Author's Response to Referee #2

We greatly appreciate the time and effort that Referee #2 has devoted to reviewing our manuscript. The comments are thoughtful and helpful in improving the quality of our paper. Below we make a point-by-point response to these comments. The response to Referee #2 is structured in the following sequence: (1) comments from the referee in blue color, (2) our response in black color, and (3) our changes in the revised manuscript in red color.

This study employs the laboratory simulation to investigate the aqueous-phase oxidation benzothiazoles (BTs), a class of emerging environmental contaminants. The work determines the kinetics, identifies and categorizes diverse oligomers and functionalized products by LC-Orbitrap MS, which are rarely reported in prior studies on BTs. Molecular formula analyses map key pathways, advancing mechanistic insights into heterocyclic pollutant transformations. Periodic carbon-number patterns empirically confirm oligomer formation, a process in SOA generation. With its analytical depth and mechanistic contributions, this paper is recommended for acceptance after minor revisions.

1. Page 1, Line 16: A grammatical issue in the abstract should be corrected, "are unclear" should be "is unclear".

Response: Taking the reviewer's advice, we have corrected this mistake.

2. Page 9: Legends in Fig. 3e are too small. It should be improved for better readability.

Response: Taking the reviewer's advice, the legends in Fig. 3e have been enlarged in the revised manuscript as follows:

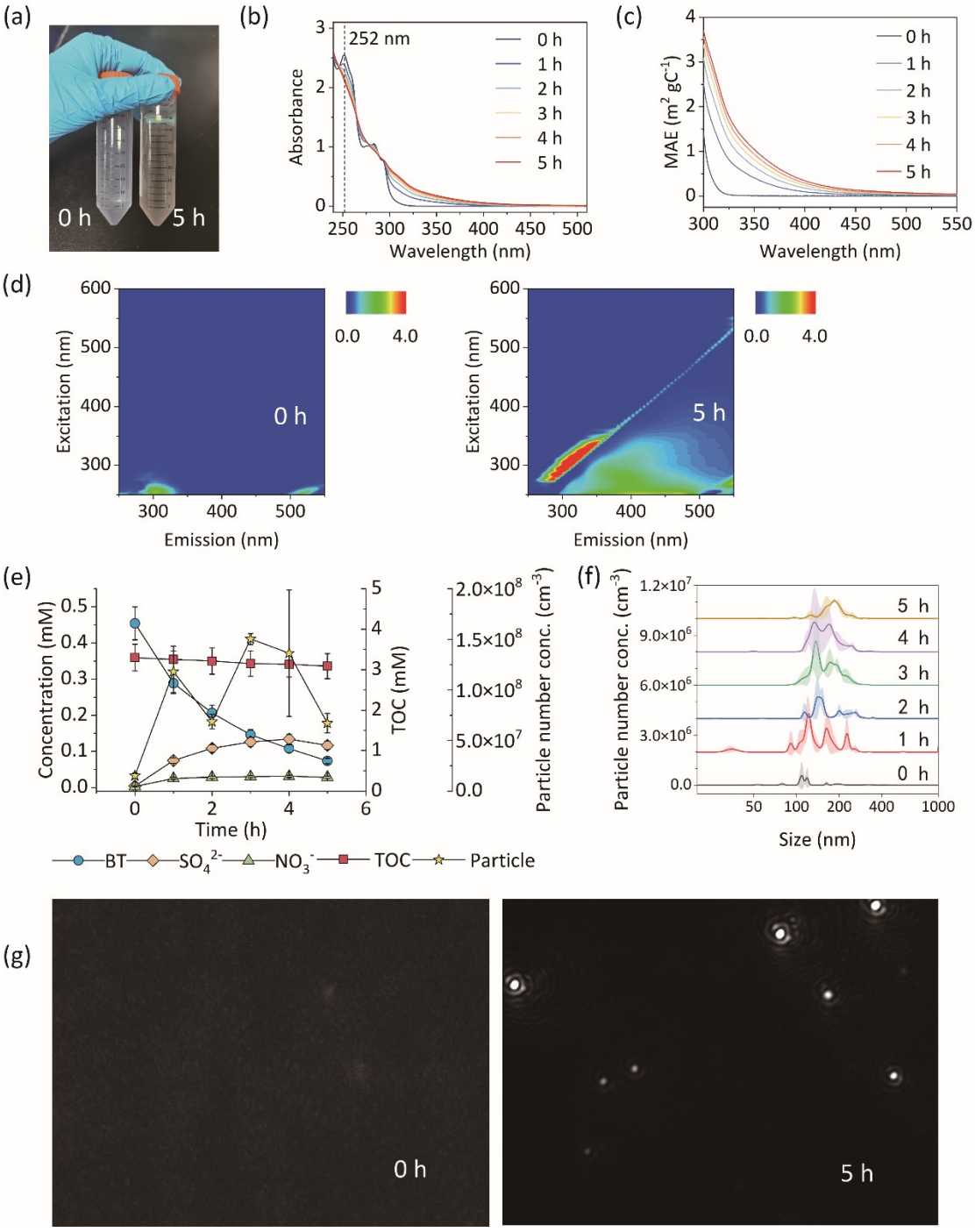

Figure 3. Characterization plots of the reaction solution in Exp. BT-pH2. The change of solution color (a). UV-vis absorption spectra (b) and Mass absorption efficiency (MAE) (c) of reaction solution collected at reaction time intervals of 1 h. The change of EEM fluorescence spectra (d). Time profiles of BT degradation, inorganic products formation (SO_4^{2-}, NO_3^-, and Cl^-), particles formation, and total organic carbon (TOC) concentration (e). Size distribution of nanoparticles formed at reaction time intervals of 1 h (f). The change of NTA images (g).

3. Page 3, Line 70: There supposed to use ", and" before "vanillic acid".

Response: Taking the reviewer's advice, ", and" has been added before "vanillic acid"

in the revised manuscript.

4. Page 3, Line 88: There supposed to use “and” before “2-chlorobenzothiazole”.

Response: Taking the reviewer’s advice, we have added “and” before “2-chlorobenzothiazole” in the revised manuscript.

5. Page 3, Lines 85-90: The units of sodium hydroxide and perchloric acid solutions are supposed to be mol L^{-1}. The format of units needs to be used consistently.

Response: Taking the reviewer’s advice, we have modified the unit “mol L^{-1}” for continuity in the revised manuscript.

6. Page 11, Line 266: The criteria used for molecular formula assignment from Orbitrap MS data should be explicitly described in this paragraph.

Response: We thank the reviewer for this suggestion. The explicit description of the criteria used for molecular formula assignment from Orbitrap MS data is indeed necessary. Following the reviewer’s advice, we have added a sentence in the second paragraph of the revised manuscript. “The number of atoms ($^{12}C \leq 30$, $^{1}H \leq 30$, $^{16}O \leq 20$, $^{14}N \leq 10$, $^{32}S \leq 10$ and $^{35}Cl \leq 5$) and a constraint of 4 ppm mass tolerance are applied as constraints to obtain the elemental composition.”

7. Sec. 3.3 and Sec. 3.4: Although the presence of oligomers and nanoparticles is well established, quantitative yield data (e.g., mass-based or molar-based) would strengthen the case for atmospheric relevance. If not available, this limitation should be acknowledged.

Response: We appreciate the reviewer’s comment on the importance of quantitative yield data to strengthen the atmospheric relevance of our findings. The current study is limited in quantifying mass- or molar-based yields of oligomers mainly due to the lack of standard substances. We did not perform LC-Orbitrap MS to complete quantitative analysis under the present experimental condition. The comparison of identified peaks of oligomers from Orbitrap MS with the formation of nanoparticles is well worth studying and this will be considered in our further experiments. We have explicitly

acknowledged the limitation of quantification in the revised manuscript, which has been added in the third paragraph of Section 3.4. "It should be noted that in this study the LC-Orbitrap MS analysis provides more qualitative insights, as quantitative determination was limited and not conducted. It can be considered and developed for further characterization of the formation and evolution of organic products."

8. The Introduction establishes that BTs themselves are potentially harmful to humans but does not foreshadow any health implications of the secondary products formed by BTs in the atmosphere. There is a mild logical disconnect between the Introduction and Conclusion on the topic of health implications. The Conclusion goes beyond what the Introduction prepares the reader for: it argues that aqueous-phase oxidation of BTs can impact climate and human health. This is a significant point – it implies the secondary aerosol products of BTs contribute to fine particulate pollution that humans could inhale, thereby affecting health. To ensure logical flow, the Introduction should at least hint that studying BTs' atmospheric oxidation is relevant not just for aerosol science but also for evaluating potential health impacts. The Introduction could include one or two sentences foreshadowing the potential health implications of BTs' oxidation products. Revise this.

Response: We thank the reviewer for this insightful suggestion. We have revised the Introduction to briefly hint at the health relevance of BTs' oxidation products. The last sentence at the third paragraph of the Introduction was modified to hint that studying BTs' atmospheric oxidation is relevant to evaluating potential health impacts. "However, the detailed aqueous-phase oxidation mechanisms of BTs in the atmosphere remain largely unexplored, hindering a holistic understanding of their atmospheric chemistry and potential health risks." This modification ensures a logical flow, preparing the readers in the Introduction for the Conclusion's discussion of the impacts of BT-derived secondary aerosols on human health.

9. The authors make a compelling case for the atmospheric relevance of BT oxidation, but the manuscript would benefit from a more detailed discussion of future research directions. For instance, what are the potential impacts on human health, or how can

the researchers study the potential impacts on human health?

Response: We thank the reviewer for the suggestion regarding future research directions. To evaluate the potential impacts on human health, it is first necessary to identify and quantify the key secondary products of BT oxidation in the ambient atmosphere. Subsequently, toxicological assessments of these key products should be conducted. The current study is limited in quantifying secondary products mainly due to the lack of standard substances, which further limits the selection of key products and their toxicological assessments. Thus, we have added a new sentence at the end of the revised Conclusion section. "Future research should also focus on selection of key secondary products from BTs oxidation in the ambient atmosphere and their toxicological assessments to evaluate the potential impacts of BTs oxidation on human health." This sentence explicitly calls for future research focusing on the toxicological evaluation of BT-derived secondary products in the atmosphere.

10. Page 17, Line 380: There supposed to use "BTs concentrations are comparable" instead of "is".

Response: Taking the reviewer's advice, we have corrected this mistake.