

Response to reviewers' comments #2

We thank the reviewers for the constructive comments and suggestions, which are very positive to improve scientific content of the manuscript. We have revised the manuscript appropriately and addressed all the reviewers' comments point-by-point for consideration as below. The remarks from the reviewers are shown in black, and our responses are shown in blue color. All the page and line numbers mentioned following are refer to the revised manuscript without change tracked.

Anonymous Referee #2

The manuscript entitled "Study on the measurement of isoprene by Differential Optical Absorption Spectroscopy" by Song et al. reports the application of DOAS technique on isoprene measurement. This study details the setup, laboratory experiments, and field applications of the DOAS. Intercomparisons of isoprene concentrations measured by the DOAS and a commercial GC-MS shows a good consistency. The content and novelty of the manuscript align well with the requirements of AMT. However, English could be improved throughout the paper as it is not easy to follow. Overall, I recommend the manuscript for publication if the authors can address the following comments.

General Comments:

1. In the calibration experiments described in Sect. 2.2, the actual concentrations (CM) must be measured more than once with parallel experiments for different cell lengths, and measuring error should be added in Table 1 and Figure 3. The equation (1) should be recalculated accordingly. In addition, it seems that the difference between CE and CM increased as the increase of cell length in Table 1. Could authors provide an explanation about the phenomenon?

R: Thank you for the suggestion. In fact, we have performed the parallel experiments for different cell lengths for several times. The measurements for each concentration point are recorded with more than 10 spectra after the system stabilizing. In the revised manuscript, we have indicated all the measured points in the Figure 4 and the standard deviation in Equation (1), as well as added the errors in the Table 2. Please refer to the revised Table 2, Figure 4, and Equation (1) in the revised manuscript.

The calibration results in Table 1 show that the difference between CE and CM increased as the increase of cell length. Even though the absolute difference between CE and CM increased, the relative deviations are constant all through the different concentration points, which can be inferred from the linear regression Figure 4 and Equation (1). As to the absolute difference, it may be due to the possible bias in the length of cell or the error of the standard gas sample.

2. Some important information is missing in the comparison experiments. Firstly, it is not given how reference spectrum was recorded during field applications. As reference spectrum plays a role in spectral fitting, uncertainty caused by reference spectrum should be discussed. Secondly, calibration methods as well as calibration frequency of

the on-line VOCs (TH-300B) are not provided. Compared with the DOAS measurements, the on-line VOCs measurements seems to have a 0.1 ppb offset during the period from 07/21 to 07/24. Could the offset be caused by the calibration of on-line VOCs? Thirdly, providing wind parameters (measured by weather station) and benzene and toluene concentrations (measured by on-line VOCs) when the comparison is inconsistent will be more persuasive, as authors speculated that wind directions and benzene and toluene concentrations would influence the comparison consistency.

R: Thank you for the suggestion. During the field measurement, the measured spectrum collected at 00:00 LT on July 1, 2018 was used as the reference spectrum. The uncertainty caused by reference spectrum have been discussed in Line 104-107 and Line 246-248 of the revised manuscript.

In order to ensure the authenticity and accuracy of the observed data, the working status and response of the TH-300B monitoring system were inspected every day. Daily calibrations were performed automatically at 00:00 to 01:00 LT. In addition, the external standard method for the FID and the internal standard method for the MS were adopted. Please refer to Line 192-197 of the revised manuscript. Regarding to the offset from 21 July, we think it could be explained by two aspects: firstly, the daily calibration operated at midnight could make the on-line VOCs observed value close to the zero point, which may deviate from the real abundance; secondly, the differences of isoprene concentration were existed between the different air masses observed by these two instruments.

Figure R1 shows the discrepancies of measured isoprene by these two instruments as a function of wind direction. It can be seen that the SE and SSE are the prevailing wind direction during the field measurement. Meanwhile, the large difference (defined as $\text{abs}(\text{DOAS}-\text{TH-300B})/\text{DOAS} * 100\%$) also tends to appear und SE and SSE wind direction, of which results of discrepancy exceeding 60% were accounted for 54% and 49%, respectively. This suggests that the differences of isoprene observed by these two instruments were impacted by the wind direction.

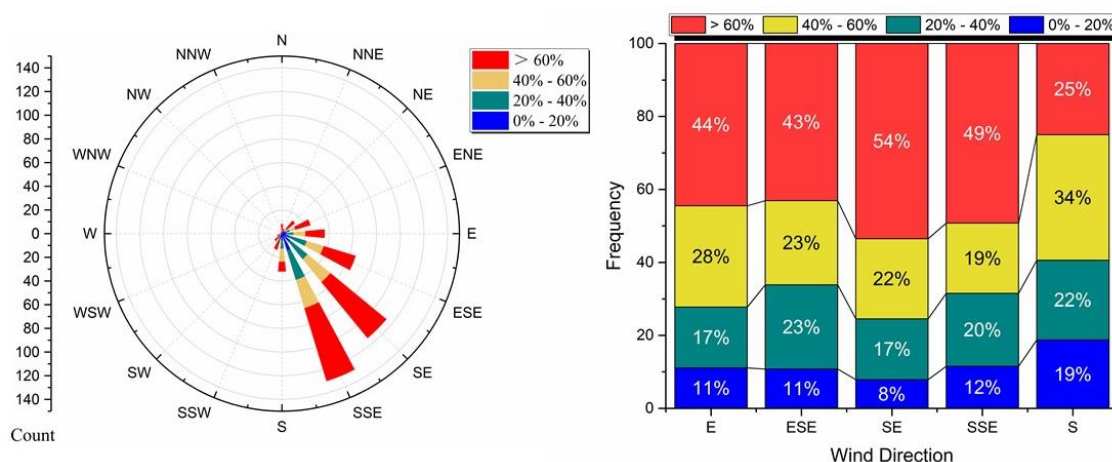


Figure R1. Differences of measured isoprene by these two instruments as a function

of wind direction.

Figure R2 shows the dependence of isoprene difference (same as mentioned above) on the benzene and toluene concentration. It can be found that the difference increased as the increases of toluene, however, not obviously benzene. Because the hourly data of benzene and toluene are only representative for the air sampled during dozens of minutes within this hour, it cannot comprehensively reflect their impacts on isoprene.

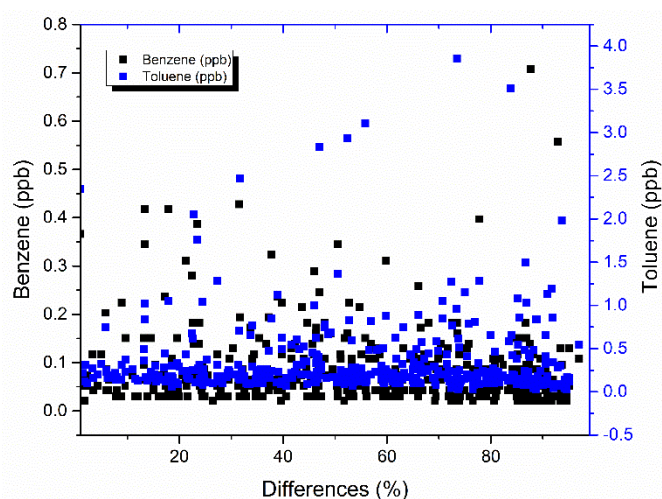


Figure R2. Dependence of isoprene difference on the benzene and toluene concentration

However, considering there lots of influencing factors can impact the observed isoprene by DOAS and VOCs analyzer, we are not able to quantify the relationship between observed differences of isoprene and these parameters. Therefore, we have decided to keep these analyses in the responses and provided these possible causes in the manuscript.

3. As authors introduced in Sect. 1, PTR-MS and CIMS can also be used to measure isoprene concentrations. The manuscript would benefit from a critical comparison of the best available performance of these four methods (i.e., DOAS, GC-MS, PTR-MS, and CIMS) together given in a table. Characteristics in the comparison could be time resolution, accuracy, precision, appropriate platforms, etc. Such a comparison would be useful to the readership and meaningful to the community.

R: Thanks for the comments. We have followed the suggestion to summarize a critical comparison of these four methods, as listed in Table R1. Please also refer to Table 1 in the revised manuscript.

Table R1. Comparison of different on-line methods for isoprene measurement.

	DOAS (this study)	GC-MS (Gong et al., 2018)	PTR-MS (Eerdekens et al., 2009)	CIMS (Leibrock et al., 2003)
Time resolution	1 min	30-60 min	0.5-2 min	1.65 s

Accuracy (Correlation with GC-MS/GC)	R=0.85	R>0.99 (with offline)	0.95	R=0.78
Detection Limit	10 ppt	4 ppt	100 ppt	<30 ppt
Platform	Stationary / conditional mobile	Stationary / mobile	Stationary / mobile	Stationary / mobile
Advantages	No sampling Easy operation Simple instrument	High precision Accurate quantification	Fast responses High precision	High time resolution Good sensitivity
Disadvantages	Impacts by weather conditions Impacts of interferences	Time consuming Calibration needed Difficult operating and maintaining	Molecule or fragment ion of the same mass cannot be differentiated	Interference of unidentified components Expensive equipment

Specific Comments:

Line 15: “202.71-227.72nm” → “202.71-227.72 nm”. Blank space should be inserted between number and unit. Such irregular expressions were used frequently elsewhere in the manuscript and should be revised.

R: Thanks for the comments. We have corrected for the irregular expressions all through the manuscript and the blank space has been inserted correspondingly in Line 14 and elsewhere in the revised manuscript.

Line 26: The “B” in BVOCs is usually the abbreviation of “Biogenic” instead of “Biological”.

R: Thank you for the suggestion. The “Biological” has been replaced with “Biogenic”. Please refer to Line 23 in the revised manuscript.

Line 42: “In the daytime, the oxidation by OH is the main chemical process of isoprene.” The sentence should specify “whose oxidation” and “what kind of chemical process” to avoid ambiguous meaning.

R: Thank you for the suggestion. We have specified this sentence as “In the daytime, the chemical process oxidized by OH is the main sink of isoprene”. Please refer to Line 35-36 in the revised manuscript.

Line 44-47: These contents are given here without references.

R: Thank you for the suggestion. Relevant literatures have been cited there, e.g. Chen et al., 2020; Lu et al., 2018; Zhu et al., 2020. Please refer to Line 39 and References in the revised manuscript.

Line 52: “BVOCs also has [: :]” → “BVOCs has [: :]”

R: We have deleted the unnecessary “also”. Please refer to Line 43 in the revised manuscript.

Line 59: “GC-MS is using the high separation ability of gas chromatography to separate the [: :]”. Simple Present Tense should be used here.

R: Thanks for the comments. Simple present tense has been used to rephrase the sentence as “GC-MS utilizes the high separation ability of gas chromatography to separate the components of environmental samples, and then measures the different compounds with the mass spectrometry”. Please refer to Line 50-51 in the revised manuscript.

Line 61-64: “Although GC-MS [: :] But the complex [: :]” These sentences should be rephased.

R: Thank you for the suggestion. These sentences have been rephrased to “With the advantages of high precision and stability, GC-MS can distinguish most VOCs qualitatively and quantitatively, however, is difficult in maintaining and operating due to the complex requirements in power, temperature control, and special carrier gas”. Please refer to Line 51-53 in the revised manuscript.

Line 63ff: A comma should go before the conjunction “and” in a list of three or more items. “[: :] in power, temperature control and special carrier gas [: :]” → “power, temperature control, and special carrier gas”. “[: :] requires sampling, preservation and pre-treatment [: :]” → “requires sampling, preservation, and pre-treatment”.

R: Thanks for the comments. We have added the comma in the corresponding places. Please refer to Line 53 and 54 in the revised manuscript.

Line 67, 77, and 78: The meaning of the abbreviations (i.e., PTR-MS, GC, and CIMS) has already been given in the previous paragraph and so it need not be defined again here.

R: Thank you for the suggestion. The abbreviations were used there. Please refer to Line 57, 63, and 66 in the revised manuscript.

Line 69-71: The sentences should be rephased.

R: Thank you for the suggestion. We have re-written as “The fixed length of the drift tube provides a fixed reaction time for the ions as they move along the drift tube. The sample air is continuously pumped through the drift tube and the VOCs in the sample react with H_3O^+ to be ionized, and then enter the mass spectrometer to be detected”. Please refer to Line 58-60 in the revised manuscript.

Line 104: “[: :] as light source, the aperture [: :]” → “as light source. The aperture”

R: Thank you for the suggestion. We have corrected it and please refer to Line 90 in the revised manuscript.

Line 106: “while, the aperture of the” → “while the aperture of the”

R: Thanks for the comments. Combined with the suggestions by Reviewer #1, we have rephrased these sentences. Please refer to Line 90-92 in the revised manuscript.

Line 109: “1024-pixel photodiode array as detector was used to record spectrum” → “1024-pixel photodiode array was used as detector to record spectrum”

R: Thanks for the comments. We have corrected this sentence. Please refer to Line 93-94 in the revised manuscript.

Line 158: “Fig. 3” → “Figure 3”

R: Thanks for the comments. We have corrected it and please refer to Line 144 in the revised manuscript.

Line 215: “[: : :] so higher measurement points will catch higher concentration of isoprene. [: :]” Reference or detailed explanations should be given here.

R: As pointed by Reviewer #1, we found that this statement is wrong and remove it from the revised manuscript.

Line 217: “[: : :] will be more or less lost during the sampling process.” Sampling loss of on-line VOCs is an important parameter which should be quantized here by performing experiments or referring to a similar research.

R: The TH-300B on-line VOC instrument uses detection technology that includes ultralow-temperature preconcentration combined with gas chromatography and mass spectrometry (GC/MS). For a complete measuring cycle, there five steps include sample collection, freeze-trapping, thermal desorption, GC-FID/MS analysis, heating and anti-blowing purification. It takes about 1h for one complete detection cycle. It's extremely difficult to evaluate the sampling loss individually from the complete detection cycle, especially for experiments. As a commercial scientific instrument, the relative error of the targets was quantized not exceeding 30% among all the detected VOCs species for the whole procedure, which is determined by the difference between the measured and guaranteed values of standard samples. As to isoprene, the R^2 reached 0.999 (Hui et al., 2019). It suggests that the detection accuracy is very high, and the total error could be contributed considerably by sampling process. We have addressed the related discussion in Line 191-192 in the revised manuscript.

Line 241-243: The authors should provide an explanation or references on the method that they used to calculate detection limit.

R: Here we have cited the National Environmental Protection Standard HJ654-2013, in which the detection limit of ambient air quality continuous automated monitoring system using open light path method, i.e. DOAS in this study, can be defined as the two times of zero noise. Please refer to Line 215 to 217 in the revised manuscript.

Line 247-249: As the stability of light source and spectrometer will influence the fitting

residual and instrumental performance, sensitivity experiments of temperature (or other relative parameters) for light source and spectrometer should be conducted.

R: Thank you for the suggestion. Considering the influences of light source and spectrometer stability on the fitting residual and instrumental performance, we have used the thermostatic apparatus to keep the operating temperature of spectrometer stable. And the air conditioner serves as thermostat model to stable the ambient temperature for the whole system of DOAS instrument. The record of thermometer show that the ambient temperature varied within ± 1 °C. We have indicated related description in Line 222-224 in the revised manuscript.

Line 293: “CIMS methods, The” → “CIMS methods, the”

R: Thanks for the comments. It has been corrected and please refer to Line 263 in the revised manuscript.

Line 304-306: The sentences should be rephased.

R: Thank you for the suggestion. We have rephrased the sentence as “Considering the differences in measurement principle and sampled air between them, the comparison results show a good agreement between these two instruments”. Please refer to Line 271-273 in the revised manuscript.

Line 308: “the paper proposes [: : :]” → “this study proposes [: : :]”

R: Thanks for the comments. “the paper” has been changed to “this study”. Please refer to the Line 275 in the revised manuscript.

References

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