General comments

The paper presents the results on aqueous-phase reactions of 4-nitrophenol (4NP) with OH radicals leading to new products formation. Depending on pH (2 or 9), about 20 to 40% of 4NP was converted into new aromatic light-absorbing compounds, with the highest contribution of 4-nitrocatechol (4NC). Besides, up to 65% of organic carbon in the reaction solution (after 4NP was completely consumed) represented the non-aromatic open-ring compounds. Consequently, the light absorption of the solution decreased with time (i.e., bleaching of the reaction solution), however with some prolongation due to initially formed aromatic compounds.

There are many open questions concerning mechanisms of brown carbon (BrC) formation, especially those in cloud droplets and aqueous particles. But, more and more studies confirmed the importance of aqueous-phase (photo)chemical processing in contribution to organic aerosol aging, and so to light-absorbing secondary aerosol formation/degradation. The topic is certainly actual.

However, the manuscript is written superficially, it is sometimes confused and not well readable, sometimes due to not precise expressions, not good choice of words or due to grammatical errors. Besides, there is too much material, too many results in the Supplement, which needs to be checked frequently to follow the results and discussion in the manuscript.

Conditionally, the manuscript could be of adequate atmospheric interest to merit publication in *Atmospheric Chemistry and Physics*, but after major revision, with addressing the following comments and/or questions. Besides, I highly recommend the English language checking, some parts should be re-written. Below, I list only very few language-related errors in the main text.

Specific comments

<u>Introduction</u>:

- Line 25: The authors may add a reference of Hems et al., ACS Earth Space Chem. 2021.
- Line 28: The authors may add a reference of Vidović et al., Atmosphere, 2020.
- Line 32: I suggest to include also the references for example: Claeys et al., Environ. Chem., 2012; Kitanovski et al., J. Chromatogr. A 2012; Frka et al., Environ. Sci. Technol., 2016.
- Line 35: The statement is not entirely true; there are other nitroaromatic compounds (NAC), which are even more important BrC components (e.g., 4-nitrocatechol, 4-NC; etc.). Xie et al., 2019 (this ref. is cited), demonstrated that among 14 NACs identified in biomass burning (BB) samples and also in simulated SOA, 4-NC contributed the most to overall BrC absorption at 365 nm (see Fig. 4. in Xie et al., 2019).
- Line 39: Here, the references Kitanovski et al., J. Chromatogr. A 2012; Claeys et al., Environ. Chem., 2012; Frka et al., Environ. Sci. Technol., 2016 should be included as well.
- Line 48: The authors could add a reference of Hems et al., ACS Earth Space Chem. 2018.
- Lines 55-57: It would be better as: "…the connection between the light absorption and chemical composition…"
- Reaction is usually written as: 4NP + OH $\rightarrow$ (check throughout the text)

- Line 71: This is not entirely true. Atmospheric aqueous particles have usually low pH (depends on their origin, but mostly below 3), while other atmospheric liquid waters (e.g., cloud droplets, fog) have mostly higher pH values (above 3); see Table 1 in Herrmann et al., 2015.

Experimental:

- Chemicals should be involved.
- Although the reactor is described in the Supplemental, I strongly suggest describing it at least briefly in the manuscript.
- Line 93: As explained in S4.1, in addition to two UVC lamps (for the photolysis of H_2O_2) also six lamps (Vis above 400 nm) were used.
- Line 96: Deionized H_2O is not good enough for such kind of experiments; usually high purity water should be used.
- Line 101 and 2.3.: Why did you use GC-MS? Wouldn't be easier and faster by LC-MS (no derivatization)?
- Line 118: Why adjusted again before UV-Vis measurements (you did this at the beginning of experiment)? In this way, you did not have the same conditions as in the reaction solution.
- Lines 116-121: Very awkwardly written, and thus unclear. From the text in the main manuscript, it should be clear how the measurements were done (the supplemental material should provide only the additional and more detailed information).
- Line 123: Non-purgeable organic carbon: What do you mean by non-purgeable OC?
- In Eq. II, change $K_{A,rmix}$ with $k_{A,rmix}$ as it is written in line 141; the same for $K_{A,}$ (first-order rate constants).
- Line 140: Instead of " bimolecular reaction rate coefficient", "second-order rate constant" should be used. Please, check throughout the manuscript and SI.
- Line 141: …first-order disappearance rate constants…. ?
- Line 147: Add d_λ (absorbing path length, it is in cm and not in cm^{-1}). I also suggest using the same characters for the same parameters as usually used for MAC (Laskin et al., Chem. Rev. 2015).
- Line 157: HCl and $HClO_4$ are acids (not buffers)!

Results and discussion

- Too much material in Supplement, more should be reasonably involved in the manuscript.
- Fig. S4 should be involved in the main MS.
- Line 167/168: Which isomers of 4NC do you have in mind?

- Fig.1: What does it present: the dependence of conc. of products vs. conc. of initial 4NP? One can conclude that with a higher initial concentration of 4NP, higher conc. of 4NC was formed (at pH 2, 3 other products as well), but only to a certain extent. Can you give some explanation?

- Fig. 1: Especially in the case at pH 9, it is not correct to derive the slope from a linear regression analysis.

- Lines 97, 181/184, etc.: “unbuffered” solution: Do you mean that the reaction solution was not adjusted to a certain pH using buffer (or only not adjusted)? However, as it can be seen you did measure the initial pH of such reaction solution (in SI, Fig. S6).

- Line 184: As I understand, the authors concluded that the distribution of products was the same in both cases (in aqueous solution with pH 2 and in that with unadjusted initial pH). I assume that your conclusion is based on fact that in both cases the reaction mixtures were acidic at the end. The authors have to be more precise in the formulation to clarify the text.

- Lines 185-245: Since the whole part is confused, I recommend shortening and writing the text more concisely explaining the mechanism with emphasize on the main formation pathways (shown in Fig. 2), and on your findings.

- Line 282: …”where it can undergo chemical and photochemical processing”: What this statement refers to, clouds or wet aerosol, or both? From what has been written, one would conclude that the processes take place only in wet aerosols.

- Line 297: Which two bleaching mechanisms: via OH reactions and via photolysis? From the results in Fig. 4, photolysis is not very effective.

Technical corrections

- All references (in parentheses) have to be written from the earliest to the latest one according to the year of publication.
- I suggest changing “absorptivity” with “absorption”: in the title and throughout the manuscript: e.g., line 26: it should be “UV-Vis absorption”; line 54: “light absorption of aqueous particles”, etc.
- Line 54: The chemical and photochemical…..result (not results).
- Line 76: Should be plural (…are strongly..).
- Line 84: Should be plural (…were monitored..).
- Line 90: Aqueous-phase reactor (here “aqueous-phase” is an adjective)
- Line 105: Delete “, the instrument was”; it should be “and equipped with…”
- Line 123: “was quantified” (or determined)
- 4-nitophenol (4-NP) can be written as 4NP, etc.
- Base-e, base-10: it is no need to write all the time; it’s obvious from the equations.
- Fig.3: Data are presented…(plural)
- Line 281: Instead of “resides” it’s better “exists”
- Line 297: …depending on [OH]
- Page 15: Authors of the first reference are missing.

Supplemental material

P. 3, line 33: Not “allowed”, but “used”
Table S1: Give the concentration ranges in mg L^{-1}.