Dear editors,

We sincerely thank you and the reviewers for your valuable time and constructive feedback on our manuscript entitled *"**The Effect of Amino Acids on the Fenton and photo-Fenton Reactions in Cloud Water: Unraveling the Dual Role of Glutamic Acid**"* (Manuscript ID: **egusphere-2025-1744** ).

We have carefully considered all the comments and suggestions, and have revised the manuscript accordingly. We have also prepared a detailed, point-by-point response to each of the reviewer's comments. The responses can be found in the following text and the modification part was highlighted at bright green in the manuscript. And the corresponding revisions are provided in the attached file.

In particular, we have addressed all of Reviewer 1's insightful suggestions, and modified the manuscript to improve the clarity, relevance, and scientific depth of our work. We believe these changes have significantly enhanced the quality of the manuscript.

We hope that the revised version meets the journal's standards and look forward to your further evaluation.

Thank you again for your attention and support.

Best regards,

Prof. Dr. Marcello Brigante

**Reviewer 1**

This is a well-written and comprehensive study investigating the complexation of glutamic acid (Glu) with Fe(II)/Fe(III) and its implications for atmospheric chemistry, particularly in cloud water. The experiments are well-designed, and the results provide valuable insights into the role of amino acids in modifying Fenton and photo-Fenton reactions. The findings are novel and contribute significantly to our understanding of atmospheric oxidative processes.

- The atmospheric relevance could be further emphasized by discussing how variations in cloud pH, light intensity, or iron/ligand ratios might influence the observed processes.

  **Response**

  We appreciate the reviewer's insightful suggestion to strengthen the discussion of the atmospheric relevance of our findings. In the revised manuscript, we have added a paragraph discussing how typical variations in cloud water pH (usually ranging from 3 to 7), diurnal changes in solar radiation, and fluctuating iron-to-ligand ratios can modulate the reaction kinetics and pathways of the studied system. This addition highlights the broader implications of our results for cloud and aerosol chemistry under realistic atmospheric conditions. The new discussion can be found on **page 26-27, lines 510-518 and lines 522-526**.

- It would be better to explicitly state in the first paragraph of "Introduction' that the role of amino acids in modifying iron redox chemistry and OH production remains poorly understood.

  **Response**

  We have revised the introduction, this sentence has been added in the first paragraph. The modification can be found at **lines 50-54**.

- Were the pH conditions (3.8–5.6) chosen to represent specific atmospheric scenarios (e.g., polluted vs. remote clouds)? A brief justification would be useful.

  **Response**

  The pH values of 3.8 and 5.6 were chosen based on both experimental needs and atmospheric relevance. pH 5.6 was used in kinetic studies to promote Fe(II)-Glu complex formation, while pH 3.8 was used in ESR experiments where •OH detection is more effective under acidic conditions. These values fall within the typical pH range of cloud water and represent different environments—pH 3.8 for polluted regions and pH 5.6 for remote areas. This allows us to study the system under realistic atmospheric conditions. A clarification has been added in the revised manuscript at **lines 133–139**.

- For the photolysis experiments, was the light spectrum adjusted to match real solar conditions?

  **Response**

  The light spectrum was not specifically adjusted, but the spectral distribution is similar to natural solar radiation, which is important for the photoreactions of Fe(III) and Fe(III)-Glu, As shown in Fig. SM2 and our previous publication. The modification is provided at **lines 169-173**.

- The reported rate constant ($1.54 \times 10^4$ M-1 s-1) is a key finding. However, how does this compare with other Fe(II)-organic complexes (e.g., oxalate, citrate)? A brief discussion would be useful.

  **Response**

  We did the comparison with our recently published value of Fe(II)-Oxalate, a brief discussion was added as well. The modifications were provided at **lines 271-276.**

- The detection of formate/acetate as primary LMCT products is interesting. Could these compounds further complex Fe(III) and influence subsequent reactions?

  **Response**

Yes, you are right. As we wrote in the part of atmospheric implications at **lines 537-539**, those generated compounds can further complex with iron and participate in the consequent photoreactions.

- The discussion of Fe-Glu fractions in cloud water is insightful, but how might these vary in highly polluted vs. marine environments?

  **Response**

  The Fe-Glu fraction in cloud water is expected to vary depending on the environmental context. In highly polluted environments, elevated levels of iron and amino acid (such as Glu from biomass burning or urban sources) may promote the formation of Fe-Glu complexes. In contrast, marine clouds often contain lower concentrations of both Fe and amino acid (like Glu is around 33 pM collected in Venice on the Sacca San Biagio Island), leading to a smaller Fe-Glu fraction. The more discussion was provided in atmospheric implications part at **lines 510-518**.

- How might these findings affect our understanding of SOA formation?

  **Response**

  Thank you for the insightful question. Our findings suggest that Fe(III)-Glu complexes can influence aqueous-phase SOA formation in two key ways. First, the photooxidation of glutamic acid generates small organic acids (e.g., formate, acetate) and ammonium, which are known precursors of SOA in cloud water. Second, the presence of Fe-Glu alters the generation of •OH radicals and introduces additional LMCT-driven pathways, potentially modifying the oxidation chemistry of water-soluble organic compounds. These results highlight a previously underappreciated mechanism by which metal–amino acid complexes may affect the oxidative capacity of cloud water and contribute to SOA formation, particularly under polluted or organic-rich atmospheric conditions. The more discussion was provided in atmospheric implications part at **lines 528-535**.

**Reviewer 2**

The article presents a detailed investigation into the potential effect of glutamic acid (Glu)-iron complexes on Fenton and photo-Fenton reactions in cloud water and on the hydroxyl radical yield. Using Glu as a model amino acid, the study offers compelling insights into how these organic compounds may interfere with iron (photo)chemistry leading to an impact on the oxidative potential of cloud water. Overall, this study makes a valuable contribution to our understanding of aqueous-phase atmospheric chemistry. I have just few comments.

- It would be interesting to compare the results with other well-known iron complexes with organic ligands that might be relevant for cloud water (for example Fe-oxalate)

  **Response**

  We fully agree that comparing our results with well-known iron-organic complexes relevant to cloud water, such as Fe-oxalate, is important. Accordingly, we have revised the manuscript to include a discussion on this aspect to enhance the environmental relevance of our study. The modification was given at **lines 271-276**.

- It would be good to further discuss the potential of forming the Glu-iron complexes in real cloud water. Are there other compounds that may complex strongly the iron? Since the Glu is only a model for AAs, I think the work is relevant because other AA-iron complexes may behaviour in the same way.

  **Response**

  The new discussion of iron-Glu complexes in real cloud water was provided and reported in **lines 510-518**. Indeed, other compounds commonly present in cloud water, such as various amino acids and low-molecular-weight carboxylic acids, are known to form stable complexes with iron and may undergo similar (photo)-Fenton reactions as observed with glutamic acid. The corresponding modifications can be found in the revised manuscript at **lines 532-535.**

- In section 2.2.1 please add the concentration of H2O2 used in the experiments (line 131).

  **Response**

  The $H_2O_2$ concentration was added in the section 2.2.1, shown at **lines 140-142**.

- In Figure 1 the letters (a, b, c and d) referred to the different plots are not very visible, probably it would be good to put them outside the plots.

  **Response**

  To maintain a consistent figure style throughout the manuscript, we did not move the panel labels (a, b, c, d) outside the plots. However, we increased their font size to enhance visibility and ensure they are clearly distinguishable. This modification can be found at **line 285** in the revised manuscript.

- From Figure 3 and Figure MS6 the degradation of Glu with and without H2O2 seems very similar, please report also the data about the irradiation of Glu alone.

  **Response**

  The similar degradation of Glu with and without 1 mM $H_2O_2$ is due to the low light absorption of $H_2O_2$ and limited •OH generation. We also tested Glu under irradiation alone, and the rate constant was $k = (1.90 \pm 0.22) \times 10^{-5}\ s^{-1}$, indicating negligible degradation. This is expected, as Glu does not absorb solar light. The data have been added to the revised manuscript (**lines 347-350**)

- In the figure caption for Figure 3 is described only the left panel and not the right panel, please add it.

  **Response**

  Thank you for very careful review. The description for the right panel is added as shown in **lines 360-363.**

- Page 19, lines 389-391, please add the reactivity constant between formic acid and hydroxyl radical.

**Response**

The reactivity constant between formic and OH radical was added and shown **on page 20 at line 409**.

- I suggest to change the colours of the lines in the figure 4a, to avoid confusion with the other part of the figures (Figure4b,c,d) where for each colour indicates a specific carboxylic acid.

**Response**

Thank you for your suggestion. We have changed the colors of the lines in the figures 4a. The modification can be found at **line 414**.

- In page 22 you discuss the TOC results, have you also performed IC (inorganic carbon) analysis? From that you could also directly measure the mineralization of the Glu. If you have these data, please add them in the manuscript (or in the SI).

**Response**

We provided measurement of total carbon (TC) and inorganic carbon (IC) and calculated the total organic carbon (TOC) accordingly. However, since the reaction system is open and acidic, a significant portion of the $CO_2$ produced during glutamate mineralization escapes from the solution, leading to an underestimation of the actual mineralization degree when using IC data. For this reason, we did not include the IC results in the manuscript. We will clarify this point in the revised SI (SM5) to avoid misunderstanding.

- Page 23, lines 456-457, please add a reference for the deamination process as you did for the other reaction involved in the overall mechanism.

**Response**

A new reference was added, the modification can be found at **lines 476-477.**