

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

to evaluate aqSOA formation (El Haddad et al., 2009; Ortiz-Montalvo et al., 2012), and in the gas phase with gasSOA formation followed by immersion of these gasSOA in homogeneous aqueous phase (Bateman et al., 2011; Liu et al., 2012a). Previous experimental studies have not been performed on a multiphase system and, as a result, they only refer to the amount of precursor consumed in aqueous phase to determine formation yields. Consequently, and contrary to SOA yields obtained in gaseous phase (gasSOA), these yields cannot be directly implemented in multiphase models because the link between aqueous and gaseous phases (transfer between the two phases) is not taken into account. These works thus lead generally to an overestimation of yields associated with gaseous precursors, whose concentrations depend on the relative importance of their loss in the gaseous phase and their transfer in the aqueous phase. Furthermore, Daumit et al. (2014) recently showed that the reactivity in a multiphase system may be substantially different from reactivity in homogeneous aqueous phase, highlighting the need to study controlled multiphase systems, which are more realistic for the atmosphere.

In the present study, taking advantage of the ability to artificially produce clouds in the CESAM simulation chamber (Wang et al., 2011), dedicated multiphase experiments were carried out to study SOA multiphase formation from isoprene in order to experimentally observe and quantify the impact of cloud-phase reactions on SOA formation. Isoprene was chosen as the precursor because it is highly reactive and it represents the most emitted VOC globally. Isoprene gas-phase oxidation is known to lead to low yields of gasSOA (Brégonzio-Rozier et al., 2015; Dommen et al., 2006; Edney et al., 2005; Kleindienst et al., 2006; Kroll et al., 2005; Zhang et al., 2011) and to large amounts of volatile water soluble compounds (such as methylglyoxal, glyoxal, glycolaldehyde and pyruvic acid) which can interact with the aqueous phase in the atmosphere and potentially lead to the formation of aqSOA after water evaporation. In this study, the formation of aqSOA from isoprene photooxidation in the presence of clouds is investigated by studying the concentration and chemistry of gaseous, aqueous and particulate phases, and the chemical exchanges between these phases.

ual air. Using this procedure, starting from dry conditions in the chamber (< 5 % RH), the first water vapour injection allowed the chamber to reach 80 % RH within less than one minute. A second water vapour injection leads to water saturation in the chamber and cloud formation. The obtained clouds were monitored, and Table 1 shows that their mean physical properties were close to those of typical atmospheric clouds. A typical droplet mass size distribution is also shown in Fig. S1. Using the above described procedure, several clouds could be generated during one experiment (typically 2 or 3).

2.1.2 Cleaning and control experiments

In order to avoid any contamination from semi-volatile organic compounds (SVOCs) off-gassing from the walls, a manual cleaning of the chamber walls was performed prior each experiment. To this purpose, lint free wipes (Spec-Wipe® 3) soaked in ultrapure water (18.2 MΩ, ELGA Maxima) were used. To complete this manual cleaning, the walls were heated at 40 °C and the chamber was pumped down to secondary vacuum in the range of 6×10^{-4} mbar for two hours at a minimum. After pumping, the chamber was cooled down to 20–22 °C, and a control experiment was performed by generating a cloud in the presence of a N₂/O₂ mixture (80%/20%), under irradiation. All of the instruments were connected to the chamber during the entire control experiment which lasted for ~ one hour after cloud generation. The aim of these control experiments was to monitor aqSOA formation arising from the dissolution of any remaining water soluble VOCs off-gassing from the walls or from contaminants introduced with water vapour. After this control experiment, the temperature of the chamber walls was increased to 50 °C before starting overnight pumping. The amount of particulate matter observed during all the control experiments was fairly reproducible with an average value of $1.5 \pm 0.4 \mu\text{g m}^{-3}$ of dried particles formed during a cloud event (Table S1).

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



2.1.3 Cloud experiments

Two types of cloud experiments were performed to study the impact of clouds on isoprene-SOA formation: (i) clouds generated during the first stages of isoprene photooxidation, prior any gasSOA formation; and (ii) clouds generated during later stages of the reaction, when gasSOA mass reached its maximum. Table 2 shows all of the experimental initial conditions, the number of generated clouds during each experiment and their maximum liquid water contents (LWC_{max}) for both types of experiments.

In the first type of experiment, a diphasic system (gas-cloud), the aim was to produce evapo-condensation cycles in the presence of gaseous isoprene oxidation products prior to any gasSOA formation. This type of experiment started under dry conditions ($< 5\%$ RH), and the first water vapour injection, leading to $\sim 80\%$ RH, was performed after 2 h of irradiation. This time corresponded to $\sim 80\%$ of isoprene consumption and to the maximum concentration of the first generation isoprene gaseous reaction products (Brégonzio-Rozier et al., 2015). After ca. ten minutes, the second water vapour injection, allowing cloud formation by saturation, was made. Two to three clouds were generated during each diphasic experiment (gas-cloud).

In the second type of experiment, a triphasic system (gas-SOA-cloud), we tested the influence of cloud generation on isoprene photooxidation during a later stage of the reaction, i.e., when the first generation oxidation gaseous products of isoprene were mostly consumed, and when maximum gasSOA mass concentration was reached. In this case, in addition to the dissolution of gaseous species in the aqueous phase, some of the condensed matter could also dissolve in droplets. In this type of experiment, the formation of gasSOA was monitored under dry conditions ($< 5\%$ RH), and the first cloud was generated when the maximum gasSOA mass concentration was reached, generally after 7 to 9 h of irradiation, in a system containing more oxidized species than in the diphasic system. One to two clouds were generated during each triphasic experiment (gas-SOA-cloud).

**SOA formation during
cloud condensation-
evaporation
cycles**

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



For each type of experiment, the protocol followed before beginning irradiation was the same as the one described in Brégonzio-Rozier et al. (2015). After overnight pumping, synthetic air was injected into the chamber to reach atmospheric pressure. This air was comprised of approximately 80 % N₂ produced from the evaporation of pressurized liquid nitrogen, and around 20 % O₂ (Linde, 5.0). A known pressure of isoprene, leading to a mixing ratio of 800–850 ppb in the chamber, was then introduced using a known volume glass bulb. Nitrous acid (HONO) was used as the OH source. HONO was produced by adding sulfuric acid (10⁻² M) dropwise into a solution of NaNO₂ (0.1 M) and flushed into the chamber using a flow of N₂. NO_x was also introduced as a side product during HONO injection. Photooxidation of the system was then initiated by turning on the lamps (reaction time 0 corresponds to the irradiation start).

2.2 Measurements

A Fourier Transform Infra-Red spectrometer (FTIR, Brucker[®], TENSOR 37) was used to measure concentrations of isoprene, MVK, MACR, formaldehyde, methylglyoxal, peroxyacetyl nitrate (PAN), formic acid, carbon monoxide (CO) and NO₂ during dry conditions. Complementary to FTIR measurements, a proton-transfer time of flight mass spectrometer (PTR-ToF-MS 8000, Ionicon Analytik[®]) was used for online gas-phase measurements in the *m/z* range 10–200 including isoprene, the sum of MACR and MVK, 3-methylfuran (3 M-F), acetaldehyde, the sum of glycolaldehyde and acetic acid, acrolein, acetone, hydroxyacetone, and a few other oxygenated VOCs (de Gouw et al., 2003). The PTR-ToF-MS was connected to the chamber through a 120 cm long Peek capillary heated at 100 °C. Its signal was calibrated using a certified gas standard mixture (EU Version TO-14A Aromatics 110L, 100 ppbV each). Considering the high amounts of water in the sampled air during and after cloud events, the sum of the primary H₃O⁺ and cluster ion H₂O · H₃O⁺ signal derived from H₃¹⁸O⁺ (*m/z* 21.023) and H₂¹⁸O · H₃O⁺ (*m/z* 39.033) count rate was taken into account for quantification. A commercial UV absorption monitor (Horiba[®], APOA-370) was used to measure ozone. NO

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



structure of the compound, the wall material and the experiment's organic loading, humidity and temperature. If production of additional semi-volatile species occurs in the droplet during cloud events, Henry's Law equilibrium suggests that these species are isolated from the walls in the droplets. After cloud dissipation, additional SOA mass is formed from these SVOCs which, at the same time, also experience a re-partitioning between particles and the walls. When the cloud is evaporated, since the available particle surface area is around 400 times smaller than the geometric wall surface area, the additional SOA mass decreases due to this equilibrium re-establishment under humid conditions. Wall loss kinetics data reported in the literature for a Teflon chamber (Matsunaga and Ziemann, 2010) has led to a characteristic time ranging from one hour for non-polar species to 8 min for carbonyls: these results are compatible with the rates of the decays observed in our experiments (20 min to one hour). Furthermore, pseudo-first order rates for loss processes of organic compounds found in Wang et al. (2011) suggest that similar wall loss kinetics are expected in the CESAM chamber.

Assuming that this observed SOA mass decay is due to wall re-partitioning, this process will not occur in the atmosphere, and aqSOA production can be determined using the maximum mass concentration measured at the end of each cloud event. In that case, aqSOA mass yield from isoprene photooxidation in the presence of clouds would be between 0.002 and 0.004 considering our results from the diphasic experiments, or between two and four times higher than mass yields observed for isoprene photooxidation experiments carried out under dry conditions with preliminary manual cleaning (Brégonzio-Rozier et al., 2015). For triphasic experiments, the observed increase of total SOA mass concentration at the end of each cloud event was at least a factor of two compared to the gasSOA mass concentrations reached under dry conditions prior cloud formation. Hence, it can be assumed that a substantial aqSOA production was observed in both types of experiments. Furthermore, the fact that additional SOA mass was formed in the triphasic system (i.e., in the second mode) seems to demonstrate that the role of cloud chemistry is not just to increase the rate of gas-phase oxidation reactions but is adding new chemistry.

3.2 Dissolution and reactivity of gaseous species in cloud droplets

The time profiles of the gas phase reactants and oxidation products during a diphasic experiment are shown in Fig. 2 (similar profiles were observed for triphasic systems, see Fig. S3) in which two clouds were generated. Ozone, NO_x and HONO showed no significant change in their concentrations during cloud events (Fig. 2b and c), with mixing ratios remaining at around 5 ppbv for HONO and NO. The concentrations of isoprene, the sum of MACR and MVK, acetone and $\text{C}_5\text{H}_8\text{O}$ (compound that may be attributed to 2-methylbut-3-enal, Brégonzio-Rozier et al., 2015) also seem not to be influenced by cloud generation (Fig. 2a and f), as their concentrations remained unchanged during cloud events. On the contrary, more water soluble species (for example, methylglyoxal and formic acid) showed a sharp decrease in their concentrations during cloud generation (Fig. 2d, e, g and h). During each cloud event and for 20 additional minutes, the PTR-ToF-MS signal was not used due to possible droplet impaction in the heated sampling line. Using the concentrations of VOCs before each cloud event (C_{before}) and 20 min after (C_{after}), we calculated the gas phase concentration changes during cloud events ($\Delta C_{\text{cloud}} = C_{\text{before}} - C_{\text{after}}$, see Table 4). From these data, it can be noted that the loss of the most water soluble VOCs (e.g., glycolaldehyde, acetic acid, methylglyoxal, formic acid and hydroxyacetone) was significant during the cloud events (higher than 32%). Isoprene was excluded from this calculation as its gas phase photochemical decay did not seem to be affected by the cloud events.

Following a hypothesis based on the kinetic determination of the mass-transport of VOCs from the gas phase to water droplets (Schwartz, 1986), Henry's Law equilibrium was considered immediate at the start of cloud generation. Hence, considering the C_{before} values for each measured VOCs, the liquid water content and assuming Henry's Law equilibrium, it was possible to estimate the potential mass of VOCs transferred into the aqueous phase (see Supplement Sect. 1). The obtained value is compared to the mass of formed aqSOA in Table 4. It can be considered that this estimated mass represents a lower limit since this calculation only considers the measured VOCs

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



second mode (which contains a large part of nitrates) is quite unlikely, and thus, that a re-partitioning between particles and the walls is far more likely.

4 Atmospheric implications and conclusion

The impact of cloud events on an isoprene/NO_x system in the presence of light and at different oxidation stages was investigated in a stainless steel simulation chamber. It was observed that a single and relatively short cloud condensation cycle in the presence of irradiation led to a significant aqSOA mass yield (0.002–0.004) with values between two and four times higher than what was observed for isoprene photooxidation experiments carried out under dry conditions (Brégonzio-Rozier et al., 2015). Even if no significant changes were noted in the SOA elemental ratios, it appears that the bulk chemical aerosol composition was significantly impacted by cloud events since an additional formation of particulate matter containing organics, nitrate and ammonium fragments was observed. This formed aqSOA seems to be metastable in the simulation chamber environment due to gas phase/wall repartitioning after cloud dissipation. However, it can be assumed that in a real cloud, in the absence of walls, the semi-volatile organic matter formed would remain in the aerosol/hydrometeor phase due to re-condensation on pre-existing aerosol or condensation/dissolution on the remaining droplets. Since clouds undergo several evapo-condensation cycles in the atmosphere, this study highlights the potentially great importance of cloud chemistry on the secondary aerosol budget.

Aqueous SOA formation was characterized by the appearance of a second mode which can be connected with the “droplet mode” which has been previously detected in the ambient atmosphere during early studies (Hering and Friedlander, 1982; John et al., 1990; Meng and Seinfeld, 1994). Evidence was obtained by John et al. (1990) that this growing second mode grew out of the condensation mode by the addition of water and aqueous phase oxidation products. Our experiment provided here a direct simulation of the origin of a “droplet mode” in the atmospheric aerosol.

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Finally, using the elemental ratios obtained in this study (Fig. 3), the aqSOA carbon mass yields obtained in this study range between 0.002 to 0.004, which is an order of magnitude lower than those predicted by a multiphase model performed on isoprene multiphase photochemistry under comparable $\text{VOC}_{(\text{ppbC})}/\text{NO}_{\text{x}(\text{ppb})}$ ratios (Ervens et al., 2008). However, the model was run using different initial conditions compared to our experiments: much lower initial concentrations of isoprene and NO_x (by a factor of $\sim 10^3$ and ~ 100 respectively), initial seed wet particles, and lower liquid water content during cloud events were used in the model. The observed difference between model and experimental results thus supports the great need for the development of simulation chamber multiphase models in order to accurately compare experimental results with the known multiphase photochemical processes. Overall, our results emphasize the need to use the same integrated multiphase approach on other chemical systems and to integrate these results in atmospheric chemistry models to improve SOA formation determinations.

The Supplement related to this article is available online at doi:10.5194/acpd-15-20561-2015-supplement.

Acknowledgements. The authors thank A. Allanic, S. Ravier, P. Renard and P. Zapf for their contributions in the experiments. The authors also acknowledge the institutions that have provided financial support: the French National Institute for Geophysical Research (CNRS-INSU) within the LEFE-CHAT program through the project “Impact de la chimie des nuages sur la formation d’aérosols organiques secondaires dans l’atmosphère” and the French National Agency for Research (ANR) project CUMULUS ANR-2010-BLAN-617-01. This work was also supported by the EC within the I3 project “Integrating of European Simulation Chambers for Investigating Atmospheric Processes” (EUROCHAMP-2, contract no. 228335). The authors gratefully thank the MASSALYA instrumental platform (Aix Marseille Université, ice.univ-amu.fr) for the analysis and measurements used in this paper.

References

- Aiken, A. C., Decarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H.,
5 Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high-resolution time-of-flight aerosol mass spectrometry, *Environ. Sci. Technol.*, 42, 4478–4485, 2008.
- Altieri, K. E., Seitzinger, S. P., Carlton, A. G., Turpin, B. J., Klein, G. C., and Marshall, A. G.: Oligomers formed through in-cloud methylglyoxal reactions: chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry, *Atmos. Environ.*, 42, 1476–1490, 2008.
- Bateman, A. P., Nizkorodov, S. A., Laskin, J., and Laskin, A.: Photolytic processing of secondary organic aerosols dissolved in cloud droplets, *Phys. Chem. Chem. Phys.*, 13, 12199–12212, 2011.
- 15 Benkelberg, H. J., Hamm, S., and Warneck, P.: Henry's law coefficients for aqueous solutions of acetone, acetaldehyde and acetonitrile, and equilibrium constants for the addition compounds of acetone and acetaldehyde with bisulfite, *J. Atmos. Chem.*, 20, 17–34, 1995.
- Betterton, E. A. and Hoffmann, M. R.: Henry's law constants of some environmentally important aldehydes, *Environ. Sci. Technol.*, 22, 1415–1418, 1988.
- 20 Bianchi, F., Dommen, J., Mathot, S., and Baltensperger, U.: On-line determination of ammonia at low pptv mixing ratios in the CLOUD chamber, *Atmos. Meas. Tech.*, 5, 1719–1725, doi:10.5194/amt-5-1719-2012, 2012.
- Brégonzio-Rozier, L., Siekmann, F., Giorio, C., Pangui, E., Morales, S. B., Temime-Roussel, B., Gratien, A., Michoud, V., Ravier, S., Cazaunau, M., Tapparo, A., Monod, A., and Doussin, J.-F.: Gaseous products and secondary organic aerosol formation during long term oxidation of isoprene and methacrolein, *Atmos. Chem. Phys.*, 15, 2953–2968, doi:10.5194/acp-15-2953-2015, 2015.
- 25 Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, 26, 185–222, 2007.
- 30

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**SOA formation during
cloud condensation-
evaporation
cycles**

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Carlton, A. G. and Turpin, B. J.: Particle partitioning potential of organic compounds is highest in the Eastern US and driven by anthropogenic water, *Atmos. Chem. Phys.*, 13, 10203–10214, doi:10.5194/acp-13-10203-2013, 2013.

Carlton, A. G., Turpin, B. J., Lim, H. J., Altieri, K. E., and Seitzinger, S.: Link between isoprene and secondary organic aerosol (SOA): pyruvic acid oxidation yields low volatility organic acids in clouds, *Geophys. Res. Lett.*, 33, L06822, doi:10.1029/2005GL025374, 2006.

Carlton, A. G., Turpin, B. J., Altieri, K. E., Seitzinger, S., Reff, A., Lim, H. J., and Ervens, B.: Atmospheric oxalic acid and SOA production from glyoxal: results of aqueous photooxidation experiments, *Atmos. Environ.*, 41, 7588–7602, 2007.

Colvile, R. N., Bower, K. N., Choularton, T. W., Gallagher, M. W., Beswick, K. M., Arends, B. G., Kos, G. P. A., Wobrock, W., Schell, D., Hargreaves, K. J., Storeton-West, R. L., Cape, J. N., Jones, B. M. R., Wiedensohler, A., Hansson, H. C., Wendisch, M., Acker, K., Wieprecht, W., Pahl, S., Winkler, P., Berner, A., Krusiz, C., and Gieray, R.: Meteorology of the great dun fell cloud experiment 1993, *Atmos. Environ.*, 31, 2407–2420, 1997.

Couvidat, F., Sartelet, K., and Seigneur, C.: Investigating the impact of aqueous-phase chemistry and wet deposition on organic aerosol formation using a molecular surrogate modeling approach, *Environ. Sci. Technol.*, 47, 914–922, 2013.

Dall'Osto, M., Harrison, R. M., Coe, H., and Williams, P.: Real-time secondary aerosol formation during a fog event in London, *Atmos. Chem. Phys.*, 9, 2459–2469, doi:10.5194/acp-9-2459-2009, 2009.

Daumit, K. E., Carrasquillo, A. J., Hunter, J. F., and Kroll, J. H.: Laboratory studies of the aqueous-phase oxidation of polyols: submicron particles vs. bulk aqueous solution, *Atmos. Chem. Phys.*, 14, 10773–10784, doi:10.5194/acp-14-10773-2014, 2014.

De Carlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem.*, 78, 8281–8289, 2006.

de Gouw, J., Warneke, C., Karl, T., Eerdekens, G., van der Veen, C., and Fall, R.: Sensitivity and specificity of atmospheric trace gas detection by proton-transfer-reaction mass spectrometry, *Int. J. Mass Spectrom.*, 223–224, 365–382, 2003.

Dommen, J., Metzger, A., Duplissy, J., Kalberer, M., Alfarra, M. R., Gascho, A., Weingartner, E., Prevot, A. S. H., Verheggen, B., and Baltensperger, U.: Laboratory observation of

**SOA formation during
cloud condensation-
evaporation
cycles**

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

oligomers in the aerosol from isoprene/NO_x photooxidation, *Geophys. Res. Lett.*, **33**, L13805, doi:10.1029/2006GL026523, 2006.

Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos Villegas, C. R., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, *Atmos. Chem. Phys.*, **7**, 2691–2704, doi:10.5194/acp-7-2691-2007, 2007.

Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W., and Claeys, M.: Formation of 2-methyl tetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x/SO₂/air mixtures and their detection in ambient PM_{2.5} samples collected in the eastern United States, *Atmos. Environ.*, **39**, 5281–5289, 2005.

El Haddad, I., Yao Liu, Nieto-Gligorovski, L., Michaud, V., Temime-Roussel, B., Quivet, E., Marchand, N., Sellegri, K., and Monod, A.: In-cloud processes of methacrolein under simulated conditions – Part 2: Formation of secondary organic aerosol, *Atmos. Chem. Phys.*, **9**, 5107–5117, doi:10.5194/acp-9-5107-2009, 2009.

Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.: Secondary organic aerosol yields from cloud-processing of isoprene oxidation products, *Geophys. Res. Lett.*, **35**, L02816, doi:10.1029/2007GL031828, 2008.

Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, *Atmos. Chem. Phys.*, **11**, 11069–11102, doi:10.5194/acp-11-11069-2011, 2011.

Ervens, B., Sorooshian, A., Lim, Y. B., and Turpin, B. J.: Key parameters controlling OH-initiated formation of secondary organic aerosol in the aqueous phase (aqSOA), *J. Geophys. Res.-Atmos.*, **119**, 3997–4016, 2014.

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, *P. Natl. Acad. Sci. USA*, **107**, 6670–6675, 2010.

Galloway, M. M., Huisman, A. J., Yee, L. D., Chan, A. W. H., Loza, C. L., Seinfeld, J. H., and Keutsch, F. N.: Yields of oxidized volatile organic compounds during the OH radical initiated

**SOA formation during
cloud condensation-
evaporation
cycles**

L. Brégonzio-Rozier et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

oxidation of isoprene, methyl vinyl ketone, and methacrolein under high-NO_x conditions, *Atmos. Chem. Phys.*, 11, 10779–10790, doi:10.5194/acp-11-10779-2011, 2011.

Giorio, C., Tapparo, A., Dall'Osto, M., Beddows, D. C. S., Esser-Gietl, J. K., Healy, R. M., and Harrison, R. M.: Local and regional components of aerosol in a heavily trafficked street canyon in Central London derived from PMF and cluster analysis of single-particle ATOFMS spectra, *Environ. Sci. Technol.*, 49, 3330–3340, 2015.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Herckes, P., Valsaraj, K. T., and Collett Jr, J. L.: A review of observations of organic matter in fogs and clouds: origin, processing and fate, *Atmos. Res.*, 132–133: 434–449, doi:10.1016/j.atmosres.2013.06.005, 2013.

Hering, S. V. and Friedlander, S. K.: Origins of aerosol sulfur size distributions in the Los Angeles basin, *Atmos. Environ.*, 16, 2647–2656, 1982.

Herrmann, H.: Kinetics of aqueous phase reactions relevant for atmospheric chemistry, *Chem. Rev.*, 103, 4691–4716, 2003.

Herrmann, H., Schaefer, T., Tilgner, A., Styler, S. A., Weller, C., Teich, M., and Otto, T.: Tropospheric aqueous-phase chemistry: kinetics, mechanisms, and its coupling to a changing gas phase, *Chem. Rev.*, 115, 4259–4334, 2015.

Hilal, S. H., Ayyampalayam, S. N., and Carreira, L. A.: Air-liquid partition coefficient for a diverse set of organic compounds: Henry's law constant in water and hexadecane, *Environ. Sci. Technol.*, 42, 9231–9236, 2008.

Huang, X.-F., Yu, J. Z., He, L.-Y., and Yuan, Z.: Water-soluble organic carbon and oxalate in aerosols at a coastal urban site in China: size distribution characteristics, sources, and formation mechanisms, *J. Geophys. Res.-Atmos.*, 111, D22212, doi:10.1029/2006JD007408, 2006.

IPCC: Climate Change 2013: The Physical Science Basis, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midg-

**SOA formation during
cloud condensation-
evaporation
cycles**

L. Brégonzio-Rozier et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

measurements using PTR-MS: calibration, humidity dependence, inter-comparison and initial results, *Atmos. Meas. Tech.*, 4, 2345–2358, doi:10.5194/amt-4-2345-2011, 2011.

Wylie, D., Jackson, D. L., Menzel, W. P., and Bates, J. J.: Trends in global cloud cover in two decades of HIRS observations, *J. Climate*, 18, 3021–3031, 2005.

5 Zhang, H., Surratt, J. D., Lin, Y. H., Bapat, J., and Kamens, R. M.: Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions, *Atmos. Chem. Phys.*, 11, 6411–6424, doi:10.5194/acp-11-6411-2011, 2011.

10 Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimojo, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species
15 in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, 34, L13801, doi:10.1029/2007GL029979, 2007.

Zhang, X., Cappa, C. D., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *P. Natl. Acad. Sci. USA*, 111, 5802–5807, 2014.

20 Zhou, X., Huang, G., Civerolo, K., and Schwab, J.: Measurement of atmospheric hydroxyacetone, glycolaldehyde, and formaldehyde, *Environ. Sci. Technol.*, 43, 2753–2759, 2009.

Zhou, X. L., Qiao, H. C., Deng, G. H., and Civerolo, K.: A method for the measurement of atmospheric HONO based on DNPH derivatization and HPLC analysis, *Environ. Sci. Technol.*, 33, 3672–3679, 1999.

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 2. Initial experimental conditions, maximum aerosol mass obtained under dry conditions and information on the generated clouds.

Experiment ^{a, b}	[Isoprene] _i (ppb)	[NO] _i (ppb)	[NO ₂] _i ^c (ppb)	[HONO] _i (ppb)	ΔM_0^d ($\mu\text{g m}^{-3}$)	T _i (°C)	Number of clouds	LWC _{max} ^e (g m^{-3})
Diphasic experiments								
D300113	817	95	71	161	/	21	2	0.75 0.38
D010213	800	103	49	133	/	21.1	2	1.17 0.55
D190313	831	123	58	99	/	19.8	3	0.41 0.65 0.50
Triphasic experiments								
T160113	846	143	27	15	< 0.1	21.5	1	0.42
T280113	833	88	45	125	2.8	18.3	2	0.60 0.69
T130313	840	66	< 1	45	2.4	17.5	1	n.m. ^f
T250313	802	137	48	121	0.15	19.7	2	0.01 0.01

^a All experiments were carried out at initial RH < 5%.

^b Experimental IDs starting with “D” indicate diphasic experiments and experimental IDs starting with “T” indicate triphasic experiments.

^c Corrected from HONO interference.

^d gasSOA mass concentration using an effective density of 1.4 g cm^{-3} (Brégonzio-Rozier et al., 2015). There is no initial gasSOA formation for diphasic experiments.

^e LWC_{max} of each cloud generated.

^f not measured.

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Table 4. Comparison between measured VOC loss, potential aqueous phase dissolution of gas phase species and particle formation during cloud events of each system.

	Diphasic system		Triphasic system		K_H (Matm ⁻¹)	Reference
	D300113	D010213	T160113	T280113		
	$\Delta C_{\text{cloud}}^a$ ($\mu\text{g m}^{-3}$) and relative change (%)					
Isoprene ^g	0	0	0	0	3.4×10^{-2}	Leng et al. (2013)
C ₄ H ₆ O ^g :	0	0	0	0		
MACR					9.5	Hilal et al. (2008)
MVK					18	Hilal et al. (2008)
Acrolein	1.1 (19%)	0.9 (16%)	2.7 (41%)	2.3 (30%)	9.5	Hilal et al. (2008)
3-methylfuran	1.7 (15%)	1.7 (14%)	0	0	6.1 ^d	Hilal et al. (2008)
Acetaldehyde	1.3 (3%)	0.7 (2%)	4.3 (9%)	5.6 (11%)	13	Benkelberg et al. (1995)
Acetone ^g	0	0	0	0	33	Poulain et al. (2010)
Formaldehyde	–	–	–	–	3.2×10^3	Staudinger and Roberts (1996)
Methylglyoxal	34.4 (49%)	32.1 (49%)	23 (52%)	31.2 (42%)	3.7×10^3	Betterton and Hoffmann (1988)
C ₂ H ₄ O ₂ :	59.4 (37%)	58.4 (36%)	141.4 (46%)	143.2 (35%)		
Acetic acid ^b					4.6×10^3	Staudinger and Roberts (2001)
Glycolaldehyde					4.1×10^4	Betterton and Hoffmann (1988)
Formic acid ^b	49.1 (41%)	47.8 (38%)	107.8 (49%)	177.2 (48%)	6.7×10^3	Staudinger and Roberts (2001)
Hydroxyacetone	15.4 (32%)	18.2 (37%)	32.1(47%)	26.3 (36%)	7.8×10^3	Zhou et al. (2009)
C ₄ H ₆ O ₂ :	1.4 (7%)	2.2 (11%)	3.6 (26%)	3.2 (18%)		
3-oxobutanal ^c					1.1×10^4	Estimated using GROMHE
hydroxyMVK ^c					1.9×10^3	(Raventos-Duran et al., 2010)
C ₅ H ₈ O ^g :						Estimated using GROMHE
2-methylbut-3-enal ^c	0	0	0	0	27.1	(Raventos-Duran et al., 2010)
C ₅ H ₈ O ₂ :						Estimated using GROMHE
2-methyl-but-2-enedial ^c	7.6 (41%)	8 (39%)	17.6 (55%)	3.2 (36%)	2.0×10^4	(Raventos-Duran et al., 2010)
C ₅ H ₄ O ₃ ^c	4.6 (43%)	5 (46%)	8.2 (69%)	3.2 (54%)	$\gg 10^4$	–
Measured VOCs loss after cloud evaporation ^e ($\mu\text{g m}^{-3}$)	176	175	341	395		
Expected VOCs dissolution in water at cloud start ^f ($\mu\text{g m}^{-3}$)	117	164	108	201		
Maximum particle mass concentration enhancement measured during cloud event ($\mu\text{g m}^{-3}$)	8.0	6.1	6.4	6.5		
LWC _{max} first cloud (g m^{-3})	0.75	1.17	0.42	0.60		

^a $\Delta C_{\text{cloud}} = C_{\text{before}} - C_{\text{after}}$. C_{after} corresponds to mixing ratios measured 20 min after cloud evaporation, when the PTR-ToF-MS signal was stabilized for all compounds.

^b The acids were considered undissociated.

^c C₄H₆O₂ was attributed to 3-oxobutanol and hydroxyMVK; C₅H₈O and C₅H₈O₂ were attributed to 2-methylbut-3-enal and 2-methylbut-2-enedial respectively, and C₂H₄O₃ could not be attributed to any known isoprene product (Brégonzio-Rozier et al., 2015).

^d Effective Henry's Law constant of 3-methylfuran was assumed identical to the one of 2-methyltetrahydrofuran.

^e Total VOC loss as measured by the PTR-ToF-MS (excluding formaldehyde for which the strong humidity-dependent sensitivity was not assessed) 20 min after cloud evaporation.

^f Dissolution of VOCs is calculated assuming Henry's Law equilibrium at cloud start (see Supplement Sect. 1). Formaldehyde cannot be accurately quantified by PTR-MS under highly variable humidity conditions (Warneke et al., 2011). As a result, formaldehyde mixing ratios used for calculations were taken at low relative humidity, before water vapour injection.

^g These species were excluded from VOCs loss calculation as their decay from gas phase chemistry did not sound affected by the cloud events.

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 5. Average elemental ratios of SOA from isoprene photooxidation under dry conditions and after cloud generation (diphasic and triphasic experiments). Values in parentheses reflect the measurement uncertainty as determined by Aiken et al. (2008).

O/C	OM/OC	H/C	Reference
0.58 (± 0.18)	1.90 (± 0.11)	1.45 (± 0.15)	Diphasic experiments
0.58 (± 0.18)	1.89 (± 0.11)	1.39 (± 0.14)	Triphasic experiments
0.60 (± 0.19)	1.92 (± 0.12)	1.43 (± 0.14)	Dry conditions (Brégonzio-Rozier et al., 2015)

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

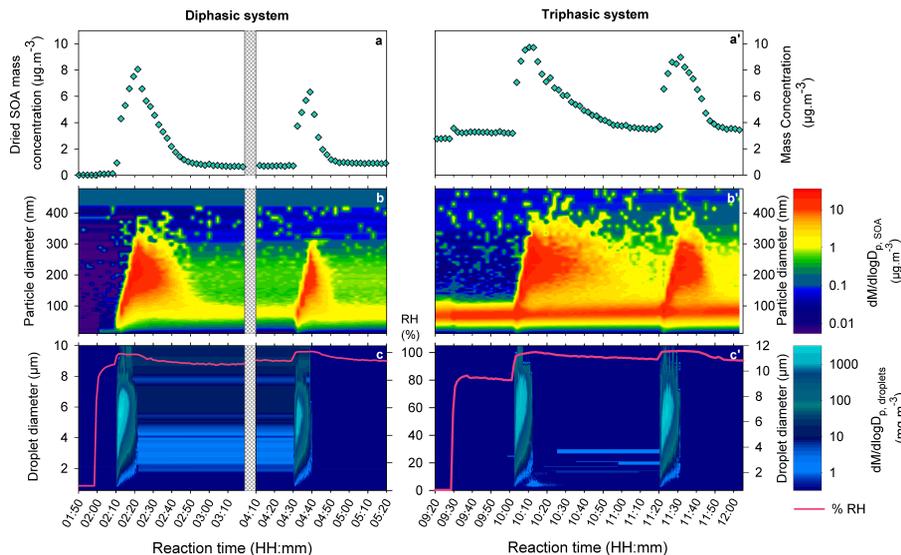


Figure 1. Effects of liquid phase clouds on SOA mass concentrations during two cloud events for typical diphasic (D300113, left panel) and triphasic (T280113, right panel) systems. Time profiles of (a and a') dried SOA mass concentration, (b and b') dried SOA mass size distribution, (c and c') cloud droplets mass size distribution and relative humidity in the simulation chamber. A particle density of $1.4 \mu\text{g m}^{-3}$ was assumed.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

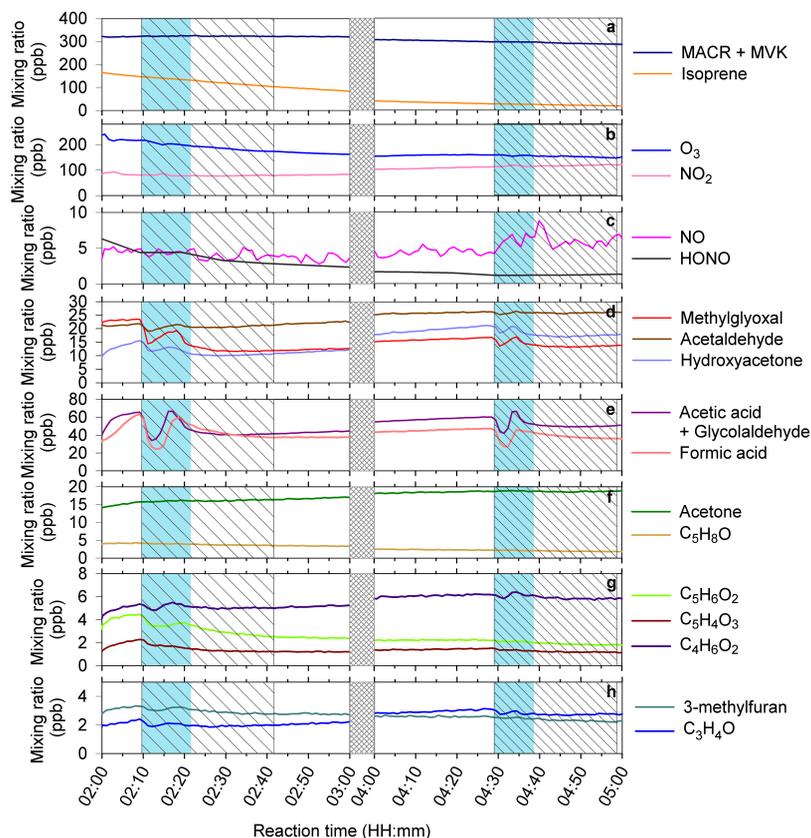


Figure 2. Time profiles of the gas phase reactants and isoprene oxidation products during a diphasic experiment (D300113). Blue areas indicate cloud events and hatched area indicate time needed for the PTR-ToF-MS signal to stabilize after the start of cloud generation (droplet and memory effects in the sampling line).

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

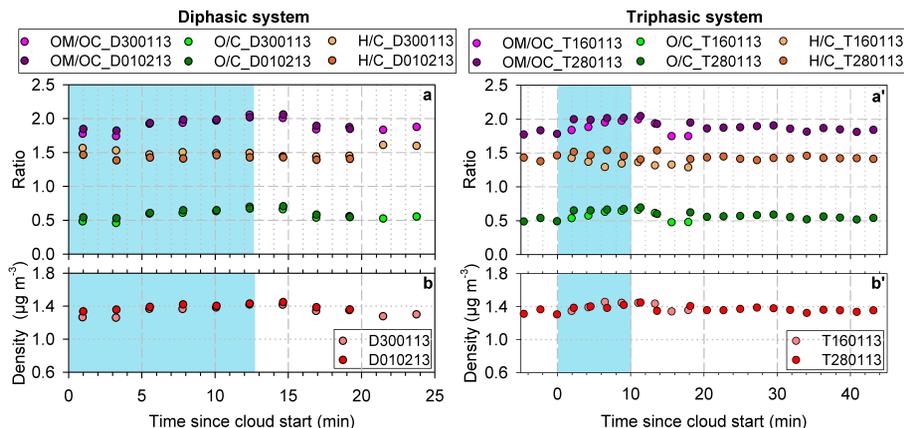


Figure 3. Time profiles of (a and a') O/C, OM/OC and H/C ratios (with the measurement uncertainty as determined by Aiken et al., 2008), and (b and b') particle density for diphasic (left panel) and triphasic (right panel) experiments. Blue areas indicate cloud events.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

SOA formation during cloud condensation-evaporation cycles

L. Brégonzio-Rozier et al.

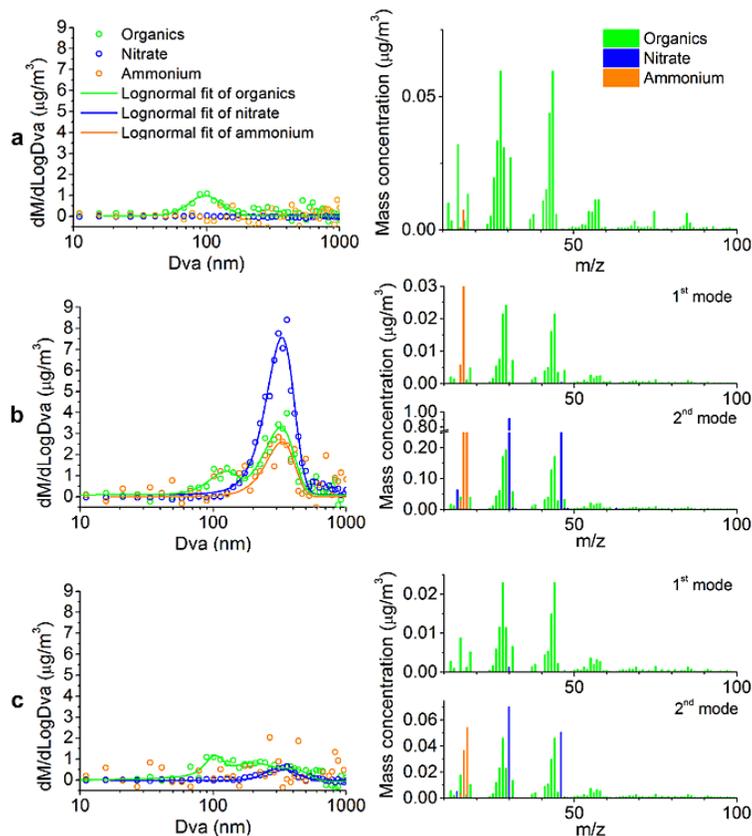


Figure 4. SOA chemical composition measured by an HR-ToF-AMS during a triphasic experiment (T280113) **(a)** before, **(b)** during and **(c)** 30 min after a cloud event. Right panels: mass spectra of dried aerosol averaged over 10 min (organic fragments are in green, nitrate fragments in blue and ammonium fragments in orange); Left panels: dried aerosol mass size distributions.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

