constant of methylglyoxal ( $K_H \approx 3.7 \times 10^3 \text{ M atm}^{-1}$ ; Betterton and Hoffmann, 1988) indicates that methylglyoxal will mainly stay in the aqueous phase even when the bulk reactor was opened. Contrary, the Henry constant of MEK was measured to be  $K_H = 7.7 - 50 \text{ M atm}^{-1}$ , thus a loss of MEK from the aqueous phase in the gas phase is possible. To proof the hypothesis, the results of blank experiment 2 can be used. As it was mentioned in the manuscript, no loss of MEK was observed. This indicates that MEK stays in the aqueous phase even during opening of the reactor.

3) p. 31898 line 7-8: please elaborate on how the relative photolysis rate constants 'confirm the experimental results'

Author`s comment

Fig. 1 B shows the molar yields of the oxidation products methylglyoxal, hydroxyacetone and 2,3-butanedione over a reaction period of 4 hours. As it can be seen, further reactions are taking place leading to lower molar yields of methylglyoxal, hydroxyacetone and 2,3-butanedione towards the end of the experiment.

The following rate constants for the OH radical reaction are reported in the literature:  $k_{OH} = 5.3 \times 10^8 - 1.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Monod et al., 2005; Ervens et al., 2003; Herrmann et al., 2005; Tan et al., 2010) for methylglyoxal,  $k_{OH} = 0.8 - 1.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (Stefan and Bolton, 1999; Herrmann et al., 2005) for hydroxyacetone and  $k_{OH} = 1.4 - 1.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (Gligorovski and Herrmann, 2004, Lilie et al., 1968) for 2,3-butanedione. Additionally, photolysis rates were determined in the present study to be  $k_P = 3 \times 10^{-5} \text{ s}^{-1}$ ,  $2 \times 10^{-5} \text{ s}^{-1}$  and  $9 \times 10^{-6} \text{ s}^{-1}$  for methylglyoxal, hydroxyacetone and 2,3-butanedione, respectively.

According to the rate constants for the OH radical reaction reported in the literature and the measured photolysis rates, a faster consumption of methylglyoxal and hydroxyacetone can be expected than for 2,3-butanedione. Such a faster consumption can be clearly seen from Figure 1B because methylglyoxal and hydroxylacetone are completely consumed at the end of the experiment whereas 2,3-butanedione was still present. This might be caused by the smaller rate constant as well as by the lower photolysis rate.

According to the Referees' comment, the following sentence was added to the manuscript:

Page 31898 Line 7-9 was changed to: *“This indicates a faster decomposition compared to 2,3-butanedione of methylglyoxal and hydroxyacetone, which showed a complete consumption at the end of the experiment (Fig. 1). 2,3-Butanedione was not completely consumed during the reaction time of 4 hours, which might be a result of the lower photolysis rate constants.”*

## References:

- Ashworth, R. A., Howe, G. B., Mullins, M. E., and Rogers, T. N.: Air water partitioning coefficients of organics in dilute aqueous-solutions, *J. Hazard. Mater.*, 18, 25-36, 10.1016/0304-3894(88)85057-x, 1988.
- Betterton, E. A., and Hoffmann, M. R.: Henry's law constants of some environmentally important aldehydes. *Environ. Sci. Technol.*, 22, 1415-1418, 1988.
- Blando, J. D., and Turpin B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623-1632, 2000.
- Buttery, R. G., Ling, L. C., and Guadagni, D. G.: Food volatiles - volatilities of aldehydes ketones and esters in dilute water solution, *J. Agric. Food Chem.*, 17, 385-&, 10.1021/jf60162a025, 1969.
- Collett, J.L., Daube, B.C., Gunz, D., and Hoffmann, M.R.: Intensive studies of Sierra Nevada cloud water chemistry and its relationship to precursor aerosol and gas concentrations. *Atmos. Environ.*, 7, 1741-1757, 1990.
- Ervens, B., Gligorovski, S., and Herrmann, H.: Temperature-dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions, *Phys. Chem. Chem. Phys.*, 5, 1811-1824, 10.1039/b300072a, 2003.
- Feng, Y. L., Wen, S., Wang, X. M., Sheng, G. Y., He, Q. S., Tang, J. H., and Fu, J. M.: Indoor and outdoor carbonyl compounds in the hotel ballrooms in Guangzhou, China, *Atmospheric Environment*, 38, 103-112, 10.1016/j.atmosenv.2003.09.061, 2004.
- Fu, T-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K.: Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *J. Geophys. Res.*, 113, 1-17, 2008.
- Fu, T-M., Jacob, D. J., and Heald, C. L.: Aqueous-phase reactive uptake of dicarbonyls as a source of organic aerosol over eastern North America, *Atmos. Environ.*, 43, 1814-1822, 2009.
- Gligorovski, S., and Herrmann, H.: Kinetics of reactions of OH with organic carbonyl compounds in aqueous solution, *Phys. Chem. Chem. Phys.*, 6, 4118-4126, 10.1039/b403070b, 2004.
- Goldan, P. D., Kuster, W. C., Fehsenfeld, F. C., and Montzka, S. A.: Hydrocarbon measurements in the southeastern United States: The Rural Oxidants in the Southern Environment (ROSE) program 1990, *Journal of Geophysical Research-Atmospheres*, 100, 25945-25963, 10.1029/95jd02607, 1995.
- Grosjean, D., and Wright, B.: Carbonyls in urban fog, ice fog, cloudwater and rainwater, *Atmospheric Environment*, 17, 2093-2096, 10.1016/0004-6981(83)90368-2, 1983.
- Grosjean, D.: Formaldehyde and other carbonyls in Los-Angeles ambient air, *Environmental Science & Technology*, 16, 254-262, 10.1021/es00099a005, 1982.
- Grosjean, D., Swanson, R. D., and Ellis, C.: Carbonyls in Los-Angeles air - contribution of direct emissions and photochemistry, *Sci. Total Environ.*, 29, 65-85, 10.1016/0048-9697(83)90034-7, 1983.
- Grosjean, D., Grosjean, E., and Moreira, L. F. R.: Speciated ambient carbonyls in Rio de Janeiro, Brazil, *Environmental Science & Technology*, 36, 1389-1395, 10.1021/es0111232, 2002.
- Herrmann, H., Tilgner, A., Barzagli, P., Majdik, Z., Gligorovski, S., Poulain, L., and Monod, A.: Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0, *Atmospheric Environment*, 39, 4351-4363, 10.1016/j.atmosenv.2005.02.016, 2005.
- Ieda, T., Kitamori, Y., Mochida, M., Hirata, R., Hirano, T., Inukai, K., Fujinuma, Y., and Kawamura, K.: Diurnal variations and vertical gradients of biogenic volatile and semi-volatile organic compounds at the Tomakomai larch forest station in Japan, *Tellus B*, 58, 177-186, 2006.
- Karl, T., Chahan, Y., Jordan, A., and Lindinger, W.: Dynamic measurements of partition coefficients using proton-transfer-reaction mass spectrometry (PTR-MS), *International Journal of Mass Spectrometry*, 12269, 1-13, 2002.
- Kawamura, K., Okuzawa, K., Aggarwal, S. G., Irie, H., Kanaya, Y., and Wang, Z.: Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai, *Atmos. Chem. Phys.*, 13, 5369 - 5380, 2013.

- Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.*, 110, 1-10, 2005.
- Lilie, J., Beck, G., and Henglein, A.: Pulse radiolysis of acetoin radicals and diacetyl anions in aqueous solution, *Berichte Der Bunsen-Gesellschaft Fur Physikalische Chemie*, 72, 529-&, 1968.
- Lin, G., Sillman, S., Penner, J. E., and Ito, A.: Global modeling of SOA: the use of different mechanisms for aqueous-phase formation, *Atmos. Chem. Phys.*, 14, 5451–5475, 2014.
- Matsunaga, S., Mochida, M., and Kawamura, K.: Variation on the atmospheric concentrations of biogenic carbonyl compounds and their removal processes in the northern forest at Moshiri, Hokkaido Island in Japan, *J. Geophys. Res.*, 109, , doi:10.1029/2003JD004100, 2004.
- Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H.: Kinetics of OH-initiated oxidation of oxygenated organic compounds in the aqueous phase: new rate constants, structure-activity relationships and atmospheric implications, *Atmospheric Environment*, 39, 7667-7688, 10.1016/j.atmosenv.2005.03.019, 2005.
- Morillon, V., Debeaufort, F., Jose, J., Tharrault, J. F., Capelle, M., Blond, G., and Voilley, A.: Water vapour pressure above saturated salt solutions at low temperatures, *Fluid Phase Equilib.*, 155, 297-309, 10.1016/s0378-3812(99)00009-6, 1999.
- Müller, K., van Pinxteren, D., Plewka, A., Svrčina, B., Kramberger, H., Hofmann, D., Bachmann, K., and Herrmann, H.: Aerosol characterisation at the FEBUKO upwind station Goldlauter (II): Detailed organic chemical characterisation, *Atmospheric Environment*, 39, 4219-4231, 10.1016/j.atmosenv.2005.02.008, 2005.
- Munger, J. W., Jacob, D. J., Daube, B. C., Horowitz, L. W., Keene, W. C., and Heikes, B. G.: Formaldehyde, glyoxal, and methylglyoxal in air and cloud water at a rural mountain site in central Virginia, *J. Geophys. Res.*, 100, 9325 – 9333, 1995.
- Ortiz, R., Hagino, H., Sekiguchi, K., Wang, Q., and Sakamoto, K.: Ambient air measurements of six bifunctional carbonyls in a suburban area, *Atmos. Res.*, 82, 709–718, 2006.
- Riemer, D., Pos, W., Milne, P., Farmer, C., Zika, R., Apel, E., Olszyna, K., Kliendienst, T., Lonneman, W., Bertman, S., Shepson, P., and Starn, T.: Observations of nonmethane hydrocarbons and oxygenated volatile organic compounds at a rural site in the southeastern United States, *Journal of Geophysical Research-Atmospheres*, 103, 28111-28128, 10.1029/98jd02677, 1998.
- Schütze, M., and Herrmann, H.: Uptake of acetone, 2-butanone, 2,3-butanedione and 2-oxopropanal on a water surface, *Phys. Chem. Chem. Phys.*, 6, 965–971, 2004.
- Sempere, R., and Kawamura K.: Comparative distribution of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban, *Atmos. Environ.*, 28, 449-459, 1994.
- Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, *Journal of Geophysical Research-Atmospheres*, 109, 20, 10.1029/2003jd003883, 2004.
- Snider, J. R., and Dawson, G. A.: Tropospheric light alcohols, carbonyls and acetonitrile - concentrations in southwestern united-states and henry law data, *Journal of Geophysical Research-Atmospheres*, 90, 3797-3805, 10.1029/JD090iD02p03797, 1985.
- Stefan, M. I., and Bolton, J. R.: Reinvestigation of the acetone degradation mechanism in dilute aqueous solution by the UV/H<sub>2</sub>O<sub>2</sub> process, *Environmental Science & Technology*, 33, 870-873, 10.1021/es9808548, 1999.
- Tan, Y., Carlton, A. G., Seitzinger, S. P., and Turpin, B. J.: SOA from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products, *Atmospheric Environment*, 44, 5218-5226, 10.1016/j.atmosenv.2010.08.045, 2010.
- van Pinxteren, D., Plewka, A., Hofmann, D., Müller, K., Kramberger, H., Svrčina, B., Bachmann, K., Jaeschke, W., Mertes, S., Collett, J. L., and Herrmann, H.: Schmucke hill cap cloud and valley stations aerosol characterisation during FEBUKO (II): organic compounds, *Atmos. Environ.*, 39, 4305–4320, 2005.
- Zhao, J., Levitt, N. P., Zhang, R., and Chen, J.: Heterogeneous Reactions of Methylglyoxal in Acidic Media: Implications for Secondary Organic Aerosol Formation, *Environ. Sci. Technol.*, 40, 7682-7687, 2006.
- Zhou, X. L., and Mopper, K.: Apparent partition-coefficients of 15 carbonyl-compounds between air and seawater and between air and fresh-water – implications for air sea exchange, *Environ. Sci. Technol.*, 24, 1864–1869, 1990.
- Zhou, X. L., and Mopper, K.: Photochemical production of low-molecular-weight carbonyl compounds in seawater and surface microlayer and their air-sea exchange, *Mar. Chem.*, 56, 201-213, 10.1016/s0304-4203(96)00076-x, 1997.

## The following changes were made to the manuscript

The term “methyl glyoxal” was changed to “methylglyoxal” in the manuscript text as well as in Fig. 1 and 4 and Table 1 and 2.

Page 31898 Line 7-9: “*This indicates a faster decomposition of methyl glyoxal and hydroxyacetone and confirms the experimental results.*” was changed to “*This indicates a faster decomposition compared to 2,3-butanedione of methylglyoxal and hydroxyacetone, which showed a complete consumption at the end of the experiment (Fig. 1). 2,3-Butanedione was not completely consumed during the reaction time of 4 hours, which might be a result of the lower photolysis rate constants.*”

Page 31898 Line 24-25: “*This is in good agreement with the experimental results obtained in the the present study.*” was changed to “*This is in good agreement with the experimental results obtained in the present study.*”

Page 31906 Line 1: The paragraph “*4. Atmospheric relevance*

*The sources of methylglyoxal in the aqueous phase are thus far not fully elucidated. Methylglyoxal can originate in the atmospheric aqueous phase through i) uptake from the gas phase, and/or ii) formation in the aqueous phase. The importance of the uptake from the gas into the aqueous phase is discussed in the literature but large discrepancies can be found. Kroll et al. (2005) investigated the uptake of methylglyoxal on inorganic seed particles under varying relative humidity. It was found that the uptake was not relevant for methylglyoxal even under high relative humidity. Contrary, Zhao et al. (2006) measured an uptake coefficient of  $\gamma = 7.6 \times 10^{-3}$  on acidic solution. They found an irreversible uptake, which decreases with increasing acidity. Fu et al. (2008, 2009) determined an uptake coefficient on aqueous particles and cloud droplets  $\gamma = 2.9 \times 10^{-3}$ , which is in good agreement with the uptake coefficient measured by Zhao et al. (2006). Lin et al. (2014) modelled an uptake coefficient for several case studies with different multiphase process mechanisms. The uptake coefficient in deliquescent particles was determined to be  $\gamma = 1.47 - 2.92 \times 10^{-5}$ . Overall,  $\gamma$  was two orders of magnitude lower compared to the values determined by Zhao et al. (2006) and Fu et al. (2008, 2009) showing the discrepancies between the different studies available in literature.*

*The in-situ formation of methylglyoxal in the aqueous phase could be an important source as well (Blando and Turpin, 2000; Sempere and Kawamura 1994). Within the present study, MEK was found as a new precursor compound for methylglyoxal in the aqueous phase yielding methylglyoxal with a molar yield of 9.5%. Although the Henry constant of MEK (up to  $K_H =$*

50 M atm I, Schütze and Herrmann, 2004) is lower compared to methylglyoxal ( $KH = 3.7 \times 10^3$  M atm<sup>-1</sup>, Betterton and Hoffmann, 1988), van Pinxteren et al. (2005) found higher concentrations in cloud water as it was expected. Thus, the phase transfer of MEK from the gas in the aqueous phase could be more important as currently derived from the available Henry constants. Besides the phase transfer, the in-situ formation of MEK in aqueous phase formation might also represents an important source.

As, the oxidation of MEK yielding methylglyoxal has not been studied much before, it should be considered as a formation process of methylglyoxal.” was included in the manuscript.

Page 31906 Line 1: “4. Summary” was changed to “5. Summary”

Page 31908 Line 13: The reference “Blando, J. D., and Turpin B. J.: Secondary organic aerosol formation in cloud and fog droplets: a literature evaluation of plausibility, *Atmos. Environ.*, 34, 1623-1632, 2000.” was included in the manuscript.

Page 31909 Line 28: The references “Fu, T-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K., Global budgets of atmospheric glyoxal and methylglyoxal, and implications for formation of secondary organic aerosols, *J. Geophys. Res.*, 113, 1-17, 2008.” and “Fu, T-M., Jacob, D. J., and Heald, C. L., Aqueous-phase reactive uptake of dicarbonyls as a source of organic aerosol over eastern North America, *Atmos. Environ.*, 43, 1814–1822, 2009.” were included in the manuscript.

Page 31911 Line 16: The reference “Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H., Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, *J. Geophys. Res.*, 110, 1-10, 2005.” was added to the manuscript.

Page 31911 Line 18: The reference “Lin, G., Sillman, S., Penner, J. E., and Ito, A., Global modeling of SOA: the use of different mechanisms for aqueous-phase formation, *Atmos. Chem. Phys.*, 14, 5451–5475, 2014.” was included in the manuscript.

Page 31912 Line 31: The reference “Sempere, R., and Kawamura K.: Comparative distribution of dicarboxylic acids and related polar compounds in snow, rain and aerosols from urban, *Atmos. Environ.*, 28, 449-459, 1994.” was included in the manuscript.

Page 31914 Line 1: The reference: “Zhao, J., Levitt, N. P., Zhang, R., and Chen, J., Heterogeneous Reactions of Methylglyoxal in Acidic Media: Implications for Secondary



*Organic Aerosol Formation, Environ. Sci. Technol.*, 40, 7682-7687, 2006.” was added to the manuscript.

### General changes made to the supplement

The term “*methyl glyoxal*” was changed to “*methylglyoxal*” in the supplement text and Fig, S1, S2 and S3.