

Response to reviewers' comments #1

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 #1

The manuscript of Sao Gong and co-authors is a very interesting work on new kind of isoprene measurements using active DOAS (Differential Optical Absorption Spectroscopy) in the deep UV spectral range between 200 and 230nm. It is to my knowledge the first manuscript presenting so clearly the possibilities for quantitative isoprene measurements with this technique and fit well in the scope of AMT. The manuscript contain all basic information on instrumentation, characterization, data analysis and a field comparison experiment. Some of the information are incomplete and should be corrected.

I recommend the publication of this manuscript after correction of the following points:

Major points:

1. Section 2.1 after line 115: It is not clear how the Reference I0 spectrum of the light source is recorded and how it is considered in the spectral fit. The shape and spectral properties should be considered. How I0 measurements are made in measurements of section 3.1?

R: Thank you for the comments. We have supplemented the related description about how the reference I0 spectrum is recorded in laboratory experiments and filed measurements, respectively. Please refer to Line 104-107 in the revised manuscript. The consideration about I0 spectrum interference was stated in Line 246-248 in the manuscript.

2. 1. 128: NO absorption cross section was recorded with a reference gas. At which concentration and slant column (cell length). Is the NO signal representative for the atmospheric concentration over 75 m? NO absorption contain narrow absorption bands which go into saturation. If the NO concentration is not representative these saturation effects should be considered.

R: The guaranteed NO gas with concentration of 3080 ppm was used to record the reference spectrum using 0.02 m cell length, which is equivalent to about 820 ppb with 75 m light path during the field measurement. Although this NO signal is not representative for the atmospheric concentration, we have performed the measurements for different NO concentrations in order to testify this NO reference can be employed for the spectral fitting of the field observation.

Considering the ambient NO levels, a series of spectra containing equivalent NO concentrations of 0, 40, 80, 160, 200 ppb under 75 m light path have been measured,

respectively. Each concentration points have been measured repeatedly multi times, as summarized in Table R1.

Table R1. The calibration results of NO in different gas cells combination

| Length of cells | C_E (ppb) | C_M (ppb) |
|--------------------|-------------|-------------------|
| empty | 0 | 0.91 ± 1.04 |
| 2 cm | 40.00 | 40.94 ± 0.78 |
| 4 cm | 80.00 | 81.02 ± 0.70 |
| 2 cm + 4 cm | 120.00 | 120.85 ± 0.76 |
| 4 cm + 4 cm | 160.00 | 160.71 ± 0.99 |
| 2 cm + 4 cm + 4 cm | 200.00 | 199.16 ± 0.94 |

Figure R1 shows the differential optical density for the equivalent NO concentration series and the correlation between equivalent and measured concentration of NO. It can be seen that the measured NO for different equivalent concentrations would not be interfered by using the reference recorded at high concentration. And the measured NO concentrations were highly consistent with the equivalent concentration showing a slope of 1.01 and correlation coefficient R^2 of 1.

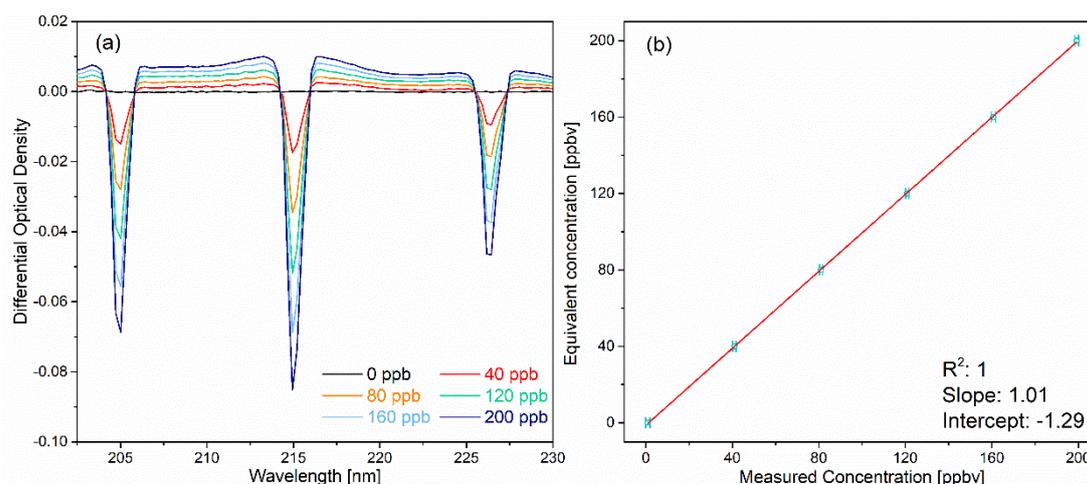


Figure R1. Differential optical density for the equivalent NO concentration series and the correlation between equivalent and measured concentration of NO.

Therefore, we consider that the NO reference is suitable used for the spectral analysis of the atmospheric measured spectrum containing less NO concentration.

3. Please explain in more detail the spectra preparation before the DOAS fit.

R: Before the DOAS fit, the measured spectra with low light intensity and high integration time were excluded from the spectral fitting, which are mainly due to the unfavorable weather condition influencing the measurements. The spectral were also corrected for offset before introducing fitting. Please refer to Line 171-172 in the revised manuscript. Regarding to the absorption cross sections of NH_3 , SO_2 , NO_2 ,

C6H6 and C7H8, these high-resolution references were convoluted with a Gaussian-shaped instrument function of 0.75 nm half-width to obtain the absorption cross section matching the spectrometer resolution. Please refer to Line 114-115 in the revised manuscript.

4. 1. 133 and following: Provide DOAS fit errors for the derived concentrations. You may use the method of Stutz, J. and Platt U., Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, Appl. Opt., 35 (30), 6041-53, 1996. Include errors of the measurements also in section 3 and 4.

R: Thank you for the suggestions. We have carefully reviewed this literature and followed the method to estimate the DOAS fit errors of this study (Stutz, J. and Platt U., 1996). Overall, the measurement errors of isoprene were estimated lower than 20%. The errors have been indicated in Line 126-127 in the revised manuscript. Besides, the errors of the measurements were also included in section 3 and 4, and summarized in Line 229.

5. Figure 1: Include all fitted reference gases.

R: Figure 1(a) and (b) shows the absorption cross section and differential absorption spectrum of isoprene in 1 ppb*km. Other interference absorption gases were showed in Figure 7. So we speculate the reviewer suggested to include all the references in the spectral fitting example (Fig. 1(c) and (d)). We have re-plotted it, as shown in Figure 2 in the revised manuscript.

6. 1. 165 show a 6.6% underestimation. Please include an error estimation. Is this within the error? What are possible reasons? Could it be due to spectrometer stray light? Did you check the spectrometer stray light below 230nm?

R: In the revised manuscript, the measuring errors have been included in the Table 2 and linear regression analysis. The 6.6% underestimation was determined from the linear regression equation. We think this underestimation may be due to the possible tiny bias in the length of cell or the uncertainty of the standard gas sample, rather than the spectrometer stray light. The spectrometer stray light is not exceeding 0.8% around 200 nm band (as mentioned in the spectrometer instruction). We would not attribute this underestimation to the impacts of stray light of spectrometer.

7. 1. 239: Your DOAS fit like in Fig. 1 is not dominated by noise but by a remaining spectral structure. This is dominating here your error. Apply a proper DOAS error calculation (see comment above). You can not simply translate the zero noise to measurement noise over 75m. In the later case you have also interference's from other gases and imperfect spectral data, and likely also changes of our light source. The zero noise estimation is a lower limit and true error will be higher.

R: As responses above, we have followed the method to estimate the DOAS fit errors of this study (Stutz, J. and Platt U., 1996).

Minor points:

I. 101: include reference “(see Figure 2)”

R: We have added it in Line 87 of the revised manuscript.

I. 105: “the aperture of the transmitting telescope is 76mm, and the primary mirror is the UV enhanced spherical mirror...”. - What is the focal length. Rephrase to make the sentence clear e.g.: The aperture of the transmitting telescope is 76mm, with a UV enhanced spherical mirror with a focal length of XXXmm. The aperture of the receiving telescope is 152mm, with a XXX mirror with a focal length of XXXmm.

R: Thank you for the comments. These sentences have been rephrased as “The aperture of the transmitting telescope is 76 mm, with a and the primary mirror is the UV enhanced spherical mirror with a focal length of 304 mm. The aperture of the receiving telescope is 152 mm with a UV enhanced spherical mirror with a focal length of 608 mm”. Please refer to Line 90-92 in the revised manuscript.

I. 116: Specify the high pass filter.

R: In this study, high pass filter is to perform a high pass binomial on the spectrum using the iterations of 500 twice. The operation will first do a low pass filter and will then divide the spectrum by the result of this low pass filter operation. The binomial filter uses the smallest binomial mask possible. This mask does the same as an averaging operation over three contiguous channels. Afterwards, the broadband structures can be eliminated effectively. Please refer to Line 101-102 in the revised manuscript.

I. 147: include the accuracy of the isoprene concentration in the bottle.

R: According to the certificate of reference material of this gas, the uncertainty of isoprene gas with 10 ppm (guaranteed values of standard samples) is 2% (confidence interval of 0.95). Please refer to the revised Figure 3.

I. 198 – 199: The isoprene observed by DOAS at night is most of the time significantly above zero and does not reach zero later in the night. Could this not be a systematic offset e.g. due to missing I0 reference spectra?

R: During the field measurement, the measured spectrum collected at 00:00 LT on July 1, 2018 was used as the reference spectrum. If the reference spectrum is pure enough without any absorption of isoprene, the DOAS retrieved data would be accurate even though it is most of the time significantly above zero at night and does not reach zero later in the night. Given that the reference spectrum was contaminated by the rare isoprene absorption, the DOAS retrieved data would be lower than the real value. The observed isoprene should be even higher in the night. On the other hand, the VOCs analyzer data series showed the isoprene concentrations were close to zero at night, which may be related to the daily calibration procedure operated at 00:00-01:00. So we would like to attribute this systematic offset to VOCs analyzer, rather than the offset from I0 spectrum.

I. 212: Here the argument for the difference is the sampling height. Before it was the night measurement. Put both arguments together in a merged explanation.

R: Thank you for the suggestions. We have re-structured this part in order to achieve a better merged explanation. Please refer to Line 186-213 in the revised manuscript.

l. 214: “Isoprene will rise up and diffuse after emission from plants, so higher measurement points will catch higher concentration of isoprene.” → This is completely wrong. Concentration can not accumulate and will always be same or lower with larger distance from the source.

R: Thank you for pointing out this wrong argument. We have removed this explanation from the text and try to explain the possible reasons causing the discrepancies between these two instrumental observed isoprene values. Please refer to Line 186-213 in the revised manuscript.

l. 216: Specify expected losses in sampling tubes.

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 (EPA, 2019). We have addressed the related discussion in Line 191-192 in the revised manuscript.

l. 217: Include estimation of (systematic) DOAS errors and if this can explain the difference.

R: Regarding to the differences in the observed isoprene by these two instruments, especially for night, we have discussed from several aspects, e.g. instrumental principle, sampled air, impacts of meteorological conditions, etc. Please refer to Line 186-213 in the revised manuscript.

l. 235: include measurement errors as example.

R: There is Figure 6 in Line 235. We are not sure if the reviewer suggested to include the measurement errors in this Figure. We have indicated the errors, as shown in Figure 6(b) in the revised manuscript.

l. 251: It is not explained how the spectral structure of the lamp is corrected.

R: We have not corrected the spectral structure of the lamp, however, included the lamp spectrum as the absorption of interfering substances in the spectral fitting. In this way, the impacts due to spectral structure of the lamp can be reduced significantly and the residual is consequently much lower. Therefore, we have stated that “the absorption of interfering substances and the spectral structure of lamp are necessary to be considered together with the isoprene absorption spectrum”. Please refer to Line 226-227 in the revised manuscript.

l. 254: “remain after the spectral fitting”, Include why they include → due to....

imperfect reference spectra

R: Thank you for the suggestions. We have included the possible reason causing the residual after spectral fitting. Please refer to Line 228-229 in the revised manuscript.

I. 260: How do you derive the influence of NO on isoprene measurements?

R: Given the absorption of NO can influence the isoprene absorption, it can be found that the occurrences of NO peak value are sometimes consistent with isoprene, as the example of a short period shown in Figure R2 (spectral temporal resolution). By investigating the spectral fitting, there were no obvious absorption of isoprene. If the isoprene concentration was subtracted by 0.3% NO concentration, some weird isoprene peaks will be disappeared. Therefore, we have inferred that the impact of NO on isoprene could be about 0.3% of its concentration.

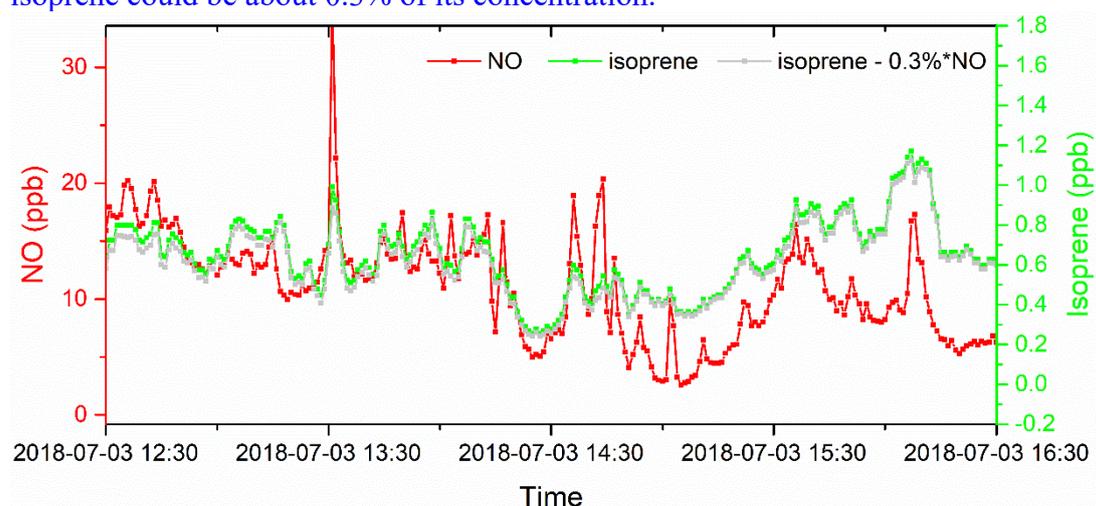


Figure R2. Time series of NO and isoprene concentration.

I. 274: Define the high pass filter for the differential absorption spectra. Is it the same like for the spectral analysis?

R: Yes, the high pass filter for the differential absorption spectra is applied same as this of the spectral fitting. We have defined it in Line 245-246 in the revised manuscript.

I. 275: Figure 7a), why these spectra are not shown as differential spectra?

R: In order to display the absorption of benzene and toluene in deep UV wavelength, we show the absorption cross sections of benzene and toluene together with isoprene. It can be found that the measured light intensity below 215 nm will be reduced significantly if the benzene and toluene concentration are high, which will further reduce the signal to noise ratio of the measured spectra and influence the spectral fitting performance. The aim of Fig. 7(b) is demonstrating the variation frequencies of differential absorption of NH₃, SO₂ and NO₂ are much higher than that of isoprene. Therefore, the interferences of NH₃, SO₂ and NO₂ absorption on isoprene can be weakened in the fitting process of differential spectra. Considering as mentioned above, we decided to display these two patterns of the absorption spectra in Figure 7 (a) and (b).

Language:

I. 19 – 21, rephrase: The correlation coefficient between DOAS and on-line VOCs instrument observed from 23 days field observation is 0.85 with a slope of 0.86.

R: Thank you for the comments. We have followed the suggestion to rephrased as “The correlation coefficient between DOAS and on-line VOCs instrument observed from 23 days field observation is 0.85 with a slope of 0.86”. Please refer to Line 18-19 in the revised manuscript.

l. 43 – 45, rephrase: Due to the existence of multiple double bonds, the additional reaction with OH will lead to the formation of a variety of products and the formation of RO₂.

R: Thank you for the comments. We have followed the suggestion to rephrased as “Due to the existence of multiple double bonds, the additional reaction with OH will lead to the formation of a variety of products and the formation of RO₂”. Please refer to the Line 36-38 in the revised manuscript.

l. 58: measure the isoprene → measure isoprene

R: We have deleted “the”, and please refer to Line 48 in the revised manuscript.

l. 61: spectrometry → spectrometer

R: We have changed the “spectrometry” to “spectrometer”, and please refer to Line 51 in the revised manuscript.

l. 63: is not easy → difficult

R: Following the suggestion by Reviewer #2, this sentence 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.

l. 91: direction → possibility

R: We have changed the “direction” to “possibility”, and please refer to Line 79 in the revised manuscript.

l. 103: space → separation or distance

R: The “space” has been replaced with “distance”. Please refer to Line 88 in the revised manuscript.

l. 104: source, → source.

R: The comma has been corrected to the dot. Please refer to Line 90 in the revised manuscript.

l. 109: record spectrum → record the spectrum

R: We have added “the” before “spectrum”. Please refer to Line 94 in the revised manuscript.

l. 115: in atmosphere → in the atmosphere

R: We have added “the” before “atmosphere”. Please refer to Line 99 in the revised manuscript.

l. 119: fitting differential → fitting the differential

R: We have added “the” between “fitting” and “differential”. Please refer to Line 103 in the revised manuscript.

l. 158: Fig. 3 is the linear fitting of the calibration → Fig. 3 shows the linear fit of the calibration

R: Combined with the suggestion from Reviewer #2, “Fig. 3 is the linear fitting of the calibration” has been changed to “Figure 4 shows the linear fit of the calibration”. Please refer to Line 144 in the revised manuscript.

l. 162: For the future → For further

R: We have removed “the”, please refer to Line 147 in the revised manuscript.

l. 171 & l. 182: of DOAS → of the DOAS

R: We have added “the” before “DOAS”, and please refer to Line 154 and Line 161 in the revised manuscript.

l. 185: with DOAS → with the DOAS

R: We have added “the” before “DOAS”, and please refer to Line 167 in the revised manuscript.

l. 189: is lightpath → is the lightpath

R: We have added “the” before “lightpath”, and please refer to Line 168 in the revised manuscript.

l. 196: 0.217ppb, → 0.217ppb respectively,

R: “respectively” has been added. Please refer to Line 176 in the revised manuscript.

l. 197: that on-line → that of the on-line

R: We have added “of the” between “that” and “on-line”. Please refer to Line 177 in the revised manuscript.

l. 252: isoprene. → isoprene absorption spectrum.

R: We have added “absorption spectrum” after “isoprene”. Please refer to Line 226 in the revised manuscript.

References

- Stutz, J. and Platt U., Numerical analysis and estimation of the statistical error of differential optical absorption spectroscopy measurements with least-squares methods, *Applied Optics*, 35, 6041-6053, 1996.
- Hui, L., Liu, X., Tan, Q., Feng, M., An, J., Qu, Y., Zhang, Y., Cheng, N.: VOC characteristics, sources and contributions to SOA formation during haze events in Wuhan, Central China, *Sci of Total Env.*, 650, 2624-2639, <https://doi.org/10.1016/j.scitotenv.2018.10.029>, 2019.

EPA, Technical Assistance Document for Sampling and Analysis of Ozone Precursors for the Photochemical Assessment Monitoring Stations Program, U.S. Environmental Protection Agency, EPA-454/B-19-004 (April, 2009).