Atmospheric Measurement Techniques Discussions

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Comment on amt-2021-407

Anonymous Referee #2

Referee comment on "Development, characterization, and application of an improved online reactive oxygen species analyzer based on the Monitor for AeRosols and Gases in ambient Air (MARGA)" by Jiyan Wu et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-407-RC2, 2022

Wu et al. presented a work on an optimization of online DTT by adding a DTT experimental module to an online sampler. The authors then compared their online system with manual DTT. The comparison yielded a slope not equal to 1 and the authors used it to calibrate their online data. The authors then measured online DTT from ambient air and compared to water-soluble ions, BC, and gases to found that photo-oxidation and secondary formation processes are important sources of DTT.

There are two major issues with the DTT protocol which will likely lead to large differences in the final DTT activities. The discussion on results and the proofreading need more work. Therefore, in my opinion, this work needs major revision.

Major comments:

- The authors compared the calibration slope from PQN in this work with those from Fang et al. (2015) and Puthussery et al. (2018) and found that their slope is less than the slopes in these two previous studies. They then concluded that “shielding from light and filling with nitrogen will reduce DTT consumption, and it also supports the accuracy of the system in determining the oxidation potential of environmental particulates”. The authors also compare the DTT obtained from their system to manual method from Cho et al. (2005), correlation scatter plot shows a slope of 1.14 (off-line methods 14% higher than online). The slope of offline DTT vs online DTT for PM2.5 sample also yielded a slope of 1.14.

All the above seem to suggest that there is a systematic deviation of the online method from this study. The initial DTT concentration used in this work is ~71 micoM (1mM x 0.5mL/7mL). Many other studies used 100uM of initial DTT concentration. In fact, the three references (Fang et al. (2015), Puthussery et al. (2018)&Cho et al. (2005)) the authors used for online-manual comparison all used 100 microM. Since initial DTT concentration makes a difference to the final DTT activity, data obtained in this work is not directly comparable to these three studies and any other studies that use a different initial DTT concentration. The authors need to justify why they used a different concentration.

In Fang et al. (2015) and Puthussery et al. (2018), the DTT consumption were blank corrected, which means the background activity of light and oxygen should be accounted for already with blank correction. Therefore, the conclusion "shielding from light and filling with nitrogen will reduce DTT consumption, and it also supports the accuracy of the system in determining the oxidation potential of environmental particulates" is not true.

- in this work, DTNB and Tris buffer were added to the TCA-DTT mixture, and the absorbance was measured every 10min to get the DTT consumption rates. However, this is wrong, at least speaking from "standard" DTT protocol. DTT consumption should be done in the presence of DTT, buffer, and sample only. This is to make sure the DTT consumption happen at pH 7.4. The correct way is withdraw the mixture of DTT-sample every 10min, then add (TCA), DTNB, and Tris buffer. The authors need to justify why they modify the Cho/Fang/Puthussery protocol while they claim that they are optimizing the DTT assay based on these studies.

- It is not clear to me what new science was obtained from this online system compared to a filter-based system. The importance of contribution of photochemistry and secondary processing to DTT is well studied in tons of previous studies. An online system has a better time resolution compared to a filter based, which is very novel but what this work have found is exceptional is not clear.

- " And through correlation analysis, we found that DTTV and PM2.5 concentration were positively correlated before rain, but negatively correlated after rain." I wouldn't say for a R value of ~0.3 or -0.2, ie, r2 of 0.09 and 0.04, there is a correlation. This sentence is not statistically supported.

Minor comments:

- More description on the light blocking and nitrogen environment system should be added? For example, how does the system look like? How to make sure it is sealed?
- What software was used to control the pumps, log data, etc?
- "Then, use pump A to suck the mixed solution in the 1ml mixing bottle and transfer it to the reaction bottle to mix it with TCA" how much was withdrawn?
- Line 264-279, the discussion of diurnal variation and before and after rain is confusing. The authors are merely listing numbers without any discussion of what the comparison imply or suggest.
- Line 285, ng m-3. Typo? microg m-3?

Technical comments:

There are many incomplete sentences and confusing use of language. The authors need to proofread the manuscript more carefully. Here are some examples:

- Incomplete sentences:
  - "In order to more conveniently and accurately detect 15 the content of reactive oxygen in atmospheric particles hour by hour."
  - "Clean the instrument 173 pipeline once a week, 5 times each time (Ultra-pure water)." A subject is missing. Many other sentences throughout the manuscript have the same problem. Please correct. Perhaps a passive tense is more appropriate.
  - "the average concentration of PM2.5 after rain was 7.80±4.18 ng m-3, PM2.5 There is a significant drop in concentration."
- Confusing sentencences:
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  - "the basis of the MARGA, which is a reliable field instrument…particle phases." MARGA is first mentioned here in the manuscript. What is field instrument? What is "transform the observation"? To what? How to transform?
  - "we divided the DTTv daily activities" this sentence appears to be some sort of

calculations but the authors meant to separate different days.

- “The levels of these substances were not high during the sampling period and decreased to varying degrees after rain.” How high is not high??