#### **Reviewer #2**

### Overview

Chen et al. report the online measurement of cycloalkanes using the PTRMS instrument equipped with the NO chemical ionization scheme. The authors utilized a selection of authentic cyclohexane standards to showcase the high sensitivity, long term stability, low humidity dependence, and low detection limit of this method for the real time characterization of cyclohexane. With this method, C10-C20 cycloalkanes were measured in the ambient air at an urban site of China as well as from vehicular emissions in a chassis dynamometer experiment. The obtained concentrations of cycloalkanes can be as much as over half of the levels of the corresponding linear/branched alkanes, suggesting an appreciable amount of this group of compounds in the urban air. Overall, the authors have demonstrated very carefully the utilization of NO+PTRMS for the rigorous quantification of cycloalkanes in the field and laboratory. Here are a few thoughts and suggestions I would like the author to consider prior to publication on AMT.

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

Specific Comments

1. Page 2, line 25: change 'undergoes' to 'undergo'.

Line 28 (and throughout the main text): 'as the result' should be 'as a result'.

Line 35: change 'demonstrates' to 'demonstrate'.

Line 38: add 'the' before 'importance'.

Reply: We thank the reviewer for the comments. We corrected all these comments and checked the grammar throughout the manuscript.

2. Page 9, line 221-225: Was there any measurement of cycloalkanes by PTRMS with the use of the NO+ ionization scheme? If so, could the authors compare their detection limits and sensitivities with those reports? If not, I am just curious why there was no attempt of using NO+PTRMS to detect cycloalkanes. After all, this ionization scheme

## has been out there for a while.

Reply: We thank the reviewer for the comment. When preparing this manuscript, we conducted a survey on the current literature, and found no relevant reports on the measurements of cycloalkanes in the atmosphere and emission sources by PTR-MS with NO<sup>+</sup> ionization, but there is a few laboratory studies have confirmed the ion chemistry (Koss et al., 2016) and use this technique to detect cycloalkanes in a smog chamber study (Wang et al., 2022). We have included the reference of this literature in Section 1 (line 102-103).

3. Page 9, line 226: Are the authors expecting a significant impact of water vapor on the instrument sensitivity? Unlike the proton transfer reaction, water cluster ion formation is not supposed to be a big issue on the ionization efficiency, right?

Reply: We thank the reviewer for the comment. Previously, it was shown that response factors of higher acyclic alkanes in NO<sup>+</sup> PTR-ToF-MS are slightly affected by air humidity, and the degree of influence is related to carbon number (Wang et al., 2020a). Therefore, we also evaluate the influence of humidity on sensitivities of cycloalkanes in NO<sup>+</sup> 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. Figure R1 shows that normalized signals of C10, C11, C13, and C<sub>14</sub> alkyl-cyclohexanes in the cylinder gas standard (Table S1) relative to dry conditions as a function of different humidity. The relative signals of the explored cycloalkanes show minor decrease (<10%) at the highest humidity (~82% RH at 25°C) compared to dry condition, and the observed changes for cycloalkanes with different carbon number are similar, suggesting little influence of humidity on measurements of cycloalkanes. The humidity-dependence curves determined in Figure R1 are used to corrected variations of ambient humidity in the atmosphere. The dependence of cyclic alkanes on humidity has been shown in Figure 4b and described in Section 3.2 in the original manuscript.



Figure R1. Humidity dependence of 1,1,3,5-teramethylcyclohexane (a), pentylcyclohexane (b), heptylcyclohexane (c), and octylcyclohexane (d).

4. Page 10, line 254: For bicyclic alkanes, compounds such as unsaturated carbonyls share the identical molecular formula at the unit mass resolution. Could the TOF-MS provide a decent separation of these bicyclic alkanes from other potential interferences?

Reply: We thank the reviewer for the comment. For those carbonyl compounds, it has been confirmed ketones will undergo association reactions with NO<sup>+</sup>, while aldehydes are ionized with NO<sup>+</sup> via hydride ion transfer (Wang et al., 2020b;Koss et al., 2016). Therefore, the unsaturated aldehydes are more likely share the identical molecular formula at the unit mass resolution with bicyclic alkanes after NO<sup>+</sup> ionization. Figure R2 shows the high-resolution peak fitting to the averaged mass spectra on a typical day (6 October 2018) in urban air measurements for m/z 165, at which masses

produced by  $C_{12}$  bicyclic alkanes ( $C_{12}H_{21}^+$ ) and other isomeric ions ( $C_8H_5O_4^+$ ,  $C_9H_9O_3^+$ , and  $C_{10}H_{13}O_2^+$ ) detected from NO<sup>+</sup> PTR-ToF-MS. These results confirmed that high-resolution mass spectrometry peak fitting can provide good separation of these bicyclic alkanes from unsaturated aldehydes and other potential interferences.



Figure R2. High-resolution peak fitting to the averaged mass spectra on a typical day (6 October 2018) for m/z 165, at which masses produced by C<sub>12</sub> bicyclic alkanes (C<sub>12</sub>H<sub>21</sub><sup>+</sup>) and other isomeric ions (C<sub>8</sub>H<sub>5</sub>O<sub>4</sub><sup>+</sup>, C<sub>9</sub>H<sub>9</sub>O<sub>3</sub><sup>+</sup>, C<sub>10</sub>H<sub>13</sub>O<sub>2</sub><sup>+</sup>, and C<sub>11</sub>H<sub>17</sub>O<sup>+</sup>) detected from NO<sup>+</sup> PTR-ToF-MS.

5. Page 10, line 255: What is the typical fraction of cycloalkanes in the overall carbon mass of organic compounds detected by NO+PTRMS? Is there any reason for smaller cycloalkanes (e.g., C6-C10) being excluded from the measurements and discussions?

Reply: We thank the reviewer for the comment. Considering the complexity of the reaction pathways between organic compounds and NO<sup>+</sup> ions, we are not able to distinguish the total carbon mass of organic compounds detected by NO<sup>+</sup> PTR-ToF-MS. As for the smaller cycloalkanes (e.g., C<sub>6</sub>-C<sub>10</sub>), we are not able to achieve accurate quantitation in this study, as the customized cylinder gas standard used in calibration experiments only contain five different alkyl-cyclohexanes (C<sub>10</sub>-C<sub>14</sub>). In addition, as

shown in Fig. 2 and Fig. S7, larger cyclic alkanes show some fragment ions that are the same to the ions for C6-10 cyclic alkanes, especially  $C_7H_{13}^+$  ion. As the result, measurements of C6-C10 may be slightly affected by fragmentation of the larger cycloalkanes, which warrants further investigation.

6. Page 11, line 276-281: Again, I would like to see more discussions on the selectivity of NO+PTRMS towards cycloalkanes. Are there any other compounds that have been routinely measured by this NO+ ionization scheme? If so, how high are the signals of cycloalkanes compared with those compounds?

Reply: We thank the reviewer for the comment. The time series of toluene and acetaldehyde shown in Fig. 7 were actually detected by NO<sup>+</sup> ionization by PTR-ToF-MS. Toluene and acetaldehyde are ionized with NO<sup>+</sup> via charge transfer and hydride ion transfer leading to major product ions of  $C_7H_8^+$  and  $C_2H_3O^+$ , respectively. As shown in Figure R3, good agreement between PTR-ToF-MS with  $H_3O^+$  and NO<sup>+</sup> chemistry was obtained for aromatics and oxygenated VOCs during the measurements of urban air, which has been reported in a recent study during the same campaign (Wang et al., 2020a). Therefore, we used toluene and acetaldehyde data from NO<sup>+</sup> measurement in vehicular emissions. The concentrations of cyclic and bicyclic alkanes are lower than acetaldehyde both in gasoline and diesel emissions, with ratios account for less than 1% of acetaldehyde, while the concentrations of cyclic and bicyclic alkanes are lower than toluene in gasoline emissions (with ratios account for 1-3% of toluene concentration) and about 5-10 times than toluene in diesel emissions.



Figure. R3 Comparisons of benzene, toluene, acetaldehyde, and pentanone measured by  $NO^+$  PTR-ToF-MS (red dots) and  $H_3O^+$  PTR-ToF-MS (blue dots) during the measurements of urban air.

The sentences in page 36 (line 728-733) are modified to:

Figure 7. Concentrations of  $C_{12}$  cyclic, bicyclic, and acyclic alkanes, acetaldehyde, toluene, and  $CO_2$  for (a) a gasoline vehicle with emission standard of China III and (b) a diesel vehicle with emission standard of China IV. The gray shadows represent the speeds of the vehicles on the chassis dynamometer. The data of toluene and acetaldehyde were detected by NO<sup>+</sup> PTR-ToF-MS.

7. Page 12, line 316: please specify the technique used in these earlier studies.Reply: We thank the reviewer for the comment. We summarized the techniques

used in these earlier studies and the results are shown in Table S2 in the revised manuscript.

The sentences in the Section 3.4 (line 354-358) are modified to:

As there are only limited measurements of bicyclic alkanes in the literature, we compare concentration ratios of cyclic alkanes to acyclic alkanes with results in previous studies, mainly using gas chromatography techniques (GC-MS/FID and GC×GC). The details of the technique used in these earlier studies are summarized in Table S2.

<b>Measurement location</b>	Measuring techniques	References
Guangzhou, China	NO <sup>+</sup> PTR-ToF-MS	This work
Algiers, Algeria	High-resolution gas chromatography-mass spectrometry (GC-MS) <sup>a</sup>	(Yassaa et al., 2001)
Los Angeles, USA	A two-channel in situ gas chromatography-mass spectrometry (GC- MS/FID) <sup>a</sup>	(de Gouw et al., 2017)
London, UK	Two-dimensional gas- chromatography time-of flight mass- spectrometry (TD-GC×GC ToF-MS) <sup>c</sup>	(Xu et al., 2020)
Northeastern Colorado, USA	GC-MS/FID <sup>a</sup>	(Gilman et al., 2013)
Lubricating oil	TD-GC×GC ToF-MS <sup>b</sup>	(Liang et al., 2018)
<b>Diesel exhausts</b>	TD-GC×GC ToF-MS <sup>b</sup>	(Alam et al., 2016)
Gasoline and diesel exhausts	GC-MS <sup>c</sup>	(Gentner et al., 2012)
Gasoline and diesel exhausts	NO <sup>+</sup> PTR-ToF-MS	This work

Table S2. Detailed information of the measurement locations and techniquesused for detection of cycloalkanes in this study and previous studies.

<sup>a</sup> The reported acyclic and cyclic alkanes were identified and quantified with gas standards

<sup>b</sup> The total ions signals of species is integrated into different regions (bin) according to the residence time of *n*-alkanes. The total ions signals of each bin were considered as the signals of acyclic and cyclic alkanes.

<sup>c</sup> The total ions signals of acyclic and cyclic alkanes were calculated by subtracted the signals of known compounds from similar chemical classes, and the remaining signals were considered to be the signals of acyclic and cyclic alkanes.

8. Page 25: It seems like the PTR sensitivities to all these cycloalkanes are pretty close. I was wondering if the obtained average sensitivity can be used to other compounds that are detected by this NO+ scheme. Do the authors have any idea what instrument parameters or compound properties may affect the sensitivity?

Reply: We thank the reviewer for the comment. Based on a series of laboratory experiments, we found that the calibrated cycloalkanes show similar sensitivities. Therefore, we use the average sensitivity of  $C_{10}$ - $C_{14}$  cycloalkanes to predict the sensitivities of cycloalkanes with higher carbon numbers ( $C_{15}$ - $C_{20}$ ).

However, we do not have much information on the parameters or compound properties that can affect sensitivities of cyclic alkanes at present. Per suggestion of reviewer #1, we checked the fragmentation of various cyclic alkanes, and we did not observe significant variations of fragmentation for cyclic alkanes with different carbon number, different sizes of the ring and the substituted alkyl group. This observation may explain similar sensitivities of cyclic alkanes. In contrast to cyclic alkanes, sensitivities of acyclic alkanes strongly correlate with the fragmentation degree of ions, with lower potential of fragmentation for acyclic alkanes with higher carbon number, as shown in Figure 4 of our previous study of NO<sup>+</sup> chemical ionization (Wang et al., 2020).

We added the description in the line 681-683: The average sensitivity of C<sub>10</sub>-C<sub>14</sub> cyclic alkanes was used to predict the concentrations of cyclic alkanes with higher carbon (C<sub>15</sub>-C<sub>20</sub>) and bicyclic alkanes (C<sub>10</sub>-C<sub>20</sub>).

# 9. Page 34: Are the authors expecting a large loss of these big alkane molecules to the sampling line?

Reply: We thank the reviewer for the comment. The perfluoroalkoxy (PFA) Teflon tubing is used for inlets in the measurements of cycloalkanes for both urban air and vehicular emissions, but gas-wall partitioning can be important for intermediate and semi-volatility compounds (Pagonis et al., 2017). In this study, we use the delay time to determine response of cycloalkanes and evaluate the interference caused by gas-wall partitioning. The delay time of cycloalkanes are summarized in Fig. 5, which

ranging from a few seconds to a few minutes. These results suggest that measured variability of cycloalkanes with higher carbon number, especially for  $C_{19}$ - $C_{20}$  or above, may only be reliable for time scales longer than 10 min. However, as shown in Fig. S13, the larger cyclic and bicyclic alkanes ( $C_{19}$ - $C_{20}$ ) exhibit very similar diurnal variations to smaller cyclic and bicyclic alkanes ( $< C_{19}$ ) during the measurements of urban air, implying that the gas-wall partitioning should not significantly affect temporal variations of larger cyclic and bicyclic alkanes reported in this study.

## **Reference:**

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