Response to reviewers' comments

Thank you and the reviewers for handling the manuscript (manuscript number: amt-2021-407). Responses to reviewers are in *italics*. The changes in the manuscript have been marked in blue. Please refer to the point-by-point response to the reviewers' comments and concerns.

Thank you again and the reviewers for such detailed suggestions for revision.

Comment on amt-2021-407
Anonymous Referee #2

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.

Response: Thanks for the question, the initial DTT concentration was not fixed, it was determined by the content of the sample (Ayres et al., 2008). This is related to the main principle of the DTT method, which is mainly divided into two parts. In the first part, when DTT is used to measure ROS in atmospheric particulates, reactive oxygen species in particulates oxidize DTT to DTT-disulfide compounds. In the second part, the reaction continues and DTT is continuously consumed. Add DTNB regularly and measure the absorbance of the solution to obtain the remaining DTT concentration. The consumption rate of DTT by particulate matter was calculated (Wang et al., 2019). Therefore, the amount of DTT is related to the sample concentration. The rate of the catalytic redox reaction can be simplified as a straight line (Sauvain et al., 2012), and the correlation of the linear regression reaches more than 0.95.

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.

Response: Thanks for your suggestion, we agree with you. Here we mainly reduce the instrument blank. We have revised the manuscript:

"As shown in Figure 4, the linear graph of DTT consumption rate and PQN concentration, the online detection slope is 3.66±0.26, and the coefficient R^2=0.992. During the on-site operation, PQN's online and offline testing is measured at least once a month to ensure online accuracy."

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.

Response: *Thank you for your question, and I agree with the reviewer. Due to ambiguity in my expression, I rewrite. We add a new text to line 151 in the revised manuscript:*

"Second (DTT determination step), after completing the first step, at 0.10.20.30.40 minutes, use pump A to draw 1ml mixed solution in the mixing bottle and add it to the reaction bottle. Then, immediately add 1 mL TCA (10% w/v; quencher) to the reaction vial (RV, wrapped in aluminum foil to prevent possible light interference) using pump A."

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.

Response: *Thanks for your question, as you said this study has better temporal resolution. In addition, this study realized the simultaneous detection of inorganic ions and trace gases (water-soluble ions Cl^-、NO_3^-、SO_4^{2-}、NH_4^+、Na^+、K^+、Mg^{2+}、Ca^{2+}) and DTT_V based on MARGA. Therefore, it is possible to further determine the source of the influence of DTT_V. For new scientific discoveries, we need more applications to discover.*

"And through correlation analysis, we found that DTT_V and $PM_{2.5}$ 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, r^2 of 0.09 and 0.04, there is a correlation. This sentence is not statistically supported.

Response: Thanks for your suggestion, we agree with you. I have made corrections. We add a new text to line 318 in the revised manuscript:

"The average concentration of $PM_{2.5}$ during the sampling period is 9.97±6.53 ug m^{-3}, the average concentration of $PM_{2.5}$ before rain is 11.13±7.21 ug m^{-3}, the average concentration of $PM_{2.5}$ after rain is 7.80±4.18 ug m^{-3}. The concentration of $PM_{2.5}$ is a significant drop. In addition, as shown in Table 1, there are differences in the correlation between $PM_{2.5}$ and DTT_V before and after rain."

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?

Response: Thank you for your question. In the DTT experimental part, we used aluminum foil to wrap all the pipes to avoid light. Each line, reaction tube, pump A, pump B, and mixing tube were sealed with sealing plugs and sealing tape. During the experiment, the valve of N_2 was kept open, and the whole DTT experimental module was filled with N_2 through pump A and pump B. We add a new text to line 123 in the revised manuscript:

"In the DTT reaction module, in order to avoid the influence of light and air on the experiment, all pipelines, reaction flasks and mixing flasks are sealed and protected from light by aluminum foil. The whole DTT experimental part was filled with N_2 by pump A and pump B before the experiment started."

What software was used to control the pumps, log data, etc?

Response: The software to control the pump is "Serial Port Utility" and "Cadent connect". The data is recorded using "Spectra Suite", a software for measuring absorbance, which has the function of automatically saving data.

"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?

Response: "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 1ml TCA"

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.

Response: Thank you for your suggestion. The main purpose here is to express that there are obvious diurnal changes in ROS content, which may be related to different pollution emission sources. I added new content on line 279:

"However, there are no obvious diurnal variation in $PM_{2.5}$ mass concentration. Therefore, the diurnal variation of DTT activity is assumed to be mainly attributed from different emission sources at the site."

Line 285, ng m-3. Typo? microg m-3?

Response: Thanks for pointing it out, I have corrected it.

"The average concentration of $PM_{2.5}$ during the sampling period is 9.97±6.53 ug m^{-3}, the average concentration of $PM_{2.5}$ before rain is 11.13±7.21 ug m^{-3}, the average concentration of $PM_{2.5}$ after rain is 7.80±4.18 ug m^{-3}. The concentration of $PM_{2.5}$ is a significant drop."

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."

Response: "In recent years, the online detection technology of ROS has been developed. However, there are few technical studies on online detection of ROS based on the DTT method."

"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.

Response: "In the DTT experimental module, DTT and DTNB solutions are prepared every 4 days. Before each test, perform a comprehensive light and nitrogen bag inspection. To ensure the accuracy of the experimental data, a standard curve was measured before each experiment. The instrument pipeline is cleaned once a week, as shown in Figure 1. The programmable pump A and pump B are connected to the ultrapure water channel. During the cleaning process, all pipelines, reaction tubes and mixing tubes are cleaned."

"the average concentration of $PM_{2.5}$ after rain was 7.80±4.18 ng m-3, PM2.5 There is a significant drop in concentration."

Response: "The average concentration of $PM_{2.5}$ during the sampling period is 9.97±6.53 ug m^{-3}, the average concentration of $PM_{2.5}$ before rain is 11.13±7.21 ug m^{-3}, the average concentration of $PM_{2.5}$ after rain is 7.80±4.18 ug m^{-3}. The concentration of $PM_{2.5}$ is a significant drop."

Confusing sentencences:

"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?

Response: Thanks for pointing it out, I have corrected it.

"In addition, the present study is developed on the basis of the MARGA, which is a state-of-art instrument. MARGA measures near-real-time water-soluble particulate species and their gaseous precursors. (Chen et al., 2017)"

"we divided the DTTv daily activities" this sentence appears to be some sort of calculations but the authors meant to separate different days.

Response: Thanks for pointing it out, I have corrected it.

"To better understand the environmental factors affecting DTT_V, hourly data obtained by running the instrument is composited to obtain a diurnal profile of the DTT activity."

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

Response: Thanks for pointing it out, I have corrected it.

"The average concentration of $PM_{2.5}$ during the sampling period is 9.97±6.53 ug m^{-3}, the average concentration of $PM_{2.5}$ before rain is 11.13±7.21 ug m^{-3}, the average concentration of $PM_{2.5}$ after rain is 7.80±4.18 ug m^{-3}. The concentration of $PM_{2.5}$ is a significant drop. In addition, as shown in Table 1, there are differences in the correlation between $PM_{2.5}$ and DTT_V before and after rain. Therefore, we suspect that the source of DTT_V is different before and after the rain. BC and the polluting gases SO_2, NO_x, NO_2, CO, Ca^{2+}, K^+, Mg^{2+} are often used as tracers of biomass burning, coal combustion, and dust storms. Compared with the early winter in the northern suburbs of Nanjing (Zhang et al., 2020), the levels of these substances decreased during the sampling period."