Reviewer #1

General comments:

This paper describes a new technique of online measurements of cycloalkanes in the atmosphere by means of NO^+ chemical ionization mass spectrometry. The authors used major product ions of $C_nH_{2n-1}^+$ and $C_nH_{2n-3}^+$ from NO^+ chemical ionization of cyclic and bicyclic alkanes, respectively, for the measurement. After characterizing this technique in the laboratory, this technique was applied for field measurements at an urban site in southern China and a chassis dynamometer study regarding vehicle emissions. I think that this paper is generally well-written. However, I can't avoid a sense of apprehension because the authors showed the results of C10-C20 cyclic and bicyclic alkanes based on mass spectra of only five C7 and C12 cycloalkanes. The authors should show, for example, each mass spectrum of C10-C20 cycloalkanes (e. g., n-alkylcyclohexane) and discuss about interferences of other species on the ion signals of the cycloalkanes before applying the technique to the filed measurements and the chassis dynamometer study. I think that the characterizations shown in this paper are not enough. In addition, I am not sure that there is no interference on the data obtained in the filed measurements and in the chassis dynamometer study. Therefore, I recommend this paper to be revised referring to my specific comments listed below.

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

In this study, we demonstrate that cyclic alkanes could be measured using the NO^+ chemical ionization via hydride ion transfer leading to M-H product ions. The major M-H ions are determined using commercially available chemicals including C_7, C_{12}, and C_{15} cyclic alkanes and C_{12} bicyclic alkanes (Table 1). These results are also complemented by the five different alkyl-cyclohexanes (C_{10}-C_{14}) in the cylinder gas standard (Table S1). It should be noted that these compounds are the only commercially available chemicals we can obtain. Though the number is limited, these compounds cover different types of cyclic alkanes, including alkyl-substituted cyclohexanes, cyclic compounds with more than 6 atom rings and also bicyclic compound. For example, we dedicatedly select all of the three types of cyclic alkanes with 12 carbons. Based on the

determined mass spectra of these cyclic alkanes, we can observe that the major product ions for all of these cyclic alkanes are M-H ions. As the result, we are convinced that other cyclic alkanes should follow the same reaction pathway with NO^+ yielding major product ions of M-H ions. To make this clear, we added the ionization results of C_{15} cycloalkanes (cyclopentadecane and nonylcyclohexane) and C_{10}-C_{14} alkyl-cyclohexanes in the revised manuscript, as shown in Fig. S5 and Fig. S6.

Fig. S5 shows mass spectra within the relevant range (*m/z* 90^+ to 240^+ Th) for C_{15} cycloalkanes. Similar with C_7 and C_{12} cycloalkanes, the product ions generated by cyclopentadecane and nonylcyclohexane ($C_{15}H_{30}$) under NO^+ ionization mainly appear at *m/z* 209 Th, corresponding to $C_{15}H_{29}^+$, but with more fragmentation ions. These results further verify that reactions of cycloalkanes with NO^+ ions follow the hydride ion transfer pathway to yield M-H product ions. Fig. S6 shows mass spectra within the relevant range (*m/z* 130^+ to 200^+ Th) for C_{10}-C_{14} alkyl-cyclohexanes during the calibration experiments. As shown in figure, five types of cycloalkanes produced regular mass spectrum peaks under NO^+ ionization, which appeared at *m/z* 139 Th, *m/z* 153 Th, *m/z* 167 Th, *m/z* 181 Th, and *m/z* 195 Th, corresponding to $C_{10}H_{19}^+$, $C_{11}H_{21}^+$, $C_{12}H_{23}^+$, $C_{13}H_{25}^+$, and $C_{14}H_{27}^+$, respectively.

As for impurities, isotope, and other potential interference, we re-checked the data and evaluated these interferences. Please find the response to individual comments from the reviewer below.

The sentence in the Section 3.1 (line 195-198) is modified to:

The product ions generated by cyclopentadecane and nonylcyclohexane ($C_{15}H_{30}$) mainly appear at *m/z* 209 Th, corresponding to $C_{15}H_{29}^+$, with slightly more fragmentation than C_{12} cyclic alkanes (Fig. S5).

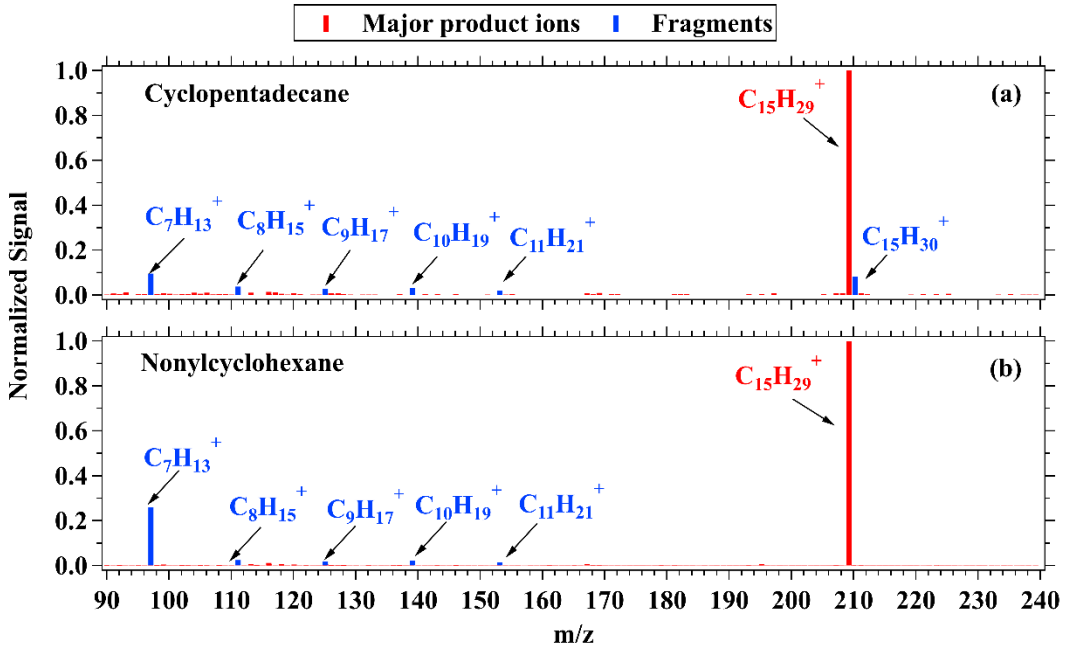

Figure S5. Mass spectra of product ions from cyclopentadecane (a), and nonylcyclohexane (b) in NO^+ PTR-ToF-MS. The major product ions are shown in red, and the fragments are shown in blue.

The sentence in the Section 3.1 (line 200-202) is modified to:

For instance, the mass spectra for C_{10}-C_{14} alkyl-cyclohexanes during the calibration experiments are shown in Fig. S6, with the same $C_nH_{2n-1}^+$ as the major product ions.

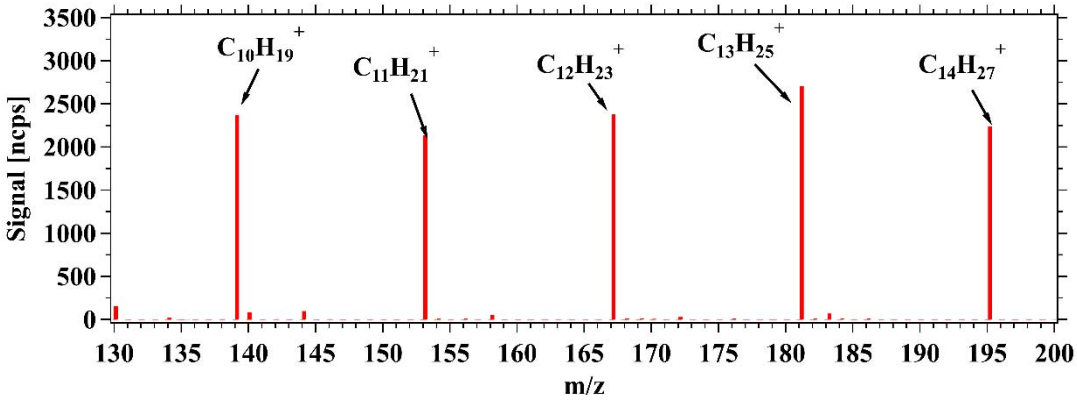

Figure S6. Mass spectra of product ions from C_{10}-C_{14} alkyl-cyclohexanes in NO^+ PTR-ToF-MS during the calibration experiment.

Specific comments:

(1) Page 5, Line 123: I would like to know ion intensities of O_2^+ and NO_2^+ relative to that of NO^+ in a flow of zero (VOC-free) -air. I guess that the O_2^+ was consumed by

reactions of VOCs in a sample air. The authors should evaluate the interference of the O_2^+ *reactions on the signals of cycloalkanes.*

Reply: We thank the reviewer for the comment. As 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^+ to NO^+, and found that the 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.

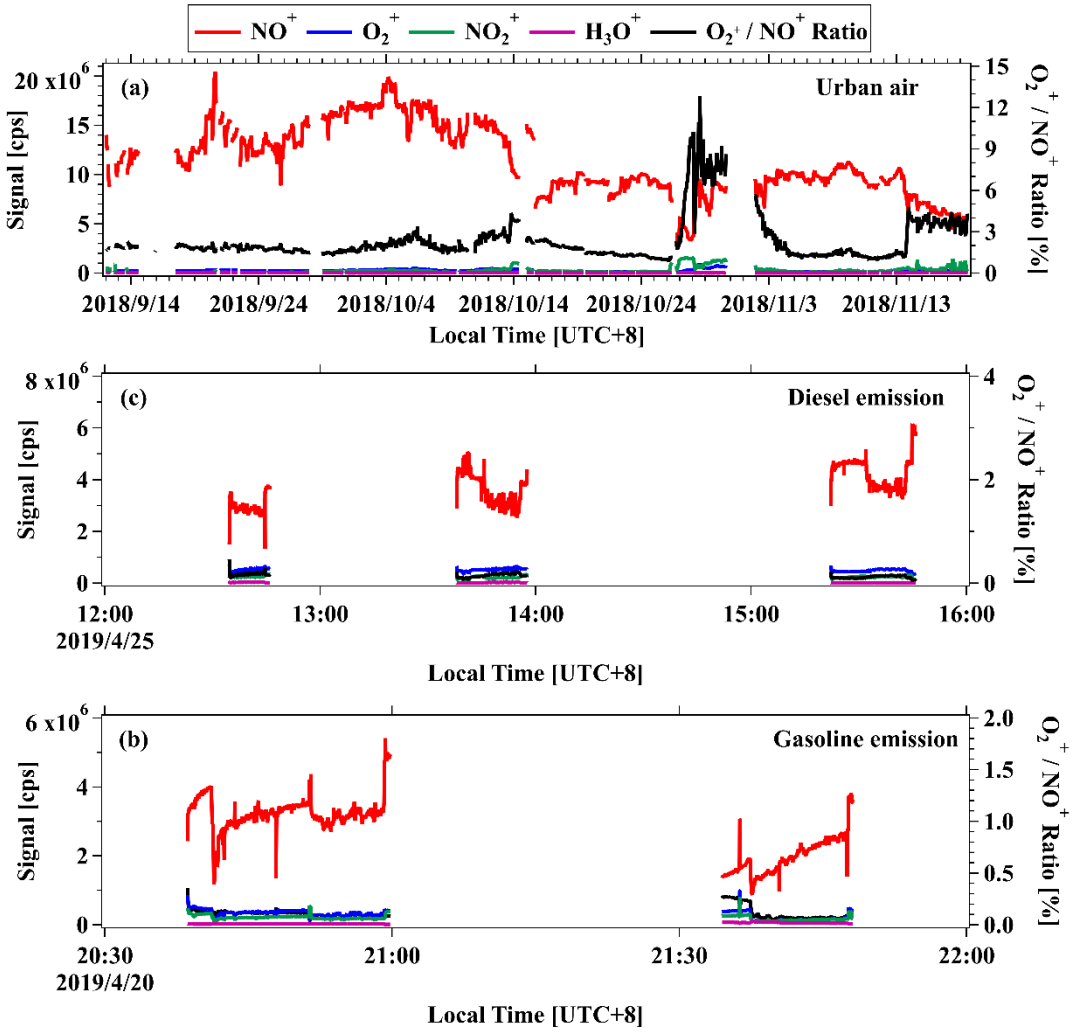

Figure S2. Time series of NO^+, O_2^+, NO_2^+, and H_3O^+ during the measurements of urban air (a), and vehicular emissions (b-c).

(2) Page 6, Line 125: I would like to know ion signals at 166.18 Th ($C_{12}H_{22+}$) in Fig. S2. If there is a signal at 166.18 Th ($C_{12}H_{22+}$), its isotopologue, $^{13}CC_{11}H_{22+}$ (166.175 Th), can be interfered on the signals of $C_{12}H_{23+}$ (168.18 Th). Did the authors check such the interference of isotopologues on ion signals of C10-C20 cycloalkenes obtained in the filed measurements and in the chassis dynamometer study?

Reply: We thank the reviewer for the comment. We re-examined the high-resolution peak fitting process for the data of urban air and the chassis dynamometer study, confirming that such isotopes would not interfere with the measurements of cycloalkanes in NO^+ PTR-ToF-MS.

During the high-resolution peak fitting, the signals contributed by ion isotopes have been calculated according to the proportional relationship between the ions and their isotopes in atmosphere (Stark et al., 2015;Timonen et al., 2016). As the result, the signals of cycloalkanes used for quantification is basically not affected by the contributions of isotopes from other ions. We added the isotopes corresponding to the identified mass spectrum peaks in Fig. S3. We also show the normalized signals of $C_{12}H_{23}^+$ and $^{13}CC_{11}H_{22}^+$ during the measurements of urban air in Fig. R1. The intensities of $^{13}CC_{11}H_{22}^+$ are significantly lower than $C_{12}H_{23}^+$, which further proved that the interference of isotopes to the measurements of cycloalkanes are little.

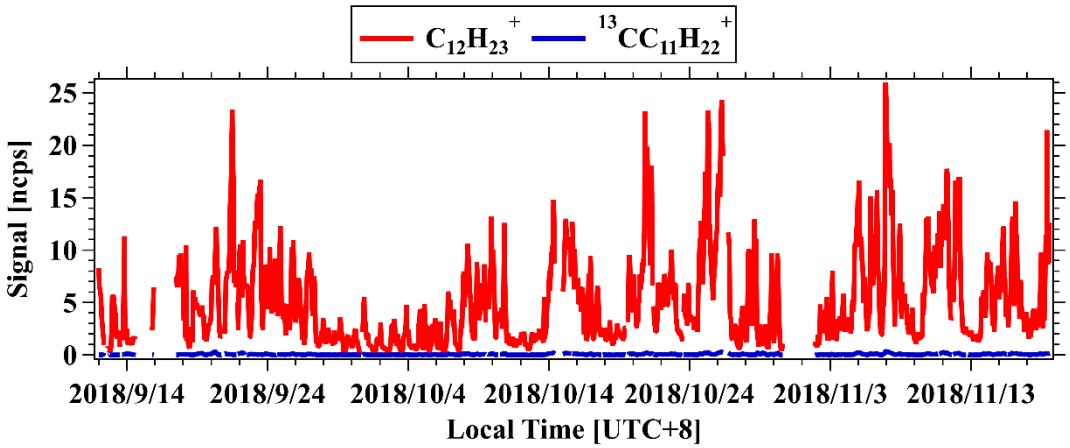

Figure. R1 Time series of $C_{12}H_{23}^+$ and $^{13}CC_{11}H_{22}^+$ during the measurement of urban air.

The sentence in the Section 2.1 (line 136-140) is modified to:

The signal of cycloalkanes used for quantification has been subtracted from the contribution of isotopes from other ions and other species such as unsaturated aldehydes that share the identical formula at the unit mass resolution (UMR) with cycloalkanes during the high-resolution peak fitting process.

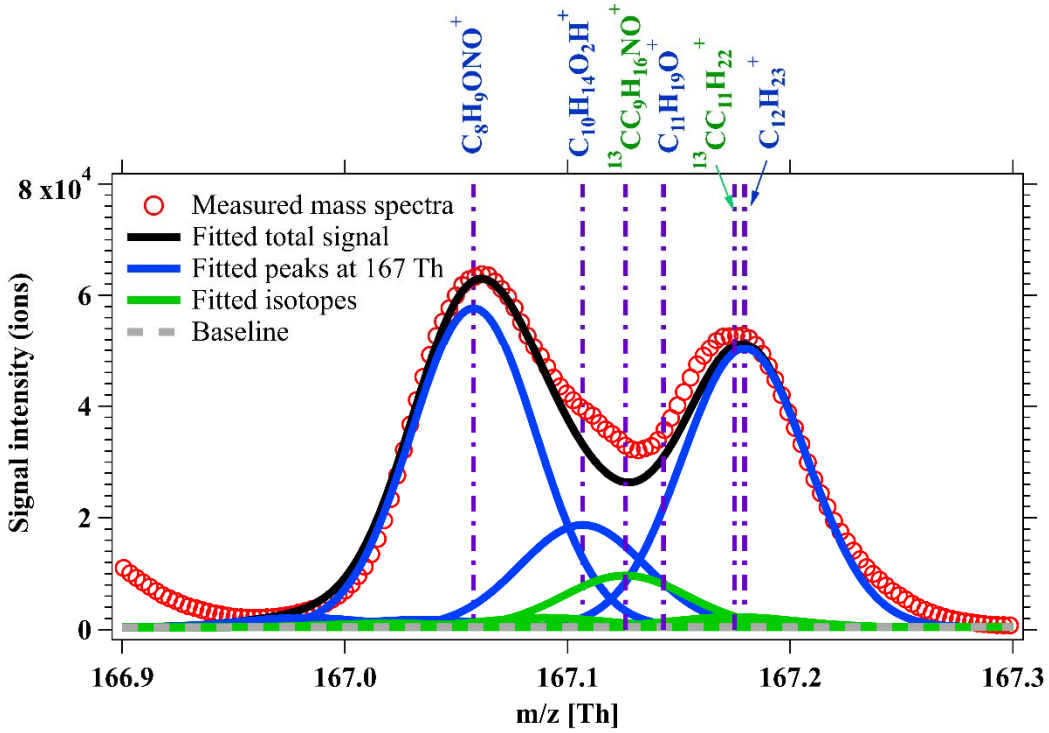

Figure S3. High-resolution peak fitting to the averaged mass spectra on a typical day (6 October 2018) for *m/z* 167 to individual ion peaks of C_{12} cycloalkanes ($C_{12}H_{23}^+$), other isomeric ions ($C_8H_9ONO^+$, $C_{10}H_{14}O_2H^+$, and $C_{11}H_{19}O^+$), and isotopes of other ion ($^{13}CC_9H_{16}NO^+$ and $^{13}CC_{11}H_{22}^+$) detected from NO^+ PTR-ToF-MS.

(3) Page 7, Line 169−Page 8, Line 192: I would like to see each mass spectrum of C10-C20 cycloalkanes (for example, n-alkylcyclohexane) and fractions of (m-1) for the cycloalkanes, like n-alkanes in Wang et al. (2020). According to Wang et al, (2020), it was reported that the fraction was relatively small for C8-C11 n-alkanes. I wonder if octylcyclohexane (C14), for example, produce strong fragment ions, leading to the interference on smaller cycloalkanes or not.

Reply: We thank the reviewer for the comment. In this study, we demonstrate that cyclic alkanes could be measured using the NO^+ chemical ionization via hydride ion transfer leading to M-H product ions. The major M-H ions are determined using commercially available chemicals including C_7, C_{12}, and C_{15} cyclic alkanes and C_{12} bicyclic alkanes (Table 1). These results are also complemented by the five different

alkyl-cyclohexanes (C_{10}-C_{14}) in the cylinder gas standard (Table S1). It should be noted that these compounds are the only commercially available chemicals we can obtain. Though the number is limited, these compounds cover different structures of cyclic alkanes, including alkyl-substituted cyclohexanes, cyclic compounds with more than 6 atom rings and also bicyclic compound. For example, we dedicatedly select all of the three types of cyclic alkanes with 12 carbons. Based on the determined mass spectra of these cyclic alkanes, we can observe that the major product ions for all of these cyclic alkanes are M-H ions. As the result, we are convinced that other cyclic alkanes should follow the same reaction pathway with NO^+ yielding major product ions of M-H ions.

We summarized the fractions of M-H ions produced by high-purity cycloalkanes species including C_7, C_{12}, and C_{15} cyclic alkanes and C_{12} bicyclic alkanes under the NO^+ ionization, as shown in Fig. S7. We observe that M-H ions account for ~100% of total ion signals for C_7 cyclic alkanes and lower but comparable fractions (74-82%) for C_{12} and C_{15} cyclic alkanes.

The sentences in the Section 3.1 (line 204-210) are modified to:

The fractions of M-H ions generated by high-purity cycloalkanes species including C_7, C_{12}, and C_{15} cyclic alkanes and C_{12} bicyclic alkanes are summarized in Fig. S7. We observe that M-H ions account for ~100% of total ion signals for C7 cyclic alkanes and lower but comparable fractions (74-82%) for C12 and C15 cyclic alkanes. These results verify that reactions of cyclic and bicyclic alkanes with NO^+ ions follow the hydride ion transfer pathway to yield $C_nH_{2n-1}^+$ and $C_nH_{2n-3}^+$ product ions, respectively.

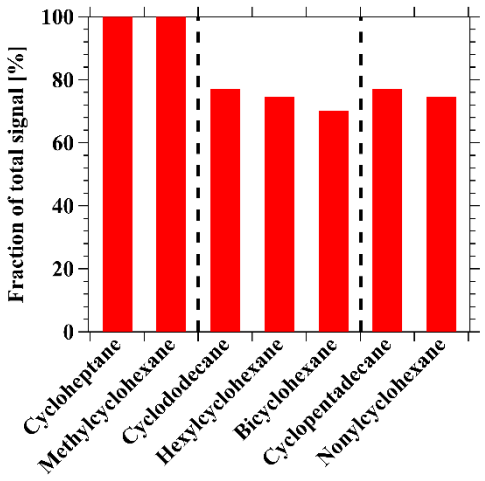

Figure S7. The fractions of product ions (M-H) from hydride abstraction of C_7, C_{12}, and C_{15} cyclic alkanes and C_{12} bicyclic alkanes in NO^+ PTR-ToF-MS.

(4) Page 8, Line 193−Page 8, Line 209: Since 2-alkenes produce C_nH_{2n+} in addition to C_nH_{2n-1+} by NO_+ ionization (Diskin et al., 2002), check ion signals of C_nH_{2n+} in the filed measurements and in the chassis dynamometer study. If there are signals, the authors should evaluate the interference.

Reply: We thank the reviewer for the comment. We calculated and compared the signals of $C_nH_{2n}^+$ and $C_nH_{2n-1}^+$ in laboratory calibration experiments, urban air measurements and chassis dynamometer study (Fig. S8). The ratios of $C_nH_{2n}^+$ to $C_nH_{2n-1}^+$ signals of pure cyclic alkanes during the laboratory experiments maintained at 2-6%, similar to the ratios measured in filed measurements (3-7%). The ratios of $C_nH_{2n}^+$ to $C_nH_{2n-1}^+$ signals for vehicular emissions maintained at 6-16% for C_{10}-C_{14} ions, which is slightly higher than those determined from cyclic alkanes, whereas the ratios for C_{15}-C_{20} ions are comparable with pure cyclic alkanes (4-8%). Based on the results in Diskin et al. (2002), 2-alkenes produce 40-45% of $C_nH_{2n-1}^+$ and 55-60% of $C_nH_{2n}^+$ ions from NO^+ ionization. If we attribute all of the differences to potential interferences from 2-alkenes and assume the same quantities of $C_nH_{2n-1}^+$ and $C_nH_{2n}^+$ ions from NO^+ ionization from 2-alkenes, the interferences from alkenes should be in the range of 1-2% for urban air measurements and 2-12% for measurements of vehicular emissions. It should be noted that these number are upper limits, as 1-alkene may dominate the

$C_nH_{2n}^+$ ions and the signals from 2-alkenes may be significantly lower. This analysis further confirms that the interferences from alkenes to cyclic alkane measurements are minor.

The sentences in the Section 3.1 (line 233-245) are modified to:

We further compare the signals of $C_nH_{2n}^+$ and $C_nH_{2n-1}^+$ from calibration experiments, urban air measurements and chassis dynamometer study (Fig. S8). The typical ratios of $C_nH_{2n}^+/C_nH_{2n-1}^+$ for cyclic alkanes are in the range of 2-6%, with similar ratios determined from urban air measurements (3-7%). The ratios of $C_nH_{2n}^+$ to $C_nH_{2n-1}^+$ from vehicular emissions maintained at 6-16% for C_{10}-C_{14} ions, which is a little bit higher than those determined from cyclic alkanes, while the ratios of C_{15}-C_{20} ions are comparable with pure cyclic alkanes (4-8%). Even though all of these differences are attributed to potential interferences from 2-alkenes and assume the same quantity of $C_nH_{2n-1}^+$ and $C_nH_{2n}^+$ ions from NO^+ ionization from 2-alkenes, the upper limits of the interferences from alkenes should be in the range of 1-2% for urban air measurements and 2-12% for measurements of vehicular emissions. Therefore, we conclude that the interferences from alkenes to cyclic alkanes measurements of cycloalkanes in most environments are minor.

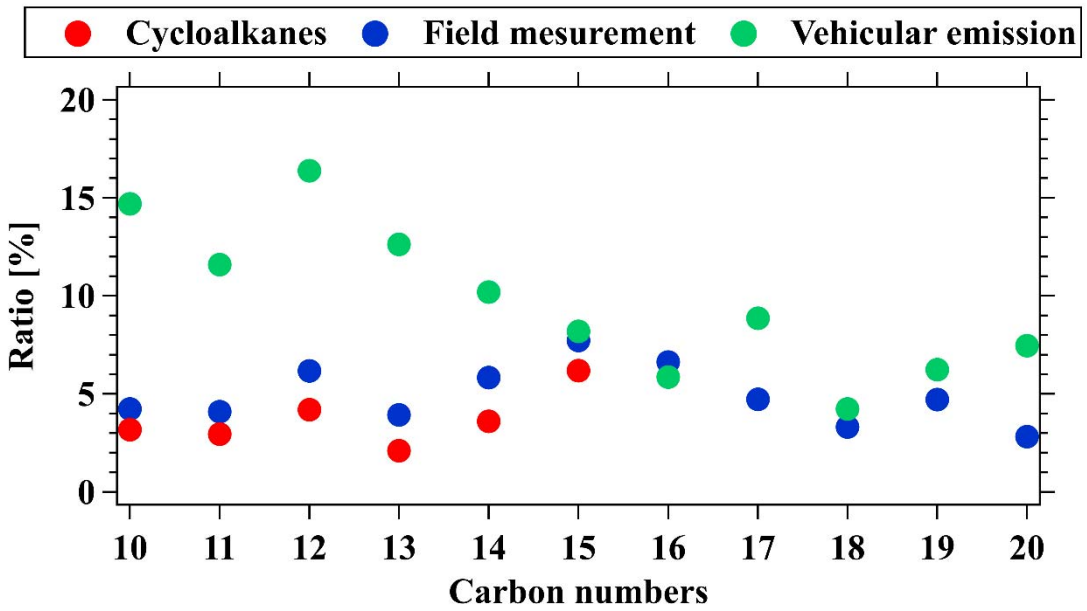

Figure S8. The ratio of $C_nH_{2n}^+$ to $C_nH_{2n-1}^+$ from cycloalkanes (red), filed

measurement (blue) and vehicular emissions (green) measured by NO^+ PTR-ToF-MS.

Reference:

Stark, H., Yatavelli, R. L. N., Thompson, S. L., Kimmel, J. R., Cubison, M. J., Chhabra, P. S., Canagaratna, M. R., Jayne, J. T., Worsnop, D. R., and Jimenez, J. L.: Methods to extract molecular and bulk chemical information from series of complex mass spectra with limited mass resolution, International Journal of Mass Spectrometry, 389, 26-38, 10.1016/j.ijms.2015.08.011, 2015.

Timonen, H., Cubison, M., Aurela, M., Brus, D., Lihavainen, H., Hillamo, R., Canagaratna, M., Nekat, B., Weller, R., Worsnop, D., and Saarikoski, S.: Applications and limitations of constrained high-resolution peak fitting on low resolving power mass spectra from the ToF-ACSM, Atmospheric Measurement Techniques, 9, 3263-3281, 10.5194/amt-9-3263-2016, 2016.