

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 comments (RC) to manuscript egusphere- 2024-4073

We thank Referee #2 for the complete and thoughtful revision of our manuscript.

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

Referee Comments #2

General comments:

This manuscript presents a well-designed laboratory study investigating the uptake of glyoxal on natural mineral dust aerosols from the Gobi Desert. The authors utilize a large simulation chamber to explore the formation of organic aerosols (OA) under varying atmospheric conditions, including different relative humidity (RH) levels and the presence of ozone. The study provides important experimental constraints on glyoxal uptake coefficients and highlights the role of mineral dust in heterogeneous atmospheric chemistry.

Major Comments:

1. Scientific Significance and Novelty

The study provides valuable insights into the uptake of glyoxal on mineral dust, yet the novelty should be more explicitly stated. How does this work go beyond previous studies such as Shen et al. (2016) or Zogka et al. (2024)? A clearer articulation of the key new findings would strengthen the introduction.

To the best of our knowledge, our paper reports on the first ever study of the interactions of natural mineral dust aerosols with volatile organic compounds, and glyoxal in particular, following the recommendation of the review paper by Tang et al. (2017). All previous studies in the literature investigated soils or soil surrogates like synthetic minerals, while our study investigate realistic airborne aerosol particles generated from a natural native soil. Our experiments considered submicron mineral dust aerosol particles generated from a natural soil (Gobi Desert) in realistic concentrations, composition and size distribution. While airborne, the dust aerosol was aged under variable conditions of relative humidity, irradiation, and ozone concentrations. Beside the realism of the tools and the experimental conditions, our study investigates, for the first time, both the rate of uptake of glyoxal and the rate of formation of the organic aerosol from the gas-phase uptake, the chemical composition of the particle formed on the dust particles, and finally the implications on the particle microphysics.

There are also several novelties with respect to previous studies on glyoxal by Shen et al. (2016) and Zogka et al. (2024). With respect to Shen et al. (2016), we extend the results to the effects on particle size and provide with the evaluation of both the coefficients of gaseous uptake and formation of the organic matter. With respect to Zogka et al. (2024), who only investigate the uptake, we provide with the investigation of the rate of particle formation, its mechanism, and the complete characterization of the organic composition formed in the particle phase, including the molecular scale. To explicit these points, we have added the reference to Zogka et al (2024) in the introduction and added some lines of text to highlight atmospheric relevance (lines 114-122).

Additionally, we modified the conclusions with the following sentences (lines 763-776) *“In this paper, we investigated the interaction between gas-phase glyoxal and mineral dust. By taking advantage of the capabilities of the CESAM atmospheric simulation chamber to perform multiphase experiments on time scales relevant to atmospheric processes and dispersion, including aerosols, our study extends the previous findings of Shen et al. (2016) and Zogka et al. (2024), who explored the uptake of glyoxal onto soils or soil surrogates like synthetic minerals. Our experiments considered submicron mineral dust aerosol particles generated from a natural soil (Gobi Desert) in realistic concentrations, composition and size distribution. While airborne, the dust aerosol was aged under variable conditions of RH, irradiation, and ozone concentrations. Beside the realism of the tools and the experimental conditions, our study investigates, for the first time, both the rate of uptake of glyoxal and the rate of formation of the organic aerosol from the gas-phase uptake, the chemical composition of the particle formed on the dust particles, and finally the consequences on the particle microphysics”*.

2. Mechanistic Understanding of Organic Aerosol Formation

The paper suggests that organic aerosol (OA) formation from glyoxal uptake on dust is significant, yet the reversibility of the process raises questions about its atmospheric relevance. Can the authors discuss potential mechanisms for OA stabilization under ambient conditions (e.g., secondary reactions, coagulation)?

Indeed our observations suggest that the uptake of glyoxal on dust exhibits a certain degree of reversibility, as the more volatile compounds, forming the majority of the organic mass concentration, revert to the gas-phase during the reaction, likely by evaporation. However, our findings also clearly indicate that the process modify in an irreversible way

the composition and the size distribution of the mineral dust particles. Molecular analysis by ESI-Orbitrap and SFE/GC-MS revealed a variety of glyoxal-derived compounds, such as glycolic acid, glyoxylic acid, oxalic acid, and several oligomers (e.g., $C_6H_6O_6$, $C_8H_{16}O_{12}$, $C_{10}H_{12}O_{11}$), on the mineral dust particles, particularly at irradiated conditions. After the reaction, the dust size distribution grows permanently to larger sizes.

These observations support the idea that although some glyoxal and its characteristic fragments may volatilize or degrade over time, the formation of lower-volatility, higher molecular weight compounds through secondary reactions—potentially including photochemistry, radical-driven oxidation, and condensation—leads to partial but significant stabilization of the organic aerosol (OA). The influence of ambient factors such as light and ozone further suggests that multiple atmospheric pathways may contribute to this process.

The stabilization of OA products depends in large part on their volatility. The formation of lower-volatility compounds through secondary processes—such as oxidation, photochemical aging, and oligomerization—contributes to their atmospheric persistence. In particular, polar oxygenated products formed from glyoxal are likely to exhibit reduced volatility and can further interact with the dust surface via hydrogen bonding, van der Waals forces, or surface complexation mechanisms.

The nature of the mineral surface and the presence of adsorbed water are critical in facilitating these interactions. Mineral surfaces often provide reactive sites (e.g., hydroxyl groups, metal cations) that can stabilize polar organics through specific interactions. Under humid conditions, a thin layer of adsorbed water may enhance glyoxal uptake and retention by promoting aqueous-phase reactions and acting as a medium for molecular diffusion and stabilization.

This water layer can also help solubilize polar products and mediate their association with surface sites, effectively reducing their volatility and enhancing their persistence. Indeed, relative humidity plays a key role in the effectiveness of the interaction. Under humid conditions, glyoxal exists predominantly in hydrated forms, which are both less volatile and more water-soluble. Using the Myrdal and Yalkowsky (1997) method to estimate saturation vapor pressures at 298 K, each hydration step of glyoxal reduces its vapor pressure dramatically: from $10^{-0.7}$ atm for glyoxal, to $10^{-4.2}$ atm for the mono-hydrate, and $10^{-8.1}$ atm for the dihydrate. These decreases in volatility strongly favor SOA formation. In parallel, the aqueous solubility of hydrated glyoxal forms is greatly enhanced, with effective Henry's law constants of $10^{8.81}$ and $10^{14.09}$ M atm⁻¹ for the mono- and dihydrated forms, respectively (Raventos-Duran et al., 2010), compared to $10^{5.56}$ M atm⁻¹ for the non-hydrated form (Zhou and Mopper, 1990). These properties promote partitioning into the condensed phase, further supporting the formation of persistent organic material.

3. Uncertainty in Uptake Coefficients

The reported uptake coefficient ($\gamma = 9 \times 10^{-3} \pm 5$) shows large variability. Given the importance of γ in atmospheric modeling, can the authors provide a sensitivity analysis on key parameters (e.g., dust surface area, chamber conditions)? How do wall losses impact the measured γ values?

We appreciate the reviewer's insightful comment regarding the variability of the reported uptake coefficient (γ) and the potential implications for atmospheric modeling. In response, we provide below a structured discussion addressing the main factors contributing to this variability, namely: (1) differences in aerosol surface area across experiments, (2) challenges in achieving reproducible glyoxal injections due to significant wall losses, and (3) the influence of chamber wall conditions on glyoxal availability and wall loss kinetics.

1) Variability in aerosol surface area

We acknowledge that the uptake coefficient γ displays some variability across our experiments. A significant factor contributing to this is the variability in the injected aerosol surface area (AS), discussed in Battaglia et al. (2025). In that study, we describe the challenges associated with generating a monodisperse mineral dust aerosol with a mobility diameter centered at approximately 300 nm. This specific size range was chosen to ensure a sufficiently long particle lifetime in the CESAM chamber, which is essential for conducting heterogeneous uptake experiments with glyoxal. However, achieving this size distribution in a consistent and reproducible manner is technically demanding.

As a result, the total injected surface area varied between experiments from 3.5×10^{-4} to $6.3 \times 10^{-3} \text{ m}^2 \text{ m}^{-3}$. This variability directly affects the value of γ , as the uptake coefficient is normalized by the available particle surface area.

2) Variability in glyoxal injection due to wall losses

Another important source of variability comes from the initial concentration of gas-phase glyoxal, which in our experiments varied between 370 and 800 ppbv. Despite efforts to standardize the injection protocol, such variability is unavoidable. Injecting glyoxal in a reproducible manner is also challenging due to its strong tendency to undergo wall loss, especially under humid conditions. These losses occur rapidly and are influenced by environmental factors such as temperature and RH, as well as by the physicochemical interactions between glyoxal and chamber walls. As consequence, the amount of glyoxal available for uptake at the particle surface can differ from one experiment to another. The kinetics of these processes, and our strategy to quantify them, are now discussed in detail in Text S2 of the Supplementary Material.

3) Influence of chamber wall condition on wall loss kinetics and glyoxal availability

Finally, an additional source of variability arises from the condition of the CESAM chamber walls themselves. The kinetics of glyoxal wall loss are not only strongly dependent on RH, but also on the surface state of the chamber—e.g., the degree of previous exposure to glyoxal, dust, ozone, or other reactive gases. The surface "history" of the chamber, including the point in time during an experimental campaign when the uptake experiment is performed, can significantly affect wall reactivity and thus the gas-phase concentration of glyoxal available to react with aerosols.

In conclusion, we recognize the importance of γ for atmospheric modeling and agree that its interpretation must account for experimental uncertainties. Together, the factors discussed explain the observed range of uptake coefficients and highlight the complexity of simulating real-world heterogeneous processes under controlled laboratory conditions.

4. Role of Relative Humidity and Surface Chemistry

The data indicate a strong dependence of glyoxal uptake on relative humidity (RH), but the underlying reasons are not fully explored. Is this due to enhanced solubility, surface adsorption, or heterogeneous reactions? Additional discussion on the molecular-level processes involved would improve clarity.

The enhanced uptake at higher RH can be attributed to several interrelated factors. First, increased RH facilitates the formation of thin water films or hydrated layers on the dust surface, which enhances glyoxal's solubility and promotes its partitioning into the aqueous phase. This aqueous environment not only allows for more efficient uptake but also creates a medium for subsequent aqueous-phase reactions.

Second, RH likely plays a key role in promoting surface-mediated and heterogeneous chemistry. The water layer acts as a solvent, enabling hydration, oxidation, and oligomerization of glyoxal—processes that are significantly less favorable under dry conditions. This is supported by our molecular analysis, which revealed the presence of a variety of oxidation products and oligomers (e.g., glycolic acid, oxalic acid, and higher-order oligomers like $C_8H_{16}O_{12}$) predominantly at high RH and under irradiation. The diversity and persistence of these products point to active aqueous-phase and surface-bound chemistry facilitated by RH.

Together, these findings suggest that RH enhances glyoxal uptake not only by increasing solubility but also by enabling a suite of heterogeneous and aqueous-phase reactions that stabilize a portion of the organic mass on the dust surface. We have clarified this point further in the revised manuscript (section 4.2).

In addition, the hydrated forms of glyoxal are significantly more polar and thus more likely to adhere to the mineral surface through hydrogen bonding or electrostatic interactions. These interactions contribute to the stabilization of glyoxal and its reaction products on the surface, reducing their volatility and favoring the formation of secondary organic aerosol.

As already discussed in our response to comment 2, hydration of glyoxal dramatically lowers its volatility—by several orders of magnitude—and increases its solubility and polarity, enhancing its ability to interact with polar sites on the mineral dust surface. These molecular characteristics reinforce the idea that RH not only increases glyoxal uptake but also promotes its stabilization on dust through strong surface interactions.

Together, these findings suggest that RH enhances glyoxal uptake not only by increasing solubility but also by enabling a suite of heterogeneous and aqueous-phase reactions and surface interactions that stabilize a portion of the organic mass on the dust surface. We have clarified this point further in the revised manuscript.

5. Optical and Hygroscopic Property Changes

The study mentions that glyoxal uptake modifies dust properties, yet quantitative data on optical and hygroscopic changes are limited. Can the authors provide experimental evidence (e.g., changes in scattering, hygroscopic growth factors) to support these claims?

The current manuscript focuses on the formation and the chemical composition of the organic aerosols on the dust particles, and provides insights on the kinetic rates, and presence of low- and high-volatility compounds on the surface of the particle dust, in particular acids and oligomers which could alter the particle's pH. The paper also shows that the formation results in the irreversible growth of the particle size, which we attribute to the enhancement of dust's hygroscopicity, and which should result in the change of the dust efficiency in scattering and absorbing the solar radiation. While the formal analysis of those data is beyond the scope of this paper, we have added a specific Section 4.3 to address the Referee's comments. A manuscript is currently being prepared to present concurrent measurements of hygroscopic growth factors and scattering and absorption efficiencies.

Minor Comments:

1. Experimental Controls and Reproducibility

While the authors conducted control experiments with ammonium sulfate, it is unclear whether repeated experiments were performed to assess reproducibility. Were there significant variations across trials, and how were they addressed?

The issue of reproducibility was significantly considered. Table 1 reports several duplicates and triplicates of experiments performed in same nominal conditions, and this is just a selection of the many more trial experiments which we performed in the laboratory to understand the chemical system that we are dealing with, and its variability. As discussed in the answer to comment #3, a large degree of variability is indeed something that we have to live with as a result of the intrinsic experimental challenges provided by both the glyoxal and the mineral dust, which are atmospherically short-lived and reactive compounds. In this respect too, our experiments are extremely realistic of the interaction that could occur in the atmosphere, and its variability due to the environmental conditions that air masses can explore.

2. Data Interpretation in Figure 1 and Figure 2

The time series data suggest transient organic aerosol formation, followed by evaporation. Could this be due to chamber dilution effects rather than desorption? A more detailed discussion would clarify the interpretation.

We thank the reviewer for raising this important point. The transient organic aerosol formation followed by apparent evaporation was carefully analyzed to distinguish real chemical processes from physical effects such as chamber dilution.

To address this, we applied a well-established dilution correction method as detailed in Text S3.1 of the Supplementary Material. This correction accounts for the dilution of gas-phase species and aerosol particles caused by the injection of particle-free nitrogen flow needed to balance the sampling flow and maintain constant chamber pressure.

In addition, size-dependent particle losses due to interactions with chamber walls and sampling lines (wall losses) were quantified and corrected for as described in Text S3.2. By combining these corrections, the reported changes in aerosol concentration and composition accurately reflect chemical uptake and transformation rather than dilution.

Therefore, the observed transient organic aerosol behavior cannot be attributed only to dilution effects but is consistent with partial reversibility of glyoxal uptake and chemical processing on mineral dust. This conclusion is further supported by molecular analyses showing the formation of less volatile glyoxal-derived oligomers and oxidation products.

In summary, dilution and wall losses were fully accounted for, and the temporal trends in Figures 1 and 2 reflect genuine heterogeneous chemistry rather than experimental artifacts.

3. Chemical Characterization of Oligomers

The study identifies C₄–C₁₀ oligomers but does not provide detailed structural assignments. Were tandem MS (MS/MS) or other advanced techniques used to confirm molecular identities? If not, adding structural information would strengthen the findings.

We thank the reviewer for this important observation. While tandem MS (MS/MS) experiments were not performed in this study, the assignment of molecular formulae was conducted using high-resolution Orbitrap mass spectrometry (mass resolution = 100,000 at m/z 400) with a stringent peak assignment protocol (Zielinski et al., 2018) allowing for mass errors within ± 4 ppm. This high mass accuracy, combined with specific elemental constraints (e.g., H/C, O/C, N/C, S/C ratios, nitrogen rule), ensures a high level of confidence in the formula assignment and supports the robustness of our chemical characterization.

Additionally, we emphasize that molecular formulas attributed to glyoxal chemistry (e.g., hydration, oxidation, and oligomerization products) were observed exclusively in the presence of both mineral dust and glyoxal. To further validate these assignments, we conducted a series of blank experiments with dust aerosol under identical chamber conditions but without glyoxal injection. In those control experiments, no glyoxal-related molecular formulas were detected, strongly supporting the attribution of these compounds to heterogeneous chemistry between glyoxal and the mineral surface.

Thus, although we acknowledge the absence of direct structural elucidation via MS/MS or NMR, the high reliability of the molecular formula assignments—combined with the fact that these species were observed only in the co-presence of glyoxal and dust—provides strong support for the proposed structures. In addition, the assignment is consistent with established glyoxal chemistry, particularly under humid conditions, where hydration promotes lower volatility and enhanced interactions with mineral surfaces. We have added a specific section to discuss the structural assignments and chemical mechanism (Section 4.2)

4. Comparison with Atmospheric Conditions

The chamber experiments are performed at controlled conditions, but how do these findings translate to real atmospheric environments? Discussion on differences in dust properties, glyoxal concentrations, and timescales in the ambient atmosphere would be beneficial.

While our experiments were conducted in a controlled chamber environment, multiple aspects of the study were designed to reflect atmospherically relevant conditions and processes.

First, the uptake of glyoxal on mineral dust was observed to occur immediately after glyoxal injection into the chamber. In this study, we employed a single, instantaneous glyoxal injection rather than a continuous flux. This design choice, combined with the rapid partitioning of glyoxal to both particles and chamber walls under humid conditions, mimics the transient interaction conditions found in the atmosphere.

Indeed, as shown by Volkamer et al. (2005), the typical atmospheric lifetime of glyoxal is on the order of 1.3 h during the day, while Alvarado et al. (2020) demonstrated that long-range transport of glyoxal is unlikely unless secondary production from longer-lived precursors is invoked. In the real world, the interaction of mineral dust with glyoxal laden-air masses from biomass burning or urban pollution, will take place within a few minutes (ref) , comparable to the timescale explored in our chamber experiments.

In addition, although the initial glyoxal mixing ratios used in our study (hundreds of ppbv) are higher than typical background atmospheric levels (generally 10–100 pptv, Fu et al., 2008), this is a common and necessary feature of chamber studies designed to yield quantifiable signals within limited experimental durations. It's important to note that due to rapid wall partitioning under humid conditions, the effective concentration of glyoxal available for heterogeneous uptake is significantly lower than the initial value. This loss suggests that the actual exposure of aerosols to glyoxal in the chamber may not be far from ambient conditions.

Moreover, the mineral dust aerosol used in this study was size-selected around 300 nm in diameter—an atmospheric size mode representative of particles that are efficiently transported over long distances, enhancing the atmospheric relevance of the experimental results. This is particularly relevant because it increases the probability that these particles will encounter pollutant plumes, including those rich in glyoxal or its precursors, during their atmospheric lifetime.

In conclusion, while absolute concentrations differ, the experimental timescales, uptake dynamics, and size selection of aerosols all support the atmospheric relevance of our findings.

Citation: <https://doi.org/10.5194/egusphere-2024-4073-RC2>

Alvarado, L. M. A., Richter, A., Vrekoussis, M., Hilboll, A., Kalisz Hedegaard, A. B., Schneising, O., and Burrows, J. P.: Unexpected long-range transport of glyoxal and formaldehyde observed from the Copernicus Sentinel-5 Precursor satellite during the 2018 Canadian wildfires, *Atmos. Chem. Phys.*, 20, 2057–2072, <https://doi.org/10.5194/acp-20-2057-2020>, 2020.

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, D15303, <https://doi.org/10.1029/2007JD009505>, 2008.

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>

Myrdal, P. B. and Yalkowsky, S. H.: Estimating Pure Component Vapor Pressures of Complex Organic Molecules, *Ind. Eng. Chem. Res.*, 36, 2494–2499, <https://doi.org/10.1021/ie950242l>, 1997.

- Raventos-Duran, T., Camredon, M., Valorso, R., Mouchel-Vallon, C., and Aumont, B.: Structure-activity relationships to estimate the effective Henry's law constants of organics of atmospheric interest, *Atmos. Chem. Phys.*, 10, 7643–7654, <https://doi.org/10.5194/acp-10-7643-2010>, 2010.
- Shen, X., Wu, H., Zhao, Y., Huang, D., Huang, L., and Chen, Z.: Heterogeneous reactions of glyoxal on mineral particles: A new avenue for oligomers and organosulfate formation, *Atmos. Environ.*, 131, 133–140, <https://doi.org/10.1016/j.atmosenv.2016.01.048>, 2016.
- Volkamer, R., Spietz, P., Burrows, J., and Platt, U.: High-resolution absorption cross-section of glyoxal in the UV–vis and IR spectral ranges, *Journal of Photochemistry and Photobiology A: Chemistry*, 172, 35–46, <https://doi.org/10.1016/j.jphotochem.2004.11.011>, 2005.
- Zhou, X. and Mopper, K.: Apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; implications for air-sea exchange, *Environ. Sci. Technol.*, 24, 1864–1869, <https://doi.org/10.1021/es00082a013>, 1990.
- Zielinski, A. T., Kourtchev, I., Bortolini, C., Fuller, S. J., Giorio, C., Popoola, O. A. M., Bogialli, S., Tapparo, A., Jones, R. L., and Kalberer, M.: A new processing scheme for ultra-high resolution direct infusion mass spectrometry data, *Atmos. Environ.*, 178, 129–139, <https://doi.org/10.1016/j.atmosenv.2018.01.034>, 2018.
- Zogka, A. G., Lostier, A., Papadimitriou, V. C., Thevenet, F., Formenti, P., Rossi, M. J., Chen, H., and Romanias, M. N.: Unraveling the Uptake of Glyoxal on a Diversity of Natural Dusts and Surrogates: Linking Dust Composition to Glyoxal Uptake and Estimation of Atmospheric Lifetimes, *ACS Earth Space Chem.*, 8, 1165–1178, <https://doi.org/10.1021/acsearthspacechem.3c00359>, 2024.