**Reply to referee comments (RC) to manuscript egusphere- 2024-4073**

The authors are grateful to anonymous reviewer 1 and 2 for providing very valuable feedbacks to the manuscript. Our detailed point-by-point response to their comments are reported below.

Both referees, implicitly or explicitly, indicated that the manuscript was presenting too many details, which were hampering the understanding the main conclusions and novelties of the research. To overcome this issue, we have reorganized the manuscript as follows

- A significant part of the experimental section is now reported in the supplementary material, only the major details remain in the main text
- The "results and discussion" section has been separated to highlight the implications of the results
- The detailed discussion of the mass spectra in the composition section has been moved in the supplementary material, to highlight the discussion on the formation of acids and oligomers

We believe that these significant modifications improved the reading and the understanding of the manuscript, fostering its significance.

**Reply to Referee # 1 comments (RC) to manuscript egusphere- 2024-4073**

We thank Referee #1 for the complete and thoughtful revision of our manuscript.

In the following the Referees' remarks and questions are in black and our replies are in light blue

**Referee Comments #1**

**General comments**

In this study, the authors investigated the heterogeneous reactions of glyoxal on real mineral dust in the CESAM simulation chamber, which is an upgraded vision of the previous studies. Multiple instruments were employed to perform complementary measurements of both gas and particle phases. Key influencing factors were carefully considered, including the presence or absence of irradiation and oxidant ozone, as well as varying humidity conditions ranging from <5% to 80% RH. The chemical composition of reaction products was characterized both online and offline, and uptake coefficients were calculated. This study highlights the substantial uptake of glyoxal by mineral dust and the resulting modifications in particle properties, including hygroscopicity, acidity, optical characteristics, and reactivity. The manuscript is well written. The contribution of this study is within the scope of ACP. There are only a few aspects that require further discussion, and the manuscript would benefit from reorganization, particularly in the results section, to enhance clarity and conciseness. Therefore, I recommend a minor revision before publication.

**Major comments:**

1. This study is impressive, with comprehensive techniques and results. However, the authors should refine the manuscript to ensure that key points are not overshadowed by excessive detail. For instance, while the methodology section contains valuable information, this is not a technical paper. Consider shortening this section and moving some details to Supporting Information (SI) if necessary. Additionally, a table summarizing the complementary functions of the instruments used would greatly enhance clarity.

Following your suggestion, we revised and shortened the methodology section in the main text (Section 2) and reported details in the supplementary material (Text S1 and S2). Additionally, we have included Table S1 in the Supplementary Information, which summarizes the complementary functions of the instruments used, to improve clarity and accessibility of the experimental setup.

In the results section (3.3 Organic Composition), the authors provide a detailed discussion of organic fragments and molecules in the particle phase but lack clear linkages between them. Given the expected diversity of organic products, it is important to highlight which ones are most significant and why. For example, the role of oligomers and organic acids deserves emphasis. Reorganizing this section to focus on key products and scientific questions, rather than structuring it around the instruments used, would improve readability and impact.

We have followed your recommendation and revised the text accordingly. We have reorganized the discussion in Section 3.4, placing greater emphasis on the most significant organic products—particularly oligomers and organic acids—and their roles in the particle phase. The section has been reorganized around key findings and scientific questions, rather than by instrumentation, to enhance readability and highlight the main outcomes of the study. Additional material, including the presentation of the mass spectra is now reported in Text S7 in the supplementary material.

2. Glyoxal concentrations play a potentially import role in the reactions. Why did the authors choose much higher concentration rather than atmospherically relevant values. i.e., 10-100 pptv? Was it due to technical limitations? Please provide an explanation.

The decision to use higher glyoxal concentrations, rather than atmospherically relevant values of 10-100 pptv, was motivated by the need to overcome the rapid wall loss of glyoxal on the chamber walls in humid conditions, when glyoxal is more likely to be adsorbed onto the chamber walls, leading to a reduction in the concentrations available for interaction with the aerosol particles. The rates of the loss of glyoxal on the chamber walls were quantified by dedicated experiments measuring the wall loss rate constant, which we now report in Text S3 of the Supplementary Material. These consisted in injecting 1 ppm of glyoxal into the chamber and then introducing water vapor to test different relative humidity (RH) conditions. The wall loss constant in dry conditions ($k_{WL,Dry}$) was found to be 4 (± 2)·$10^{-5}$ $s^{-1}$, and roughly two orders of magnitude in humid conditions ($k_{WL,Humid}$; 1.8 (± 0.9)·$10^{-3}$ $s^{-1}$. Such increase in concentration was aimedto ensure the measurements of the organic aerosol composition, with both online and offline techniques.

3. Wall loss is a critical factor in accurately calculating the uptake coefficient and warrants further discussion. While its size dependence is addressed in the SI, it is important to clarify whether wall loss also varies with different RH conditions. Additionally, the authors

state that the uptake coefficient in humid air is independent of concentration. To support this claim, please provide evidence or relevant references.

We thank Reviewer #1 for those comments, and, as also discussed in the previous answer, we agree with the statements indicating the importance of the mechanisms of wall loss, both for dust particles and the gas-phase. For sake of clarity, we address those separately.

- The wall losses for dust particles are corrected as presented in the Text S4 in the supplementary material. These are based on the deposition model by Lai and Nazaroff (2000), which provides a theoretical framework for estimating particle lifetime inside a reactor. The model assumes a one-dimensional vertical flux and neglects particle rebounds from the walls, which act as a perfect sink removing particles upon impaction. These conditions are not completely met in the CESAM chamber as a consequence of two phenomena: the presence of an internal fan operated to enhance mixing, inducing an additional horizontal movement to the particles, and physical properties of dust particles, which are electrostatically active and can rebound from the walls. As discussed in Battaglia et al. (2025), in dry conditions, the size-average rate of deposition loss rate coefficient rate is 2.5 (±0.8) $10^{-5}$ $s^{-1}$, resulting in calculated particle lifetime between 9 and 11 h, significantly lower than the expected from the theoretical calculations, indicating a particle lifetime of the order of 24h (see Alfarra et al. 2023a). In the presence of water vapor, the average lifetime reduced to 2-3 hours (not shown in Battaglia et al., 2025).
- The wall loss of the gas phase is certainly depending on RH. This dependence was considered by developing a specific kinetic model, which is now described in Text S3 in the supplementary material. Regarding the losses (uptake) of glyoxal on dust particles, Reviewer #1 notes our sentence saying "*results indicate that natural Gobi dust is an effective sink of glyoxal, with initial uptake coefficient independent of glyoxal concentration, pointing to a first order removal process*...", Indeed, our experimental results of glyoxal uptake on mineral dust could be described with a first-order kinetic model, which assumes that the uptake rate is independent of the initial concentration of the gas-phase reagent. Similar first-order uptake behavior has been reported in previous studies across a range of particle substrates. Shen et al. (2016) studied glyoxal uptake on clean and $SO_2$-aged mineral particles; Zogka et al. (2022) investigated uptake on a wide variety of natural dusts and mineral proxies; Go et al. (2018) examined reactions on methylammonium-containing inorganic salts; and Liggio et al. (2005) focused on glyoxal uptake onto ammonium sulfate particles. Despite the diversity of substrates, all these studies support a first-order uptake process, reinforcing our interpretation of the glyoxal uptake mechanism under the experimental conditions presented in this work.

4. The authors did not observe uptake under dry condition. However, given that glyoxal is highly water-soluble—more soluble than methylglyoxal, which can undergo hydration in the gas phase even at <5% RH (Axson et al., 2010). One might expect some uptake to still occur in relatively dry air (though not necessarily at 0% RH) but it did not. Can the authors provide potential explanations for this observation? Additionally, a closer look at

the volume concentration curve,   it shows a slight enhancement after glyoxal injection, though less pronounced than under humid conditions. I recommend exploring alternative methods to better illustrate and analyze the results in dry air.

We thank Referee #1 for verifying the observation in such a detail. Indeed, based on the results of Shen et al. (2016) and Zogka et al. (2024) we expected some uptake in dry conditions too. While it is possible that the light enhancement in the volume concentration curve might indicate that some uptake is occurring, this and the concentration of the organic aerosol formed are below the detection limit of our experimental techniques.

The absence of glyoxal uptake under dry conditions in our experiments could be due to the limited reactive surface area available for heterogeneous interactions. In contrast to our study, Shen et al. (2016) and Zogka et al. (2024) examined glyoxal uptake on deposited soils, with a significantly higher availability of reactive sites. Shen et al. (2016) used model powders with BET (Brunauer-Emmett-Teller) surface areas ranging between 1.4 and 440 $m^2\ g^{-1}$, respectively. In the conservative assumption that only 5 mg of the model powder was used, the total reactive surface area was up to 2.2 $m^2$. Zogka et al. (2024) reported that the BET surface areas of the Gobi soil used in their experiments was 10.5 ± 1.0 $m^2\ g^{-1}$. Using even just 1 g would yield a surface area of the order of 10.5 $m^2$.

On the other hand, in our study we privileged the realism with respect to the dust conditions in the atmosphere. The generated aerosols were distributed in a single mode centered around 300 nm (mobility diameter). This approach inherently limits the total available surface area. The aerosol surface area calculated from the size distribution measurements across our experiments was in the range 0.35-6.3 × $10^{-3}\ m^2\ m^{-3}$. The corresponding total surface area ranged from approximately 0.002 to 0.026 $m^2$ (the CESAM chamber volume is 4.2 $m^3$), several orders of magnitude lower than in the experiments by Shen et al. (2016) and Zogka et al. (2024). This discussion is now added in the main text of the revised manuscript (section 3.2).

**Minor comments:**

Line 116: Give full name of OA.

We have corrected the text accordingly by providing the full name of OA (organic aerosol) at line 116.

Line 127: Give full name of CESAM or add some explanation, e.g, the abbreviation in French for Experimental Multiphase Atmospheric Simulation Chamber.

We have revised the text at line 127 to include the full name of CESAM, specifying that it stands for "Chambre Expérimentale de Simulation Atmosphérique Multiphasique", the French abbreviation for Experimental Multiphasic Atmospheric Simulation Chamber.

Line 181: Please show the FTIR spectra, e.g., in SI.

We have now included the FTIR spectra in Figure S1 of the Supplementary Material.

Line 457: Fig 1 a) RH=0%, is it real 0%? Or some value < 5% which is the lowest RH listed in table1. Please revise. Same comment for Fig. S4.1.

The RH measurements in our study were conducted using the Vaisala® HMP234 transmitter, which is designed for accurate humidity measurements across a full range of

0–100% RH. According to the manufacturer's specifications, the HMP234 is capable of measuring RH values down to 0%.

In the context of our experiments, the "RH = 0%" condition refers to measurements taken in a dry environment where the RH was effectively at or near zero. Given the capabilities of the HMP234, we are confident in the accuracy of these low RH measurements.

Line 485-486: Consider putting the result in presence of ozone in the SI.

In response, we have moved the results in the presence of ozone to the Supplementary Information and integrated them intoFigure S2. This figure presents the timeline of ageing experiment $D_{14}$, where submicron dust was exposed to gas-phase glyoxal under humid conditions (78% RH) at 293 K and 1450 ppbv of ozone.

Line 502: It is not clear why Fig 2 can confirm the statements above. Please reshape.

This is now discussed in Section 3.4

Line 573: Fig 4, please add the legend for the red and blue curves.

Done

Line 610: Table 2: Do not use the symbol γ for OA formation. Consider using e.g., Y (yield) instead.

As a matter of fact, we do not report a yield of OA formation but rather a rate. Therefore, for consistency with the gas phase, we prefer to keep using the symbol γ. We have revised the text to clarify.

Line 625: Shen et al. (2016) also used α-Al2O3. Please add it.

Done

Line 627: How long was the exposure time?

The exposure time of glyoxal to mineral dust, corresponding to the period between the glyoxal injection and the stabilization of aerosol mass concentration and chemical composition, was of the order 5 to 10 minutes. As also detailed in response to one of the minor comments of Reviewer #2, this short interaction time is since in our experiments we performed a single injection of glyoxal, which, due to its high solubility and reactivity, rapidly partitioned to both the aerosol surface and the chamber walls.

Our exposure time is realistic of atmospheric conditions, and shorter than previously reported in the literature. Shen et al. (2016) exposed mineral dust to glyoxal for approximately 30 minutes (see Section 2.3.2 of the revised manuscript). The experiments reported by Zogka et al. (2024) used an exposure time between 40 to 60 minutes, and reached a quasi-steady-state uptake (see Sections 2.4.3 and 2.4.4).

Line 631: Change “AlO3” to “α-Al2O3”.

Done

Line 685: Change 28 m/z to m/z 28. Same for 44 m/z and the other fragments. Please go through the whole manuscript and revise accordingly.

This is now done

Line 783: Do not use “seem to”. Please change to another more appropriate word.

We have revised the sentence, accordingly changing it from “Light and the presence of ozone seem to favor its formation” to “Light and the presence of ozone favor its formation” at line 830 in the revised manuscript.

Line 929-936: Please add the comparison of uptake coefficients with Shen et al. (2016).

This is now done

## References

Alfarra, R., U. Baltensperger, D. M. Bell, S. G. Danelli, C. Di Biagio, J.-F. Doussin, P. Formenti, M. Gysel-Beer, D. Massabo, G. McFiggans, et al. 2023a. Preparation of the experiment: Addition of particles. In A practical guide to atmos. simulation chambers, ed. J.-F. Doussin, H. Fuchs, A. Kiendler-Scharr, P. Seakins, and J. Wenger, 163–206. Cham: Springer International Publishing.

Battaglia, F., Baldo, C., Cazaunau, M., Bergé, A., Pangui, E., Picquet-Varrault, B., Doussin, J.-F., & Formenti, P. (2025). Protocol for generating realistic submicron mono-dispersed mineral dust particles in simulation chambers and laboratory experiments. Aerosol Science and Technology, 59(3), 357–369. https://doi.org/10.1080/02786826.2024.2442518

Go, B. R., Gen, M., Chu, Y., & Chan, C. K. (2019). Reactive Uptake of Glyoxal by Methylaminium-Containing Salts as a Function of Relative Humidity. ACS Earth and Space Chemistry, 3(2), 150–157. https://doi.org/10.1021/acsearthspacechem.8b00154

Lai, A. C., & Nazaroff, W. W. (2000). Modeling indoor particle deposition from turbulent flow onto smooth surfaces. Journal of aerosol science, 31(4), 463-476.

Liggio, J., Li, S., & McLaren, R. (2005). Reactive uptake of glyoxal by particulate matter. Journal of Geophysical Research: Atmospheres, 110(D10), 2004JD005113. https://doi.org/10.1029/2004JD005113

Loza, C. L., Chan, A. W., Galloway, M. M., Keutsch, F. N., Flagan, R. C., & Seinfeld, J. H. (2010). Characterization of vapor wall loss in laboratory chambers. Environmental science & technology, 44(13), 5074-5078.

Shen, X., Wu, H., Zhao, Y., Huang, D., Huang, L., & Chen, Z. (2016). Heterogeneous reactions of glyoxal on mineral particles: A new avenue for oligomers and organosulfate formation. Atmospheric Environment, 131, 133–140. https://doi.org/10.1016/j.atmosenv.2016.01.048

Zogka, A. G., Lostier, A., Papadimitriou, V. C., Thevenet, F., Formenti, P., Rossi, M. J., Chen, H., & Romanias, M. N. (2024). Unraveling the Uptake of Glyoxal on a Diversity of Natural Dusts and Surrogates: Linking Dust Composition to Glyoxal Uptake and Estimation of Atmospheric Lifetimes.