Reviewer #3

Overview

The authors investigate the simultaneous detection of cycloalkanes and acyclic alkanes using a PTR-TOF-MS with NO^+ ionization chemistry. The measurement technique was tested in a laboratory before applied in the field, here the city of Guangzhou, China and at a chassis dynamometer. The authors confirm that cyclic alkanes are ionized via hydride ion transfer while isomers of alkanes, alkenes, cluster with NO^+. Using a gas standard containing cyclic and acyclic molecules their sensitivity was determined. Effects of humidity and tubing were also considered by the authors. Their motivation is the contribution of cyclic and bicyclic alkanes to the formation of SOA in urban environments or from vehicle exhaust. They also report different ratios for cyclic and acyclic alkanes in diesel and gasoline exhaust.

Further investigation of the application of PTR-TOF-MS with NO^+ ionization chemistry is of great interest for the field if VOC detection. The results provide a new dataset for C10 to C20 alkanes under polluted conditions. I thus recommend that the work is published.

Reply: We would like to thank the reviewer for the insightful comments, which helped us in improving the quality of our work. Please find the response to individual comments below.

Specific comments:

1. Line 100: This sentence sounds as if cycloalkanes and acyclic alkanes have never been measured simultaneous in ambient air before, but Koss et al., 2016 did that to my knowledge.

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 1 (line 100-103) as **"These evidences suggest that NO^+ ionization scheme could provide a possibility for measuring cycloalkanes along with acyclic alkanes, as demonstrated in two recent work (Koss et al., 2016;Wang et al., 2020) ".**

2. Line 118: The authors show one part of the ionization sequence, but the formation of NO^+ ions in the ion source is more complex. See Karl et al., 2012 (doi:10.5194/acp-12-

11877-2012).

Reply: We thank the reviewer for the comment. We supplemented the ionization sequence of the formation of NO^+ ions in manuscript.

The sentences in the Section 2.1 (line 115-122) are modified to:

In order to generate NO^+ ions, 5 sccm ultra-high-purity air (O_2+N_2 ≥ 99.999%) is directed into to the hollow cathode discharge area of ion source, NO^+ ions are produced by ionization as follows (Federer et al., 1985;Karl et al., 2012):

$$N^+ + O_2 \rightarrow NO^+ + O \qquad (a)$$

$$O^+ + N_2 \rightarrow NO^+ + N \qquad (b)$$

$$N_2^+ + O_2 \rightarrow O_2^+ + N_2 \qquad (c)$$

$$O_2^+ + NO \rightarrow NO^+ + O_2 \qquad (d)$$

3. Line 120: The authors state that impurities are minimum, but no values are given. Also it is known from Yuan et al., 2016 that primary ion signals as well as signals of the impurities can be influenced by the ion guide. This study used an instrument including an ion guide, thus it would be important to rule out artefacts arising from that.

Reply: We thank the reviewer for the comment. When NO^+ ions are used as parent ions in PTR-ToF-MS, the impurities such as O_2^+ and NO_2^+ do exist and may affect the measurements. Here, we present the intensities of NO^+ ions and other impurities including O_2^+, NO_2^+, and H_3O^+ during the measurements of urban air and vehicular emissions (Fig. S2). As shown in the two figures, the abundances of O_2^+, NO_2^+, and H_3O^+ ions are significantly lower than the NO^+ ions. We also calculated the ratio of O_2^+ ions to NO^+ ions, and found that ratio was below 5% during the measurements of urban air expect for the period from 26 October to 2 November, 2018 (7-10%), while the O_2^+/ NO^+ ratio was lower during the measurements of vehicular emissions, which is generally below 2%. Thus, the impurities inducing little interference to cycloalkanes detection.

The sentence in the Section 2.1 (line 128-134) is modified to:

The intensities of primary ions NO^+ and impurities including O_2^+, NO_2^+, and

H_3O^+ and the ratio of O_2^+ to NO^+ during the measurements of urban air and vehicular emissions are shown in Fig. S2. The abundances of O_2^+, NO_2^+, and H_3O^+ are significantly lower than NO^+ ions and the ratio of O_2^+ to NO^+ is basically below 5% during the measurements of urban air expect for the period from 26 October to 2 November, 2018 (7-10%), while the ratio of O_2^+/NO^+ is basically below 2% during the measurements of vehicular emissions.

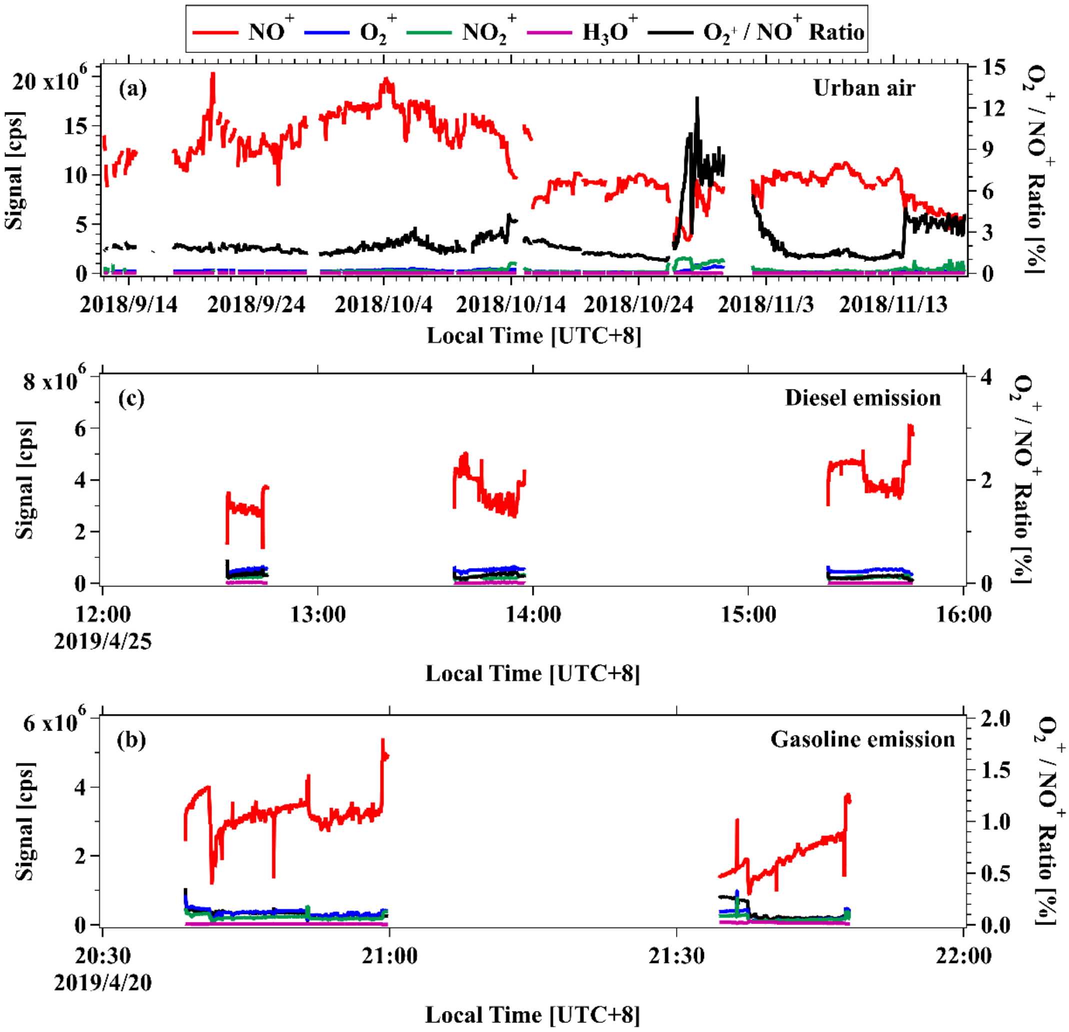

Figure S2. Time series of NO^+, O_2^+, NO_2^+, and H_3O^+ during the measurements of urban air (a), and vehicular emissions (b-c).

4. Line 130: VOCs can also cluster with H3O+, I suggest writing: Compared to proton transfer reactions occurring mostly between H3O+ ions and VOCs species…

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 2.1 (line 144-146) as **“Compared to proton transfer reactions occurring mostly between H_3O^+ ions and VOCs species, NO^+ ions show a variety of reaction pathways with VOCs, which can be roughly summarized as follow”.**

5. Line 209: As far as I understood the interferences can still be up to 15 %. To my opinion this is worth mentioning like (< 15 %).

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 3.1 (line 230-233) as **“However, concentrations of 1-alkenes and trans-2-alkenes in the atmosphere are usually significantly lower than cycloalkanes (about 25% and <15%, respectively)”.**

6. Line 211: The authors mention before that the calibration experiments were done with a gas standard containing compounds listed in Table S1, but the information would be very helpful in this chapter as well.

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 3.2 (line 247-249) as **“The calibration experiments of cycloalkanes (see details of gas standard in Table S1) are carried out in both dry conditions (<1% RH) and humidified conditions (Fig. S9)”.**

7. Line 238: The authors show how vehicular emissions drop to 10 %, but how did they measure that technically. Was the inlet brought close to the cars exhaust? How was the switching from detecting exhaust to clean air done? I imagine they used a dilutive flow of synthetic air, but this is not described in the manuscript.

Reply: We thank the reviewer for the comment. The delay time of cycloalkanes in vehicular emissions was calculated based on the results of chassis dynamometer study, so the sampling methods are same as mentioned in Li et al. (2021) and Wang et al. (2022). A custom-built sampling and dilution system for vehicles combining online and offline sampling techniques was used during this campaign. The vehicles were pushed onto a chassis dynamometer and driven through short transient driving cycle for

3~5 times. During the test, vehicle exhaust is diluted by a factor of 10-100 by zero air using the custom-built dilution system. In other words, the drop of signals of cyclic alkanes for vehicular emissions are as the result of switching from diluted vehicular exhausts to zero air.

The sentence in the Section 3.2 (line 271-274) is modified to:

For the species not in the gas standard, we also take advantage of vehicular emissions measurements associated with high concentrations of cycloalkanes, and the sampling methods are same as mentioned in Li et al. (2021) and Wang et al. (2022).

8. Line 249: Did the authors calculate average sensitivities for cyclic and bicyclic alkanes separately? The fragmentation seems to be different.

Reply: We thank the reviewer for the comment. We did not calculate the average sensitivities for cyclic and bicyclic alkane separately, as bicyclic alkanes are not contained in the gas standard. For bicyclic alkanes, we also use the average sensitivity of C10-C14 monocyclic alkanes.

The fragmentation of various compounds is shown in Figure S7 in the revised manuscript. From Figure S7, the fractions of product ions (M-H) from hydride abstraction in the total product ions for bicyclohexane is 71%, which is only slightly lower than monocyclic alkanes with the same carbon number (cyclodecane~77% and hexylcyclohexane~75%). Based on this only information for the fragmentation of bicyclic alkanes, we tentatively assume bicyclic alkanes fragment similar with other compounds and the average sensitivity of C10-C14 monocyclic alkanes.

We added the description in the line 681-683: **The average sensitivity of C_{10}-C_{14} cyclic alkanes was used to predict the concentrations of cyclic alkanes with higher carbon (C_{15}-C_{20}) and bicyclic alkanes (C_{10}-C_{20}).**

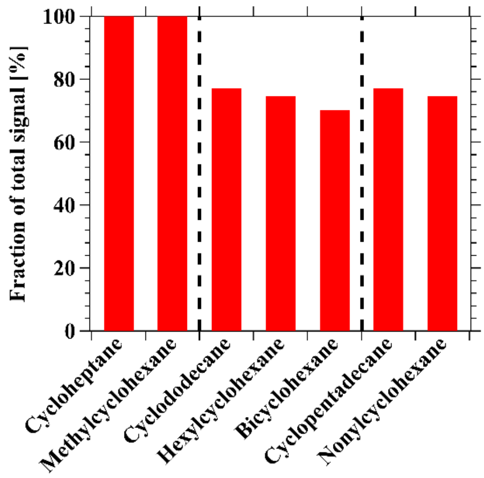

Figure S7. The fractions of product ions (M-H) from hydride abstraction of C_7, C_{12}, and C_{15} cyclic alkanes and C_{12} bicyclic alkanes in NO^+ PTR-ToF-MS.

9. Line 269: Since there are also cases where cyclic alkanes are more abundant than acyclic alkanes I suggest writing: … suggestion they predominantly came from same emission sources.

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 3.3 (line 305-308) as **"Based on both time series and correlation analysis (Fig. 6c), cyclic and bicyclic alkanes showed strong correlation with acyclic alkanes, suggesting they predominantly came from same emission sources"**.

10. Line 289: The authors report completely different emission pattern from diesel vehicles compared to gasoline. Has this been detected before for other compounds? Is there a known explanation for the difference?

Reply: We thank the reviewer for the comment. In addition to cycloalkanes and alkanes, other compounds such as aromatics and oxygenated VOCs also presents similar different emission pattern between gasoline and diesel vehicles, which has been reported in a recent study during the same campaign (Wang et al., 2022). The different emission patterns from diesel vehicles compared to gasoline vehicles for cycloalkanes and alkanes can be explained by chemical compositions of gasoline and diesel fuels are different. The gasoline fuel used in China is mainly comprised of C_4-C_7 hydrocarbons, including alkanes (55%-62%), alkenes (12%-17%), aromatics (27%-32%), and methyl tert-butyl ether (MTBE, 1%-4%) (Tang et al., 2015;Sun et al., 2021;Qi et al., 2021;Huang et al., 2022), while heavy hydrocarbons, mainly C_8-C_{10} alkanes and aromatics account for major fractions in diesel fuel, including alkanes (70%-79%), alkenes (1%-7%), and aromatics (21%-25%) (Yue et al., 2015).

The sentences in the Section 3.3 (line 329-332) are modified to:

In addition to cycloalkanes and alkanes, other compounds including aromatics and oxygenated VOCs also demonstrate large differences between gasoline and diesel vehicles, which were mainly attributed to different chemical compositions of gasoline and diesel fuels (Wang et al., 2022).

11.Line 315: For some alkanes (C_{15}, C_{16}, C_{18}) the ratio observed in London is much larger than detected in this work. This is not similar. I would appreciate a more detailed discussion at this point.

Reply: We thank the reviewer for the comment. We re-checked measurement results of cyclic and acyclic alkanes from Xu et al. (2020), and found an error in processing this dataset from London. We corrected the ratios obtained in London and modified Fig. 9. The ratios obtained in London are higher than the ratios obtained in the urban region of Guangzhou, but the ratios in London are similar to diesel exhausts in our work for C_{13}-C_{18} range. These results are likely due to the measurement location in London is proximity to a main road, where cyclic and acyclic alkanes may be dominated by traffic emissions with high fractions of diesel vehicles in the fleet. Although some variations observed in different urban environments, nevertheless, these ratios are broadly within the range between gasoline and diesel emissions.

The sentences in the Section 3.4 (line 358-367) and Fig. 9 are modified to:

As shown in the Fig. 9, the ratios obtained in the urban region of Guangzhou in this work (0.2-0.4) are similar to other measurements in urban area, including Algiers, Algeria (Yassaa et al., 2001). The ratios obtained in London, UK (Xu et al., 2020) are higher than the ratios obtained in Guangzhou, but similar to the diesel exhaust in our work for C_{13}-C_{18} range. These results are likely due to the

measurement location in London is proximity to a main road, cyclic and acyclic alkanes may be dominated by traffic emissions with high fractions of diesel vehicles in the fleet. Although some variations observed in different urban environments, nevertheless, these ratios are broadly within the range between gasoline and diesel emissions.

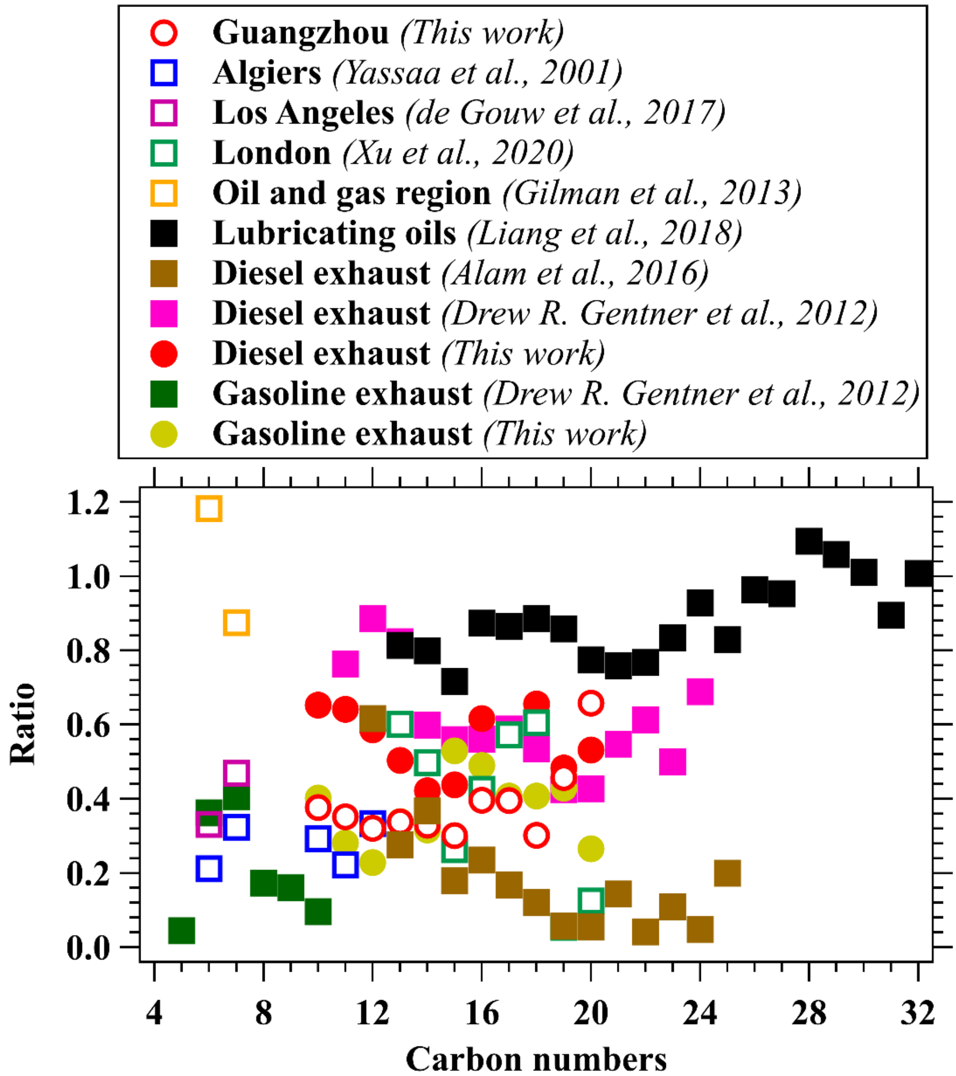

Figure 9. The concentrations ratios of cyclic alkanes to acyclic alkanes for different carbon number. Measurements in various urban areas, including Guangzhou in China, London in UK (Xu et al., 2020), Los Angeles in US (de Gouw et al., 2017), Algiers in Algeria (Yassaa et al., 2001), and an oil and gas region in Colorado of US (Gilman et al., 2013) are also shown for comparison. Emission sources, including vehicle exhausts (Alam et al., 2016;Gentner et al., 2012) and lubricating oils (Liang et al., 2018) are also included.

12. Figure 8: Here it would be very helpful to see error bars. AS the authors present averaged values the variability is important to proof significance, especially for the comparison of the ratios.

Reply: We thank the reviewer for the comment. We have added error bars on the corresponding figure. Figure 8 (line 728-733) is modified to:

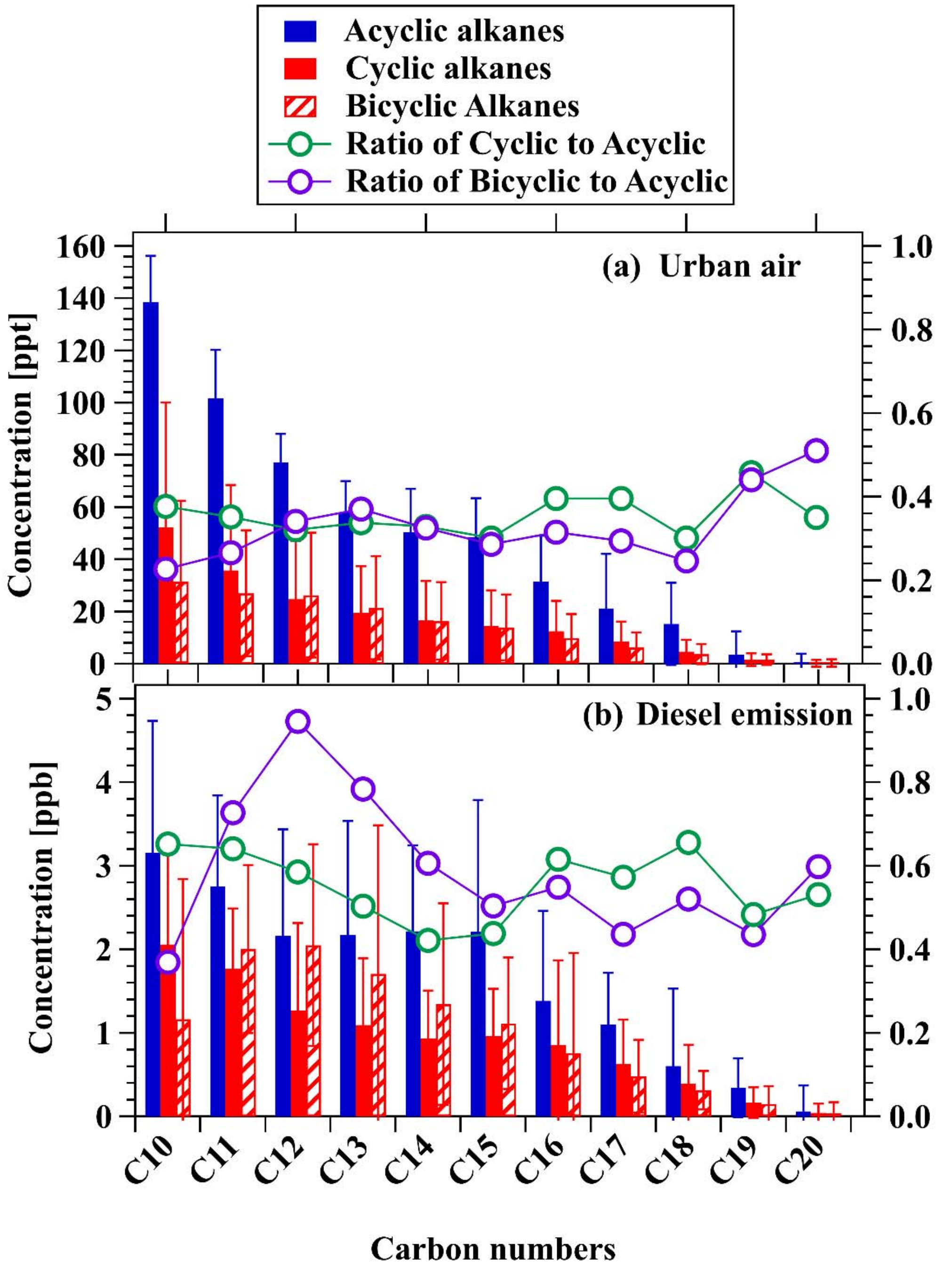

Figure 8. Mean concentrations of cyclic and bicyclic alkanes and alkanes (branched + linear) with different carbon numbers measured by NO+ PTR-ToF-

MS in the urban air (a) and diesel emissions (b). The green and purple lines with circles represent the ratios of cyclic and bicyclic alkanes to acyclic alkanes under the same carbon numbers, respectively. Error bars represent standard deviations of the concentration for the acyclic, cyclic and bicyclic alkanes.

Technical corrections:

1. Line 31: For a better reading I recommend writing: Appling this method, cycloalkanes were successfully measured at an urban site in southern China and during a chassis dynamometer study for vehicular emissions.

Reply: We thank the reviewer for the comment. We corrected this sentence in Abstract (line 30-32) as **"Appling this method, cycloalkanes were successfully measured at an urban site in southern China and during a chassis dynamometer study for vehicular emissions"**.

2. Line 35: These results demonstrate that NO+ PTR-ToF-MS…

Reply: We thank the reviewer for the comment. We corrected this sentence in Abstract (line 35-38) as **"These results demonstrate that NO^+ PTR-ToF-MS provides a new complementary approach for fast characterization of cycloalkanes in both ambient air and emission sources, which can be helpful to fill the gap in understanding the importance of cycloalkanes in the atmosphere"**.

3. Line 45: Components and concentration levels of organic compounds largely affect atmospheric chemistry, …

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 1 (line 45-48) as **"Components and concentration levels of organic compounds largely affect atmospheric chemistry, atmospheric oxidation capacity, and radiation balance (Wu et al., 2020;Monks et al., 2015), as well as human health (Xing et al., 2018) "**.

4. Line 75: For a better understanding I recommend writing: Based on measurements *of gas chromatographic techniques, the signals of unspeciated cyclic compounds can be determined. This is done by subtracting the signal of speciated IVOC from the total signal for each retention time bin according to the series of n-alkanes.*

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 1 (line 75-78) as **"Based on measurements of gas chromatographic techniques, the signals of unspeciated cyclic compounds can be determined. This is done by subtracting the total signal for each retention time bin according to the series of n-alkanes (Zhao et al., 2016;Zhao et al., 2014) ".**

5. Line 103: Typo: … ambient air and from emission sources…

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 1 (line 104-105) as **"In this study, we discuss the potential of online measurements of cycloalkanes in ambient air and emission sources utilizing NO^+ ionization in PTR-ToF-MS".**

6. Line 105: I suggest to write: The results of laboratory experiments to characterize product ions,…

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 1 (line 105-107) as **"The results of laboratory experiments to characterize product ions, calibration, and response time will be shown".**

7. Line 113: mass resolution instead of mass resolving

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 2.1 (line 112-115) as **"A commercially PTR-ToF-MS instrument (Ionicon Analytik, Austria) equipped with a quadrupole ion (Qi) guide for effective transfer of ions from drift tube to the time-of-flight mass spectrometer is used for this work (Sulzer et al., 2014), and the mass resolution approximately reach about 3000 m/Δ m (Fig. S1)".**

8. Line 147: In this study, we investigate characteristic ions of cycloalkanes generated *by the NO+ ionization…*

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 2.2 (line 161-162) as **"In this study, we investigate characteristic ions of cycloalkanes generated by NO+ ionization from a series of species identification experiments".**

9. Line 149: I suggest using species instead of chemicals.

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 2.2 (line 162-164) as **"The information of cycloalkanes species used in these experiments is listed in Table 1".**

10. Line 160: Typo: sensitivities

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 2.2 (line 173-176) as **"Therefore, we evaluate the influence of humidity on sensitivities of cycloalkanes in NO+ PTR-ToF-MS using a custom-built humidity delivery system (Fig. S4), and the results are applied to explore the relationship between sensitivities of cycloalkanes and humidity".**

11. Line 186: The sentence is confusing to me, I suggest writing: As mentioned above, thecharacteristic peaks of cycloalkanes under NO+ ionization are consistent with the ions that are received at the attempts to utilize H3O+ PTR-MS. For the latter method though sensitivities are reported to be lower.

Reply: We thank the reviewer for the comment. We corrected the sentences in the Section 3.1 (line 210-213) as **"As mentioned above, the characteristic peaks of cycloalkanes under NO^+ ionization are consistent with the ions that are received at the attempts to utilize H_3O^+ PTR-MS. For the latter method though sensitivities are reported to be lower (Yuan et al., 2014;Gueneron et al., 2015;Warneke et al., 2014;Erickson et al., 2014)".**

12. Line 193: The isomers… (without 'as')

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 3.1 (line 218-219) as **"The isomers of cyclic alkanes, alkenes may interfere with measurements of cycloalkanes".**

13. Line 202: I recommend adding: …which are similar fragmentation ions from NO+ ionization of the two species and …

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 3.1 (line 225-228) as **"Based on the mass spectra, alkenes produce the $C_nH_{2n-1}^+$ product ions at fractions of <5%, which are similar fragmentation ions from NO^+ ionization of the two species and other 1-alkenes determined from a selected ion flow tube mass spectrometer (SIFT-MS) (Diskin et al., 2002)".**

14. Line 212: Figure S4 is never mentioned in the manuscript.

Reply: We thank the reviewer for the comment. We have re-checked the figure name of the manuscript and found that it was wrongly marked, which has been modified in the corresponding position of this manuscript.

The sentence in the Section 3.2 (line 247-249) is modified to:

The calibration experiments of cycloalkanes (see details of gas standard in Table S1) are carried out in both dry conditions (<1% RH) and humidified conditions (Fig. S9).

15. Line 241: Typo: …but relatively lower than determined for those acyclic alkanes.

Reply: We thank the reviewer for the comment. We corrected this sentence in the Section 3.2 (line 277-280) as **"The delay time of various cycloalkanes generally increases with the carbon numbers, ranging from a few seconds to a few minutes, but relatively lower than determined for those acyclic alkanes within C10-C15 range (Wang et al., 2020) ".**

16. Line 307: Fig. 8b instead of Fig. 9

Reply: We thank the reviewer for the comment. We corrected this sentence in the

Section 3.4 (line 348-350) as **“Similar results are obtained for gasoline vehicles, with cyclic alkanes/acyclic alkanes and bicyclic alkanes/acyclic ratios of 0.27-0.53 for and 0.21-0.52, respectively (Fig. 8)”.**

Reference:

Alam, M. S., Zeraati-Rezaei, S., Stark, C. P., Liang, Z., Xu, H., and Harrison, R. M.: The characterisation of diesel exhaust particles – composition, size distribution and partitioning, Faraday Discussions, 189, 69-84, 10.1039/c5fd00185d, 2016.

de Gouw, J. A., Gilman, J. B., Kim, S. W., Lerner, B. M., Isaacman-VanWertz, G., McDonald, B. C., Warneke, C., Kuster, W. C., Lefer, B. L., Griffith, S. M., Dusanter, S., Stevens, P. S., and Stutz, J.: Chemistry of Volatile Organic Compounds in the Los Angeles basin: Nighttime Removal of Alkenes and Determination of Emission Ratios, Journal of Geophysical Research: Atmospheres, 122, 11,843-811,861, 10.1002/2017jd027459, 2017.

Diskin, A. M., Wang, T. S., Smith, D., and Spanel, P.: A selected ion flow tube (SIFT), study of the reactions of H_3O^+, NO^+ and O_2^+ ions with a series of alkenes; in support of SIFT-MS, International Journal of Mass Spectrometry, 218, 87-101, 10.1016/s1387-3806(02)00662-0, 2002.

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NO^+ chemical ionization in PTR-ToF-MS: important contributions of higher alkanes to secondary organic aerosols in China, Atmospheric Chemistry and Physics, 20, 14123-14138, 10.5194/acp-20-14123-2020, 2020.

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