Evidence of ketene emissions from petrochemical industries and implications for ozone production potential

Chinmoy Sarkar et al. (acp-2020-1103)

We would like to thank Prof. Wisthaler and both the referees for the interactive comments/suggestions on the manuscript. The comments from the referees are in black and our responses are in blue. The texts that have been added to the manuscript are in **bold blue**. We have also included Sanjeevi Nagalingam and Nicole Jenna Gross as co-authors in the revised manuscript who helped us to carry out laboratory experiments.

Interactive comment from Prof. Armin Wisthaler:

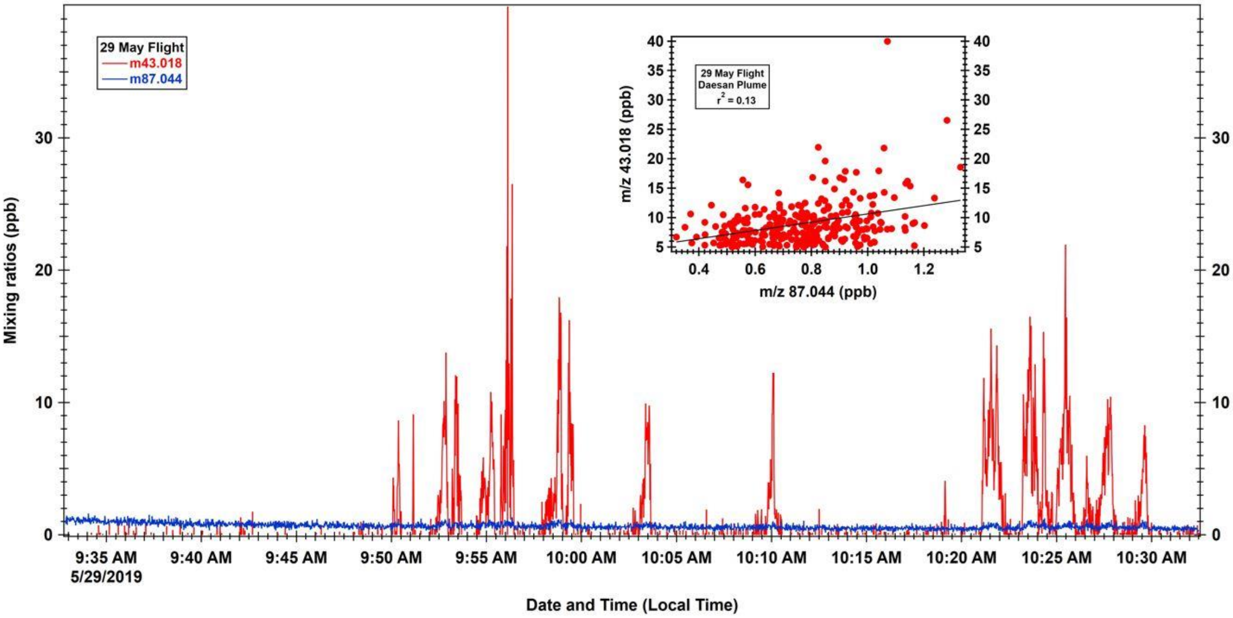
I am posting a quick comment for saving some time to the reviewers.

I think the assignment of the m/z 43.018 (CH_3CO^+) signal to ketene is incorrect. We flew our PTR-TOF-MS instrument on the NASA DC-8 during KORUS-AQ, and we also observed a high m/z 43.018 signal over the Daesan petrochemical complex. The signal was highly correlated with the m/z 87.044 ($C_4H_7O_2^+$) signal and a laboratory study confirmed that the signal ratio was the same as for vinyl acetate. Vinyl acetate produces a strong acetylium ion fragment upon protonation in the PTR-MS analyzers, especially under the PTR-MS operating conditions (high E/N) the authors were using. Vinyl acetate is expected to be emitted from the ethylene vinyl acetate (EVA) plants at Daesan.

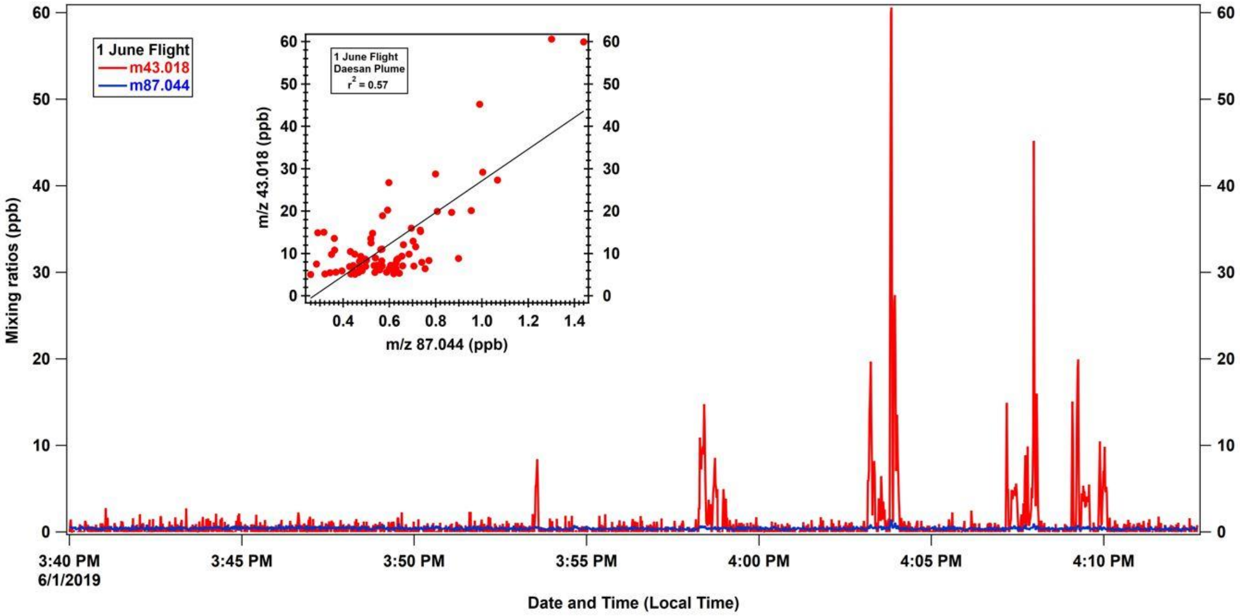
Thank you for pointing out the possible contribution of vinyl acetate (m/z 87.044) to the m/z 43.018 signal using PTR-TOF-MS.

We have not observed any high peaks similar to the m/z 43.018 (attributed to ketene) in the timeseries of m87.044 signal. Following figures show the timeseries of m/z 87.044 and m/z 43.018 (ketene) and their correlation plots for the plume episodes (in the inset) during all the flights.

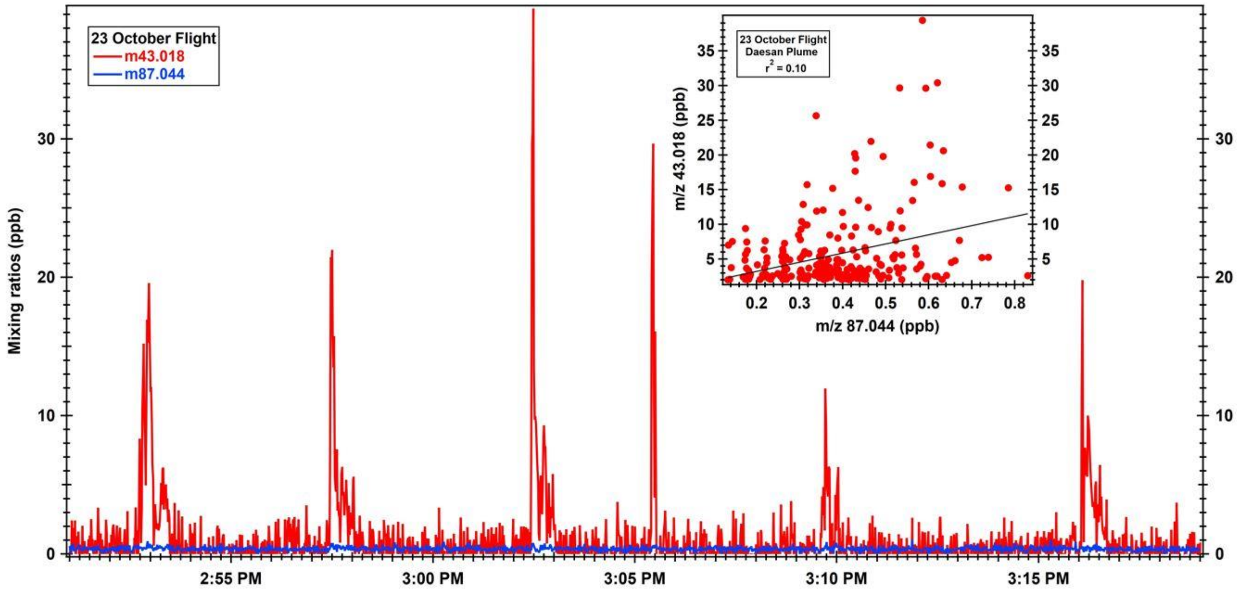
29 May Morning Flight:



1 June Afternoon Flight:



23 October Afternoon Flight:



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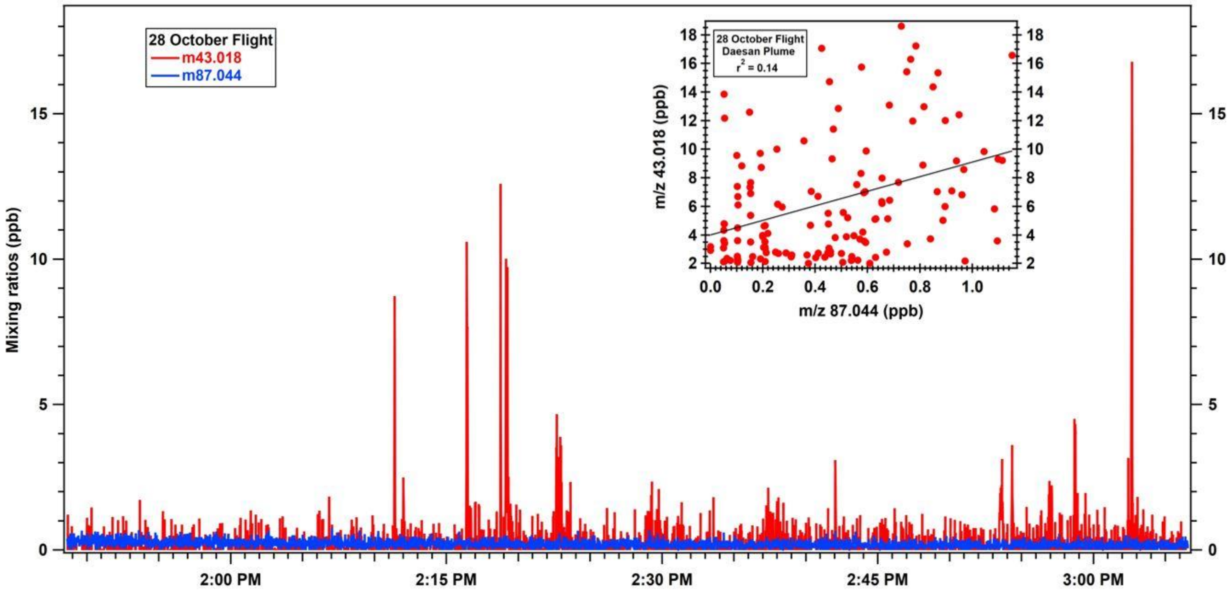

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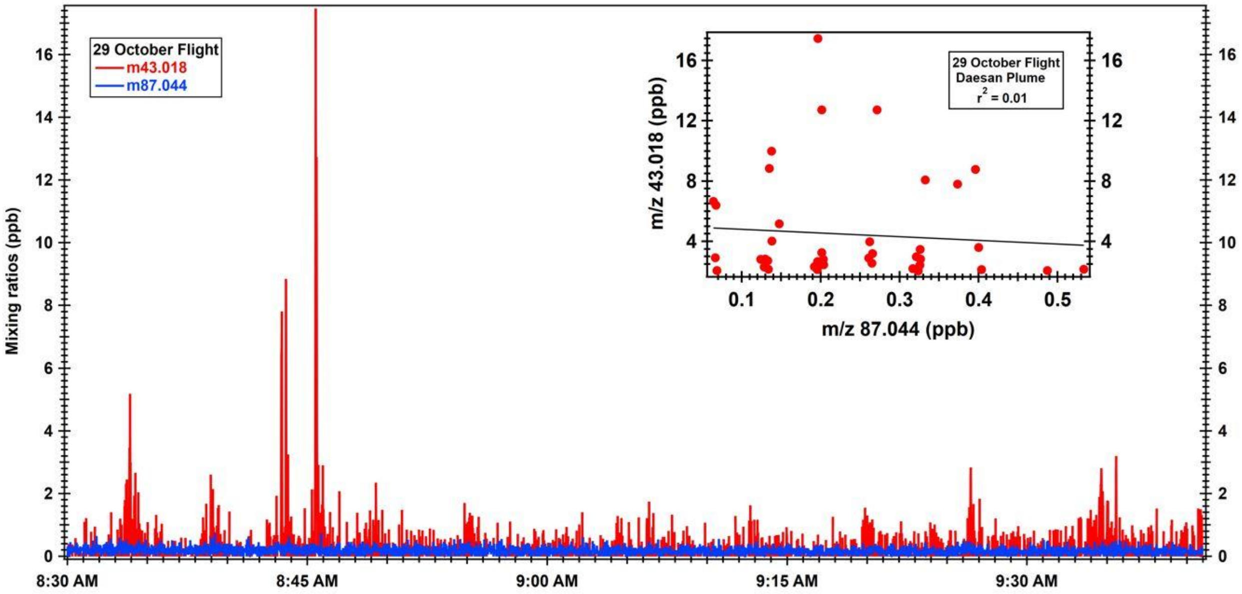

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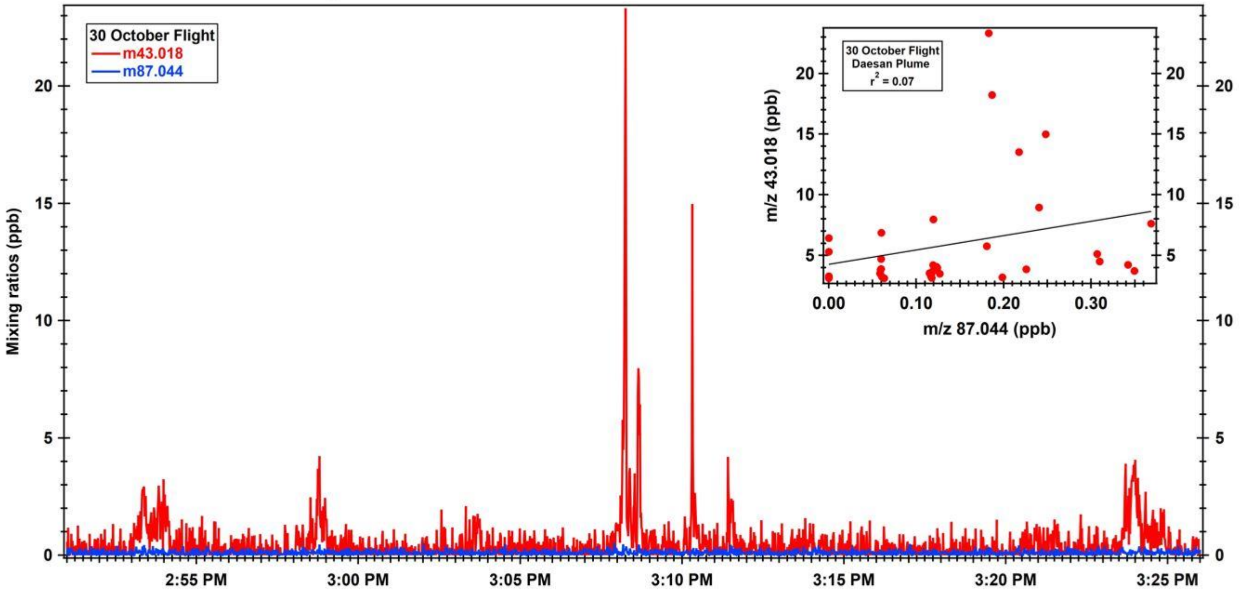

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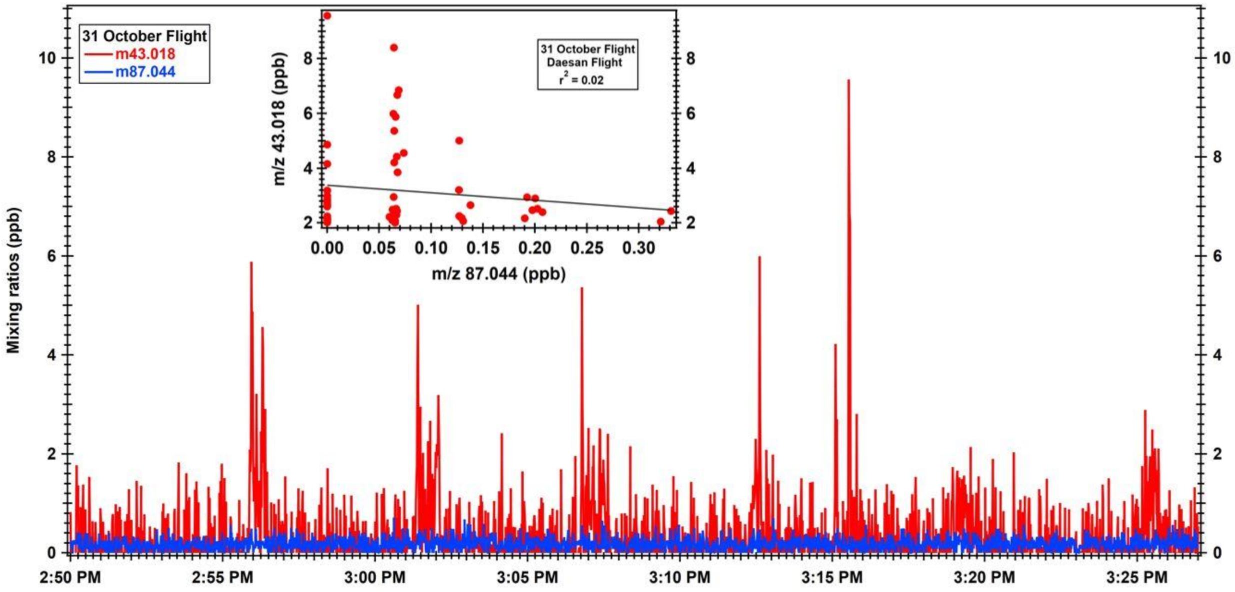
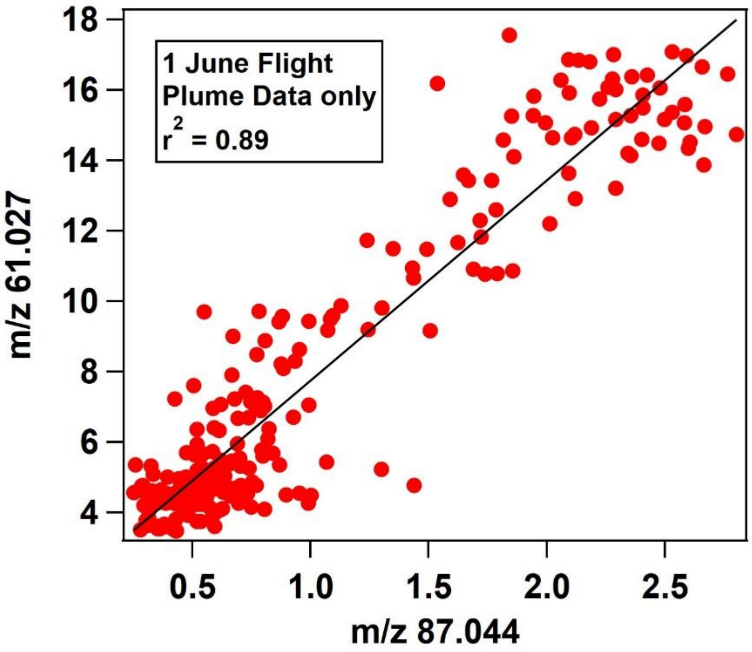


As we can see from the timeseries plots during all the flights, m/z 87.044 did not show any high peaks that we observed in the case of m/z 43.018 (attributed to ketene). In addition, no significant correlations were observed (Figures in the inset) between m/z 43.018 and m/z 87.044 when data corresponding to the plume episodes were utilized. This indicates that high peaks of m/z 43.018 cannot be attributed to the fragmentation of m/z 87.044 and the signal at m/z 43.018 had a different source.

During the plume episodes at Daesan, the concentrations of vinyl acetate (m/z 87.044), which is an acetate ester, showed excellent correlations with the concentrations of m/z 61.027 (acetic acid

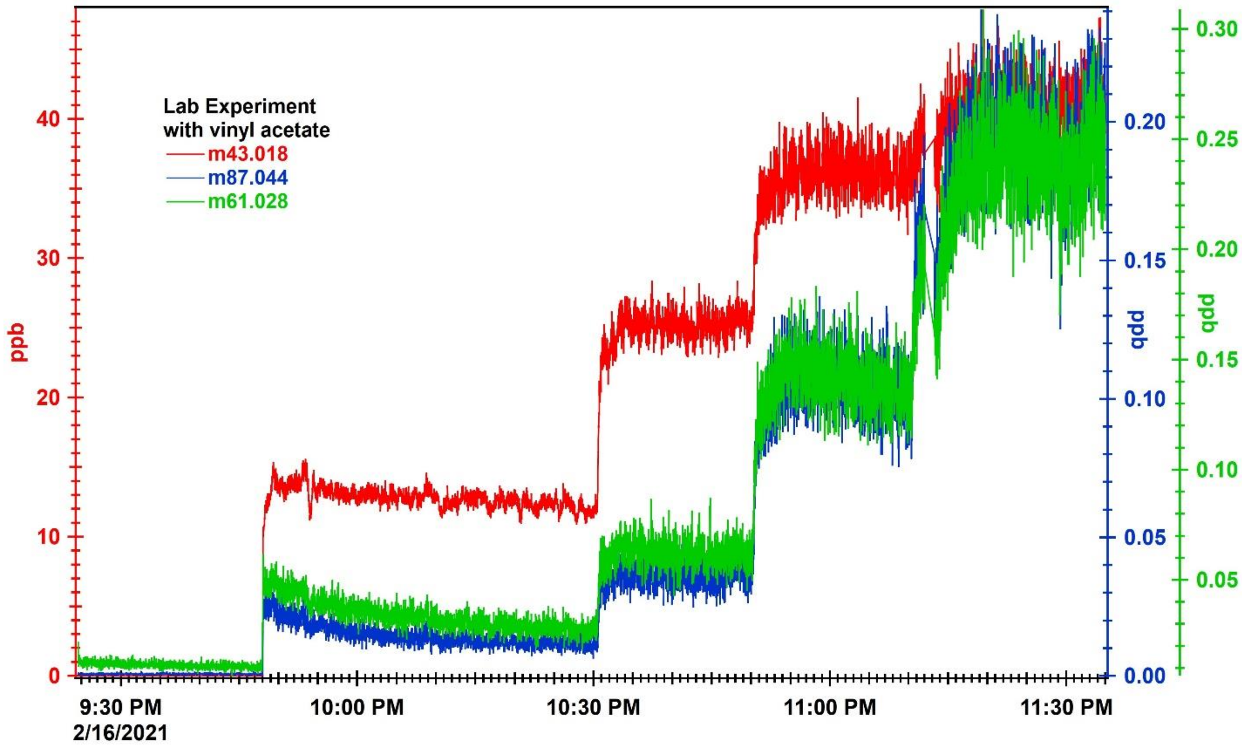
and glycolaldehyde, as mentioned in the original manuscript; P5 L66-67) as shown in the following figure. The excellent correlation (r^2 ~ 0.9) between m/z 87.044 and m/z 61.027 for the plume episodes during 1 June flight indicates that vinyl acetate and acetic acid had similar sources in Daesan. We have already corrected the ketene signal at m/z 43.018 for the contribution of acetic acid and glycolaldehyde which is mentioned in the original manuscript (P6, L177-178).

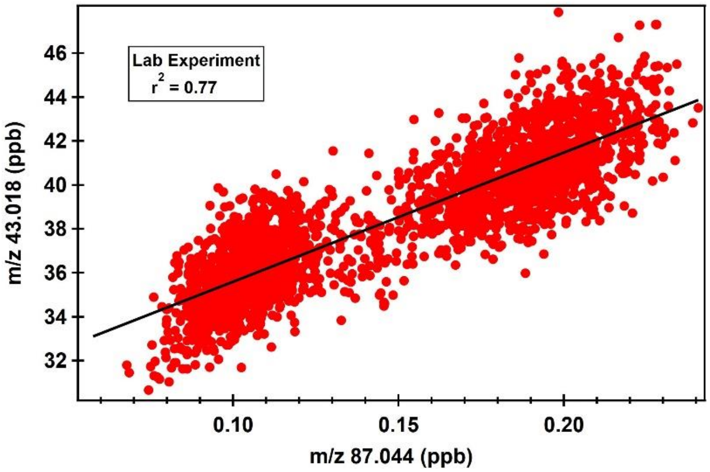


This further indicates that m/z 43.018 (ketene) has a direct emission source at Daesan and it does not originate from the fragmentation of vinyl acetate (m/z 87.044) within the PTR-TOF-MS.

Lab Experiments with vinyl acetate:

We have also carried out laboratory experiments by introducing different known concentrations of vinyl acetate standard into the PTR-TOF-MS (PTR-TOF1000) and observed that the signals at m/z 87.044 (vinyl acetate) correlates strongly with m/z 43.018 (acylium ion) as well as m/z 61.028 (acetic acid and glycolaldehyde). The timeseries of the experiment and the correlation plot (r^2 for the correlation ~ 0.77) between m/z 43.018 and m/z 87.044 are shown in the figures bellow. We have purposefully selected the data for higher concentration steps for the correlation analysis to be consistent with the high concentrations of m/z 43.018 that we measured in the field. This observation is similar to the laboratory observation mentioned by Prof. Wisthaler. If the m/z 43.018 signals were originated from the fragmentation of m/z 87.044, we would have observed similar correlations during our airborne measurements over Daesan. However, since we have not observed any such correlation in our field observations (as shown earlier), we believe the signal at m/z 43.018 does not originate from the fragmentation of vinyl acetate.

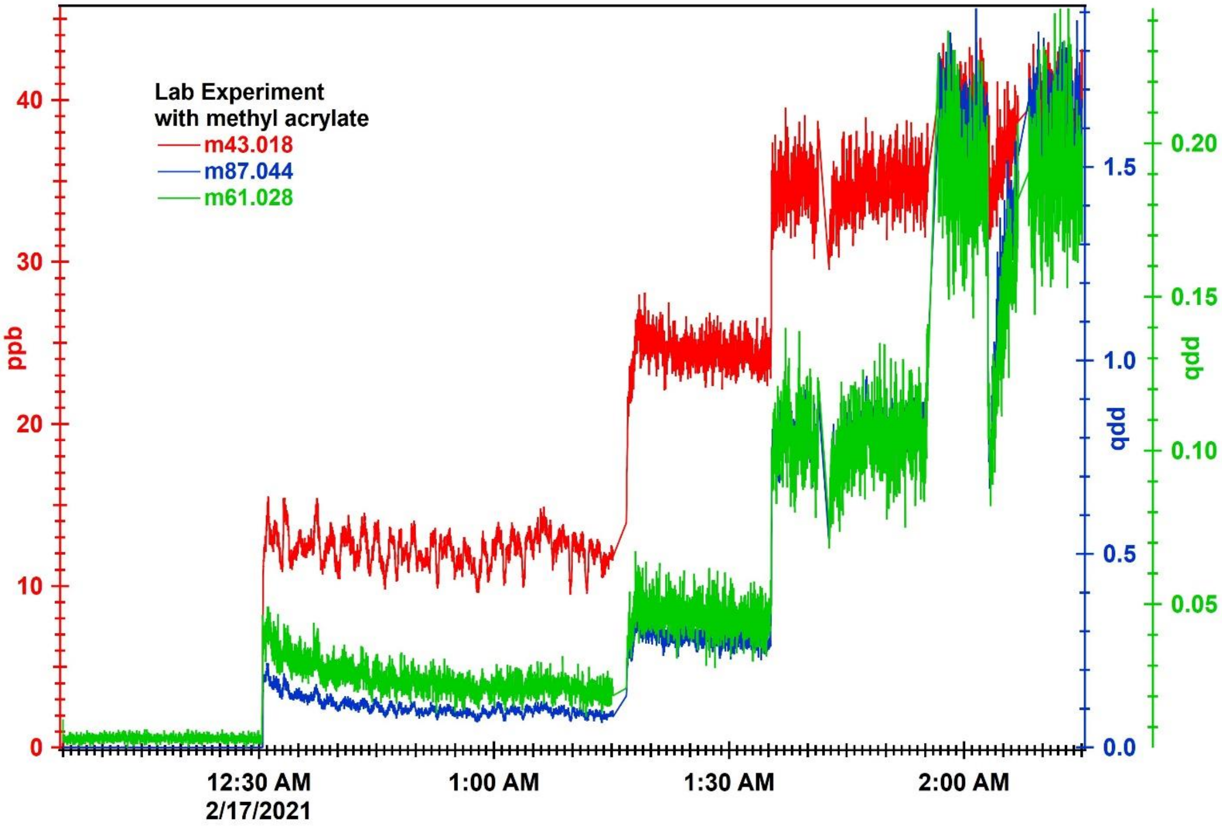


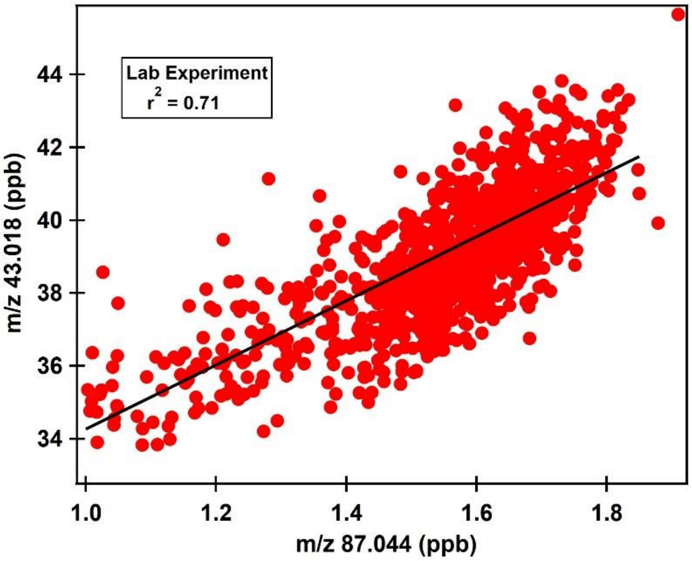


Lab Experiments with other possible contributing VOCs:

Previous studies have reported that m/z 87.044 signal can also be due to VOCs like 2,3-butadione and methyl acrylate (Müller et al., 2016;Koss et al., 2018). These compounds are reported to be emitted from incomplete combustion/biomass burning sources. We have carried out lab experiments with 2,3-butanedione and methyl acrylate standards to observe whether we observe any changes in the signal at m/z 43.018 when we introduce these two standards. We observed the similar response like vinyl acetate when we introduced different concentrations of these two standards into the PTR-TOF1000 (figures for the methyl acrylate experiment is shown below).

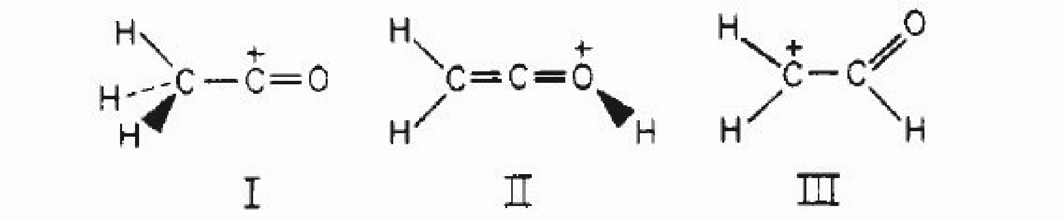
The strong correlations (e. g. $r^2 = 0.71$ for methyl acrylate) clearly indicate that 2,3-butanedione and methyl acrylate are also not contributing to the m/z 43.018 signals at Daesan.





Detection of ketene using PTR-TOF-MS:

Ketene has a proton affinity of 196 kCal/mol which is much higher than that of water (166 kCal/mol) and therefore, it is possible to detect protonated ketene using PTR-TOF-MS. The direct protonation of ketene can result in three different structural conformations and the most stable structure of protonated ketene is the acylium ion (Vogt et al., 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005) which is detected at m/z 43.018 using PTR-TOF-MS. The following are the three different possible conformations upon protonation of ketene and acylium ion (I) is the most stable structure as reported by several previous studies (Yarkony and Schaefer, 1975;Vogt et al., 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005).



Fragmentation of m/z 87.044 can also result in the formation of acylium ion at m/z 43.018 as we observed during our lab experiments and also mentioned by Prof. Wisthaler. However, during our field observations, we have not observed any correlation between m/z 43.018 and m/z 87.044 when we used the data for the plume episodes. Therefore, even we have detected the same acylium ion (at m/z 43.018) that can be formed from direct protonation of ketene as well as fragmentation of vinyl acetate, our results suggest that the origin of the acylium ion detected during our field campaign is the protonation of directly emitted ketene and not the fragmentation of vinyl acetate.

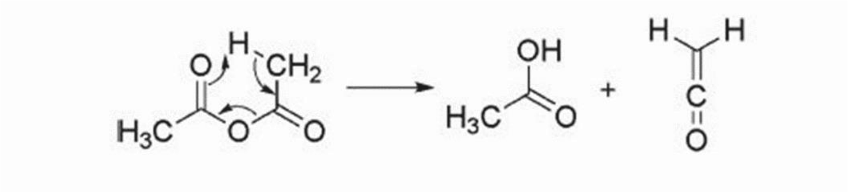
We have now added the following paragraph in the revised manuscript (P6 L180-202):

"Fragmentation of vinyl acetate (detected at m/z 87.044) could also potentially contribute to the signal at m/z 43.018. However, during our airborne measurements, m/z 87.044 did not show any high peaks that we observed in m/z 43.018 (attributed to ketene). In addition, no significant correlations were observed between m/z 43.018 and m/z 87.044 when data corresponding to the plume episodes were utilized. The signal-to-noise (S/N) ratio for m43.018 and m87.044 were 6 ppt and 2 ppt, respectively which indicates that the instrument sensitivity was good enough to observe the linearity between m43.018 and m87.044. This indicates that high peaks of m/z 43.018 cannot be attributed to the fragmentation of m/z 87.044 and the signal at m/z 43.018 had a different source. Previous studies have reported that m/z 87.044 signal can also be due to VOCs like 2,3-butadione and methyl acrylate (Müller et al., 2016;Koss et al., 2018). These compounds are reported to be emitted from incomplete combustion/biomass burning sources. We have carried out laboratory experiments with these two VOC standards and found that similar to vinyl acetate, these two VOCs were unlikely to be contributing to the m/z 43.018 peaks observed during our airborne measurements over Daesan. Ketene has a proton affinity of 196 kCal/mol which is much higher than that of water (166 kCal/mol) and therefore, it is possible to detect protonated

ketene using PTR-TOF-MS. The direct protonation of ketene can result in three different structural conformations and the most stable structure of protonated ketene is the acylium ion (Vogt et al., 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005) which is detected at m/z 43.018 using PTR-TOF-MS. Therefore, even we have detected the same acylium ion (at m/z 43.018) that can be formed from direct protonation of ketene as well as fragmentation of vinyl acetate/methyl acrylate/2,3-butanedione, our results suggest that the origin of the acylium ion detected during our field campaign is the protonation of directly emitted ketene and not the fragmentation of vinyl acetate."

Potential sources of ketene in the atmosphere:

Pyrolysis of acetic anhydride was reported to be a potential source of ketene in the atmosphere and follows the chemical mechanism shown below (Atkinson et al., 2016):



Louie et al. (2015) previously reported that pyrolysis of cellulose and lignins, which are the principal components of plants, produces various organic compounds, which, upon further pyrolysis, generate ketene as a major byproduct. Pyrolysis of acetone can also produce ketene (Brown et al., 1989) while Kahan et al. (2013) reported that pyrolysis of furan at 295 K could also be a potential source of ketene.

We have now added the following sentence in the revised manuscript (P2 L59-60):

"Pyrolysis of acetic anhydride is also reported to be a potential source of ketene in the atmosphere (Atkinson et al., 2016)."

Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to ketene, the possibility of the contribution from vinyl acetate cannot be ruled out completely and therefore, further studies focusing on this aspect needs to be carried out. Since the rate coefficient of vinyl acetate with OH radical is 2.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate was found to be ~ 20-25% less than that of ketene. Following table shows a comparison of the estimated OH reactivity and O_3 production potential for both ketene (already shown in Table 2b of the original manuscript) and vinyl acetate:

Research Flights	OH reactivity (s^{-1})*		O_3 production potential (ppb h^{-1})*	
	Ketene	Vinyl acetate	Ketene	Vinyl acetate
29 May	5.42 (33.76)	4.01 (24.96)	4.84 (30.10)	3.58 (22.28)

1 June	7.75 (51.24)	5.73 (37.88)	6.91 (45.70)	5.11 (33.82)
23 October	7.35 (33.33)	5.44 (24.64)	6.56 (29.80)	4.85 (22.00)
28 October	5.28 (15.74)	3.90 (11.64)	4.71 (14.00)	3.48 (10.39)
29 October	3.79 (14.77)	2.80 (10.92)	3.38 (13.20)	2.50 (9.75)
30 October	3.33 (19.71)	2.47 (14.57)	2.98 (17.60)	2.20 (13.01)
31 October	4.56 (8.09)	3.37 (5.98)	4.07 (7.22)	3.01 (5.34)

***** values in the parenthesis corresponds to the maximum OH reactivity and O_3 production potential, respectively.

We have included the following sentences as a short paragraph in the Conclusions section (P11-12 L382-389 of the revised manuscript):

"Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to ketene, the possibility of the contribution from vinyl acetate cannot be ruled out completely and therefore, further studies focusing on this aspect needs to be carried out. Since the rate coefficient of vinyl acetate with OH radical is 2.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate can be ~ 20-25% less than that of ketene. Since ketene as well as vinyl acetate can significantly contribute to the OH reactivity and O_3 production, it is important to explore these new and understudied oxygenated VOCs and their impact on secondary pollutants formation."

References:

Atkinson, S. J., Noble-Eddy, R., and Masters, S. L.: Gas-Phase Structures of Ketene and Acetic Acid from Acetic Anhydride Using Very-High-Temperature Gas Electron Diffraction, The Journal of Physical Chemistry A, 120, 2041-2048, 10.1021/acs.jpca.6b00704, 2016.

Brown, A. C., Canosa-Mas, C. E., Parr, A. D., and Wayne, R. P.: Temperature dependence of the rate of the reaction between the OH radical and ketene, Chemical Physics Letters, 161, 491-496, https://doi.org/10.1016/0009-2614(89)87026-5, 1989.

Kahan, T. F., Ormond, T. K., Ellison, G. B., and Vaida, V.: Acetic acid formation via the hydration of gas-phase ketene under ambient conditions, Chemical Physics Letters, 565, 1-4, https://doi.org/10.1016/j.cplett.2013.02.030, 2013.

Koss, A. R., Sekimoto, K., Gilman, J. B., Selimovic, V., Coggon, M. M., Zarzana, K. J., Yuan, B., Lerner, B. M., Brown, S. S., Jimenez, J. L., Krechmer, J., Roberts, J. M., Warneke, C., Yokelson, R. J., and de Gouw, J.: Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment, Atmos. Chem. Phys., 18, 3299-3319, 10.5194/acp-18-3299-2018, 2018.

Leung-Toung, R., Peterson, M. R., Tidwell, T. T., and Csizmadia, I. G.: Protonation of ketene and vinylketene: Relative stabilities of isomeric cationic products, Journal of Molecular Structure: THEOCHEM, 183, 319-330, https://doi.org/10.1016/0166-1280(89)80013-2, 1989.

Louie, M. K., Francisco, J. S., Verdicchio, M., Klippenstein, S. J., and Sinha, A.: Hydrolysis of Ketene Catalyzed by Formic Acid: Modification of Reaction Mechanism, Energetics, and Kinetics with Organic Acid Catalysis, The Journal of Physical Chemistry A, 119, 4347-4357, 10.1021/jp5076725, 2015.

Müller, M., Anderson, B. E., Beyersdorf, A. J., Crawford, J. H., Diskin, G. S., Eichler, P., Fried, A., Keutsch, F. N., Mikoviny, T., Thornhill, K. L., Walega, J. G., Weinheimer, A. J., Yang, M., Yokelson, R. J., and Wisthaler, A.: In situ measurements and modeling of reactive trace gases in a small biomass burning plume, Atmos. Chem. Phys., 16, 3813-3824, 10.5194/acp-16-3813-2016, 2016.

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Prakash, G. K. S., Bae, C., Rasul, G., and Olah, G. A.: The question of C- vs. O-silylation of ketenes: Electrophilic triethylsilylation of diphenylketene, Proceedings of the National Academy of Sciences of the United States of America, 102, 6251, 10.1073/pnas.0501813102, 2005.

Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J., and Smurthwaite, P. I.: Kinetics and mechanisms of the reactions of OH with some oxygenated compounds of importance in tropospheric chemistry, International Journal of Chemical Kinetics, 26, 113-130, https://doi.org/10.1002/kin.550260112, 1994.

Vogt, J., Williamson, A. D., and Beauchamp, J. L.: Properties and reactions of ketene in the gas phase by ion cyclotron resonance spectroscopy and photoionization mass spectrometry. Proton affinity, site specificity of protonation, and heat of formation of ketene, Journal of the American Chemical Society, 100, 3478-3483, 10.1021/ja00479a032, 1978.

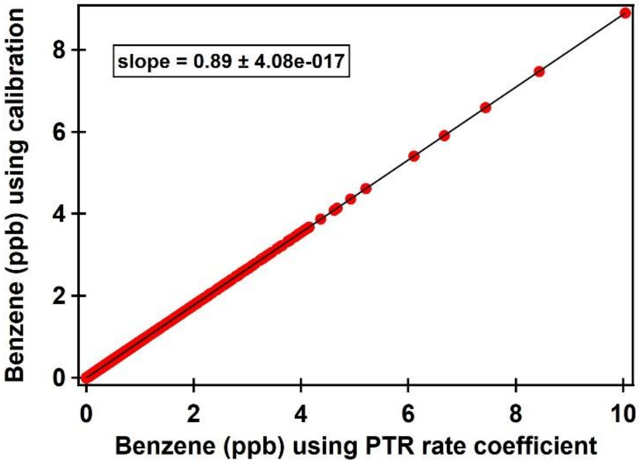
Yarkony, D. R., and Schaefer, H. F.: The acetyl cation and its geometrical isomers, The Journal of Chemical Physics, 63, 4317-4328, 10.1063/1.431148, 1975.

Reviewer #1:

The manuscript presents aircraft measurements of PTR-ToF-MS from a petrochemical facility in South Korea. It applies a horizontal adventive flux approach adapted from the top-down emission rate retrieval algorithm (TERRA) to estimate emission strength. It focuses on a single species, Ketene, and its emissions and impact on OH reactivity and tropospheric ozone formation. The idea about an understudied VOC could be exciting and potentially point to new areas to explore. However, it appears that there are several weaknesses that the paper would need to address.

1. For a study addressing a single species, I'd hope that authors could do a better job in the quantification than just using a proton transfer reaction rate coefficient to estimate its concentration. The rate coefficient could easily go wrong by more than 200%, and all conclusions would depend on the quality in quantification. Why not do a calibration of ketene in the laboratory? It could also help with the compound identification question raised by Prof. Armin Wisthaler in the Interactive Comment.

VOCs for which there are no calibration standards available or not developed yet, the widely used method in the atmospheric chemistry and VOC measurements community is to calculate the concentrations using the proton transfer reaction rate coefficient of the respective VOCs. The estimation of VOC concentrations using proton transfer reaction rate coefficients as compared to using available calibration standards mostly varies by < 20%. For example, if we estimate the measured benzene concentrations for the 23 October flight data using the proton transfer rate coefficient, the concentrations were found to be ~ 11% higher as compared to the concentrations estimated using the sensitivity factors (ncps/ppb) obtained from the calibration as shown in the following correlation plot (slope = 0.89):



Till date, no calibration standard is developed for ketene, in fact studies on atmospheric ketene measurements are rare, as mentioned in the manuscript. One of the future directions of this study would be to develop standards for ketene and carry out more laboratory studies which would help us to perform more accurate quantification (with lower uncertainty) of ketene.

Regarding the ketene identification question, we have mentioned in detail in the response to Prof. Wisthaler showing why the m/z 43.018 signal observed at Daesan is more likely to be due to protonation of directly emitted ketene and unlikely to be from vinyl acetate/methyl acrylate/2,3-butanedione. The probable contribution from acetic acid and glycolaldehyde to the m/z 43.018 signal was already corrected and this corrected data were used for the analysis purpose as mentioned in the original manuscript (P6, L177-178).

2. Specie identification needs to be better addressed, which should be easy to check as a correlation to m/z 87.044, and other potential ions. Again, laboratory experiments could help. Again, I refer to the interactive comment.

We have shown the laboratory experimental results as well as the comparison with our airborne measurement results and correlations while replying to Prof. Wisthaler which reads as follows:

We have not observed any high peaks similar to the m/z 43.018 (attributed to ketene) in the timeseries of m87.044 signal. Following figures show the timeseries of m/z 87.044 and m/z 43.018 (ketene) and their correlation plots for the plume episodes (in the inset) during all the flights.

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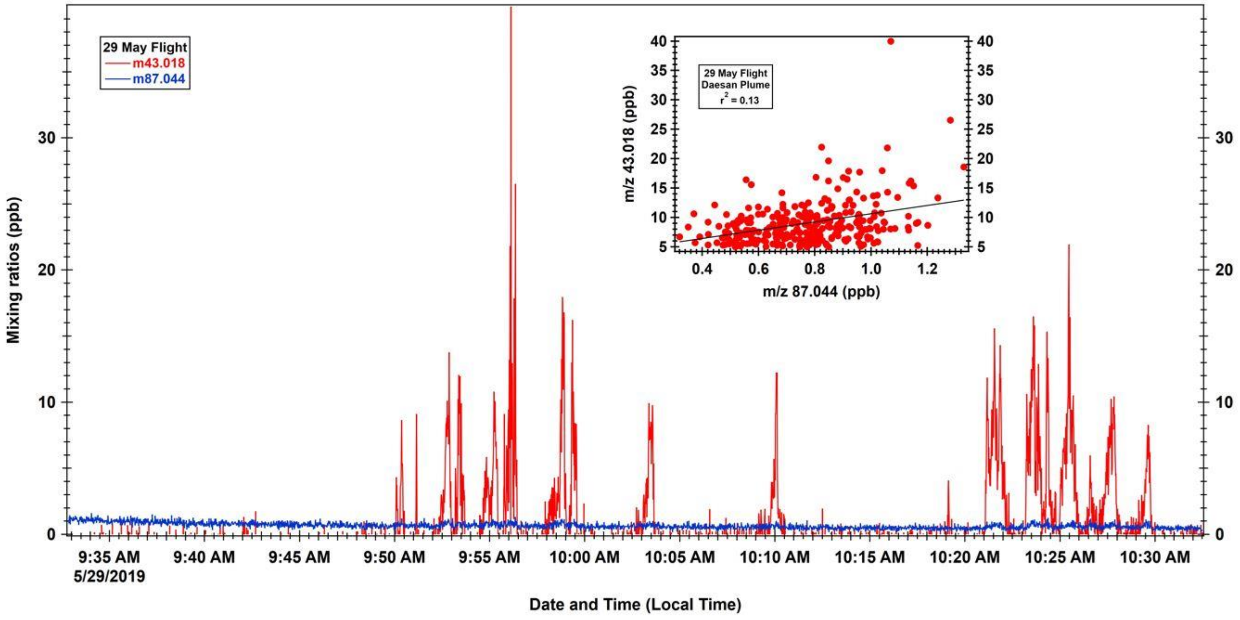

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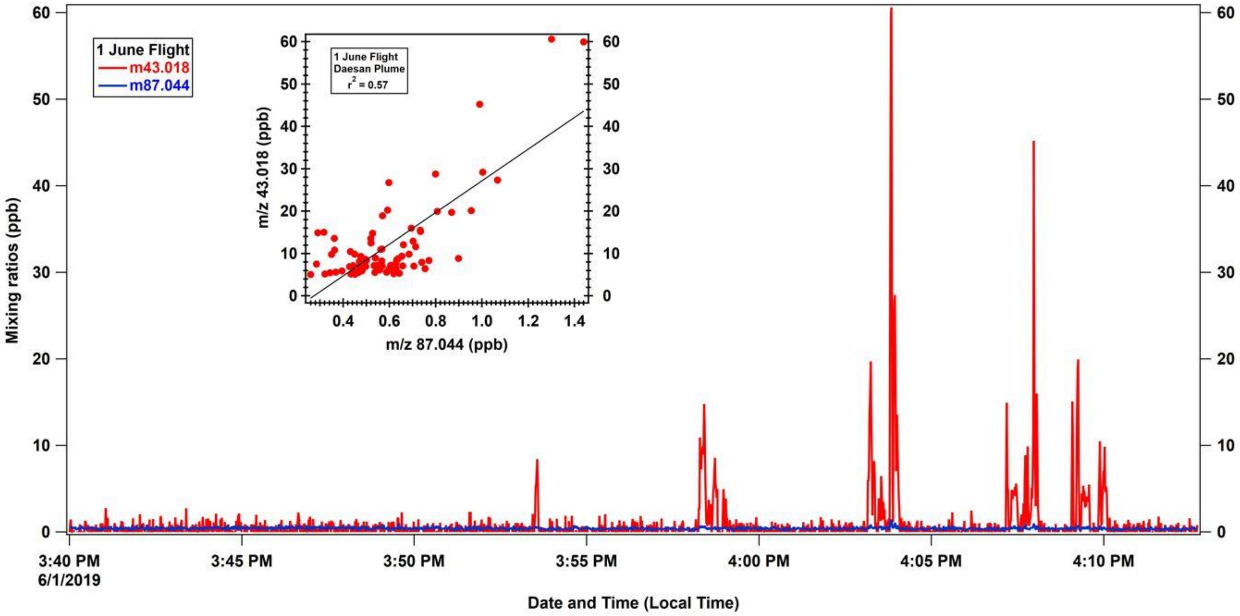
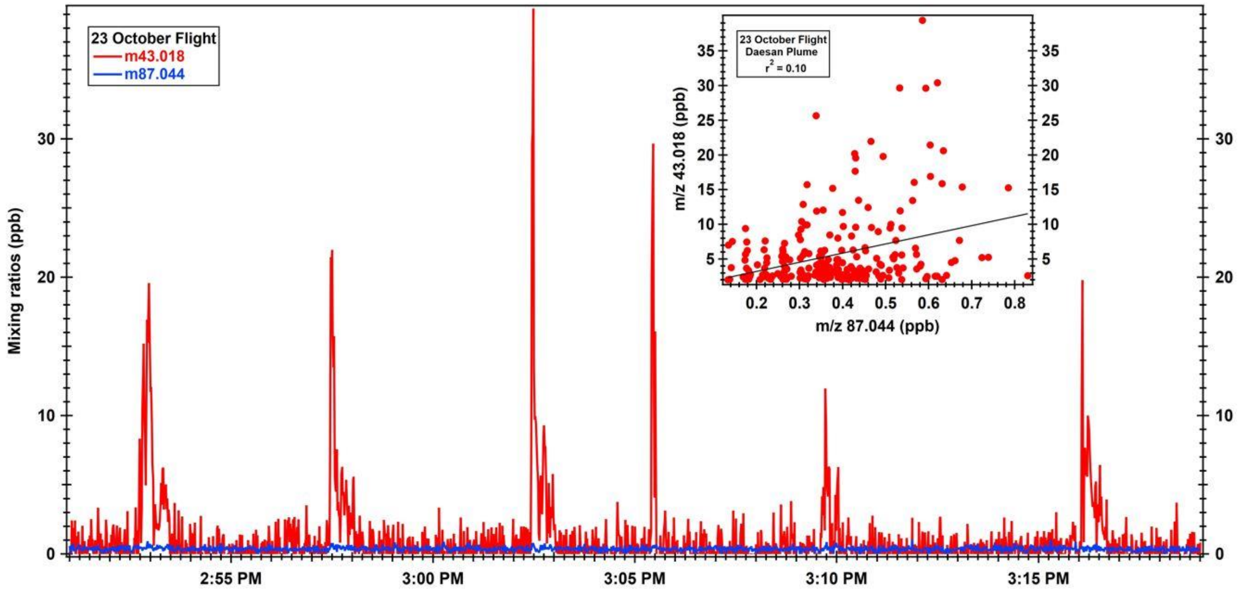


23 October Afternoon Flight:



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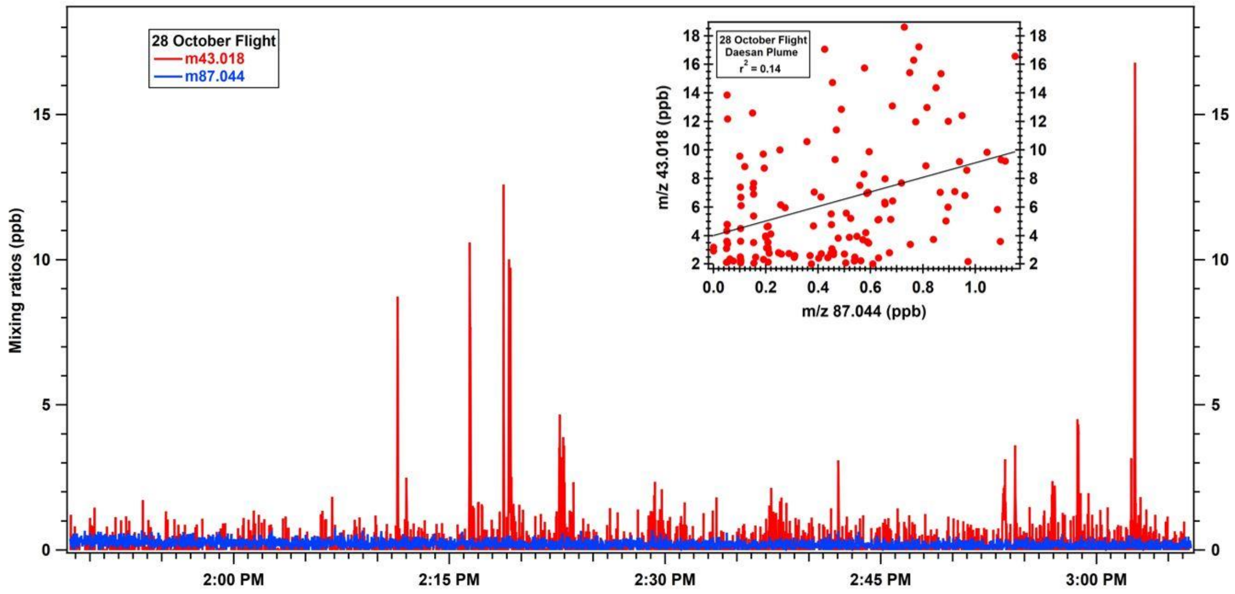

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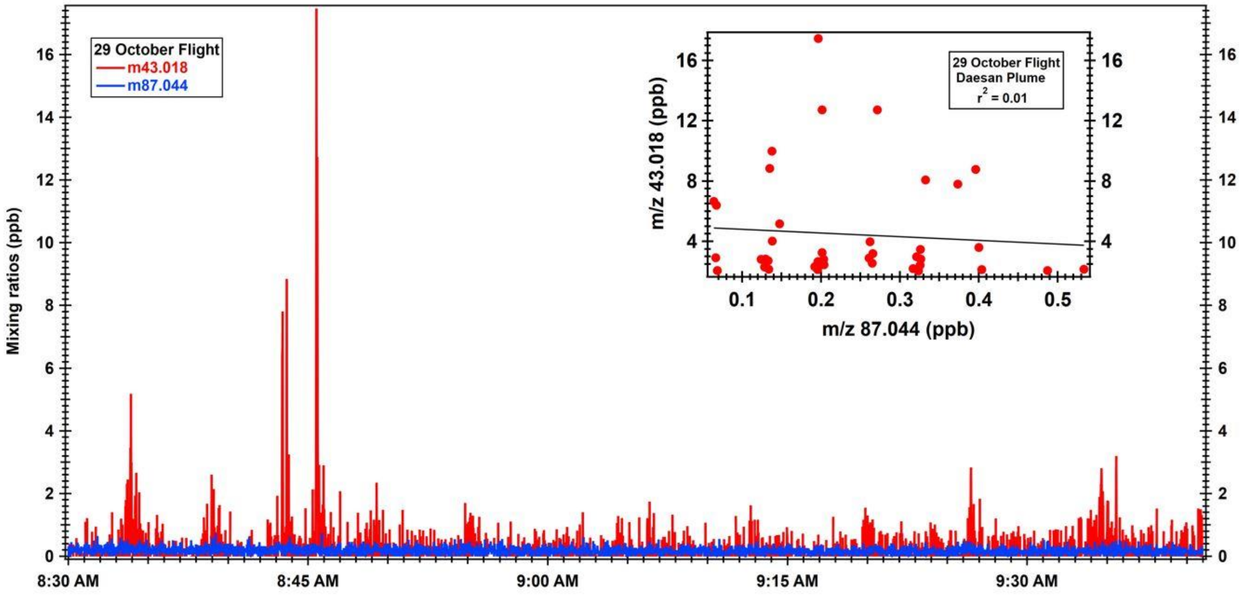

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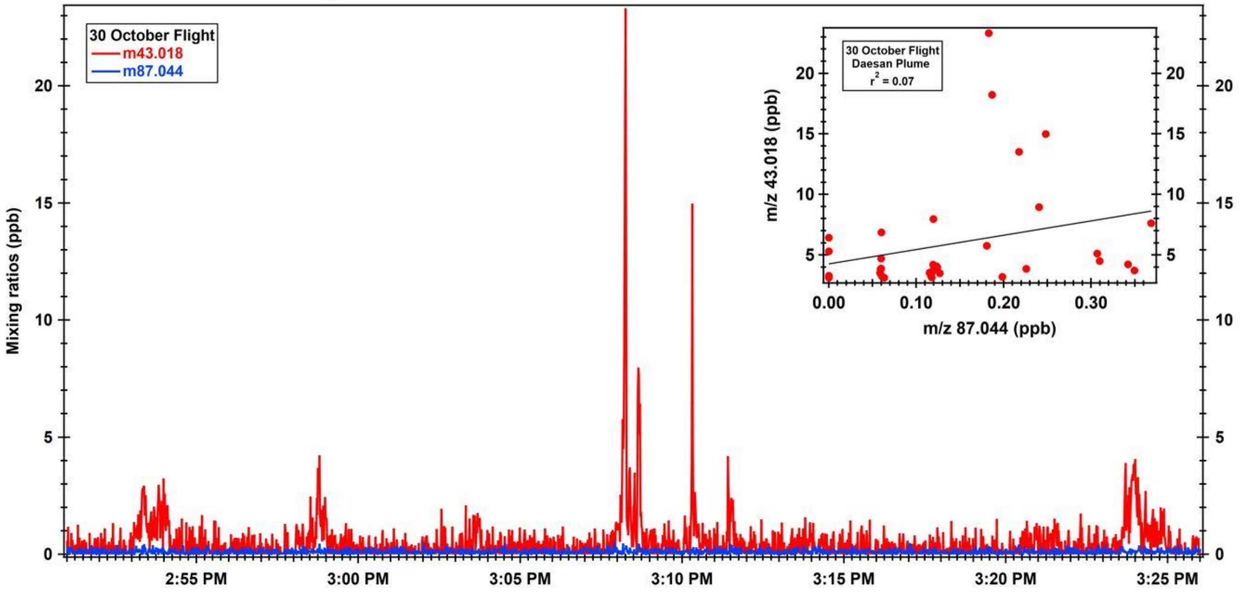

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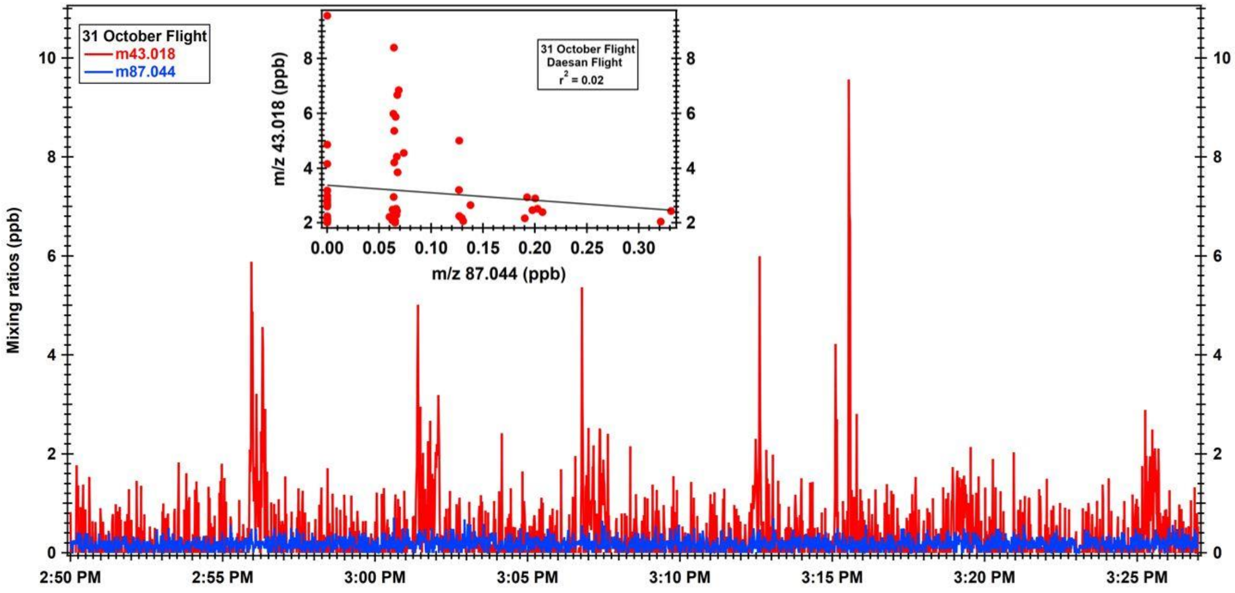

As we can see from the timeseries plots during all the flights, m/z 87.044 did not show any high peaks that we observed in the case of m/z 43.018 (attributed to ketene). In addition, no significant correlations were observed (Figures in the inset) between m/z 43.018 and m/z 87.044 when data corresponding to the plume episodes were utilized. This indicates that high peaks of m/z 43.018 cannot be attributed to the fragmentation of m/z 87.044 and the signal at m/z 43.018 had a different source.

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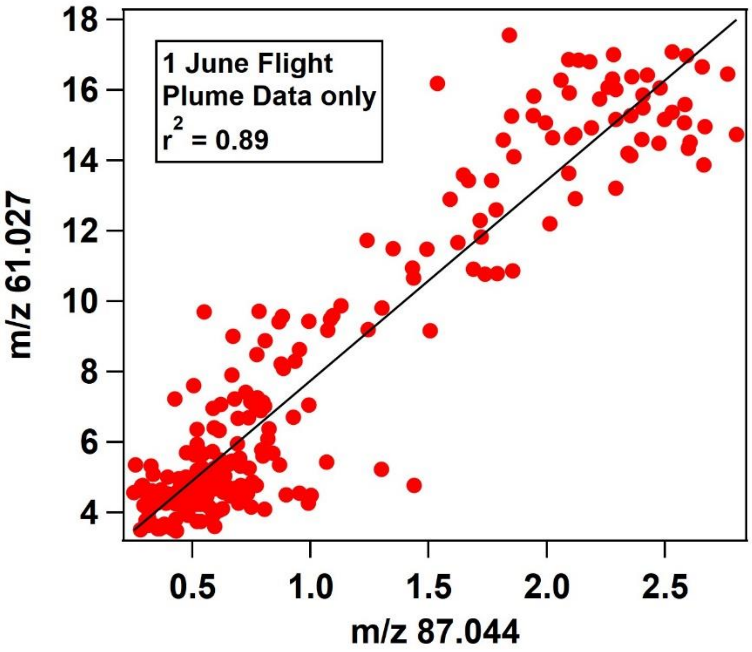
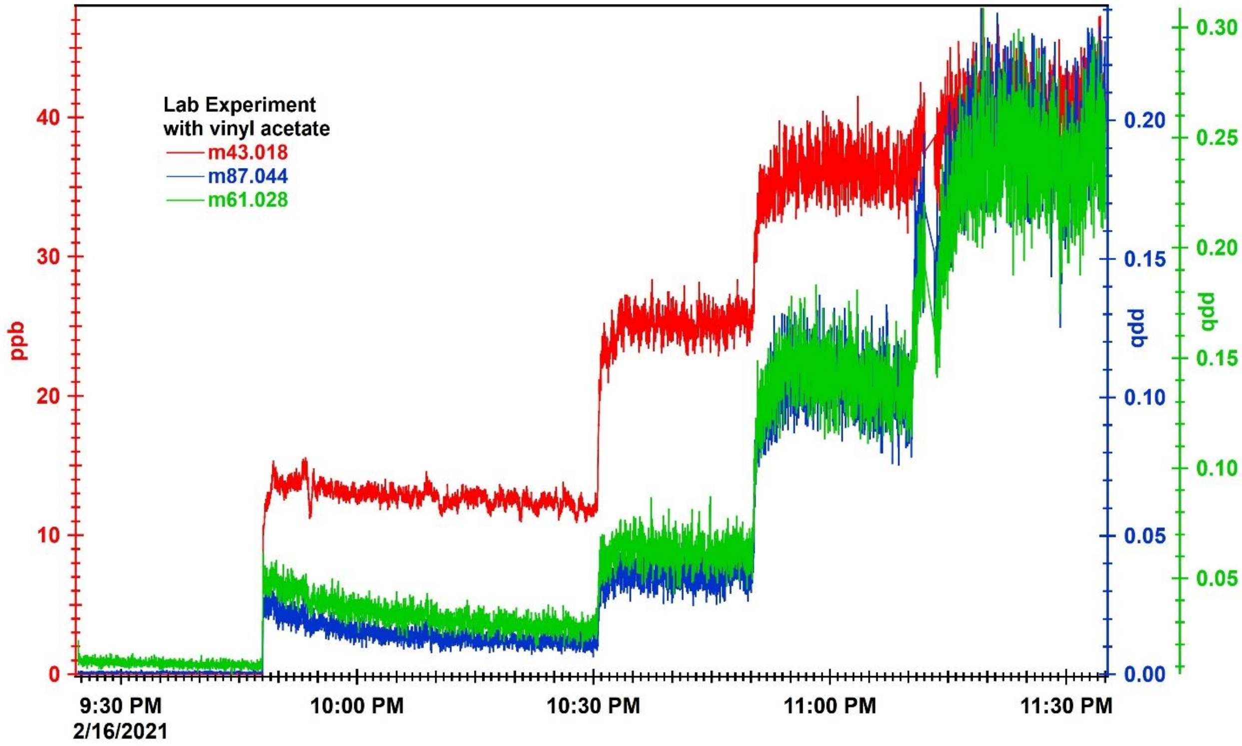
and glycolaldehyde, as mentioned in the original manuscript; P5 L66-67) as shown in the following figure. The excellent correlation (r^2 ~ 0.9) between m/z 87.044 and m/z 61.027 for the plume episodes during 1 June flight indicates that vinyl acetate and acetic acid had similar sources in Daesan. We have already corrected the ketene signal at m/z 43.018 for the contribution of acetic acid and glycolaldehyde which is mentioned in the original manuscript (P6, L177-178).

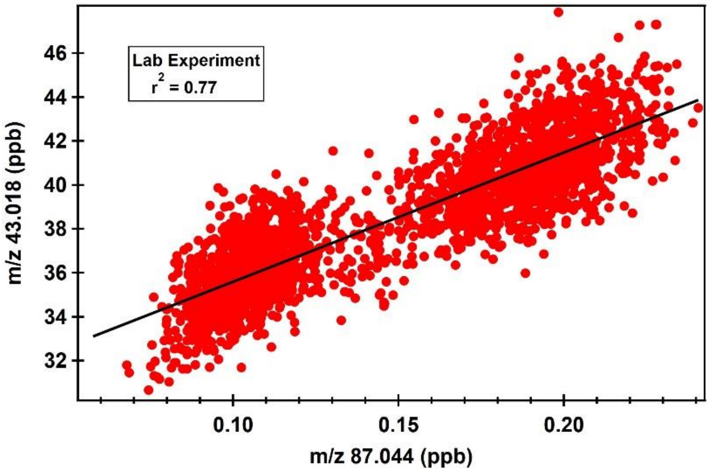


This further indicates that m/z 43.018 (ketene) has a direct emission source at Daesan and it does not originate from the fragmentation of vinyl acetate (m/z 87.044) within the PTR-TOF-MS.

Lab Experiments with vinyl acetate:

We have also carried out laboratory experiments by introducing different known concentrations of vinyl acetate standard into the PTR-TOF-MS (PTR-TOF1000) and observed that the signals at m/z 87.044 (vinyl acetate) correlates strongly with m/z 43.018 (acylium ion) as well as m/z 61.028 (acetic acid and glycolaldehyde). The timeseries of the experiment and the correlation plot (r^2 for the correlation ~ 0.77) between m/z 43.018 and m/z 87.044 are shown in the figures bellow. We have purposefully selected the data for higher concentration steps for the correlation analysis to be consistent with the high concentrations of m/z 43.018 that we measured in the field. This observation is similar to the laboratory observation mentioned by Prof. Wisthaler. If the m/z 43.018 signals were originated from the fragmentation of m/z 87.044, we would have observed similar correlations during our airborne measurements over Daesan. However, since we have not observed any such correlation in our field observations (as shown earlier), we believe the signal at m/z 43.018 does not originate from the fragmentation of vinyl acetate.

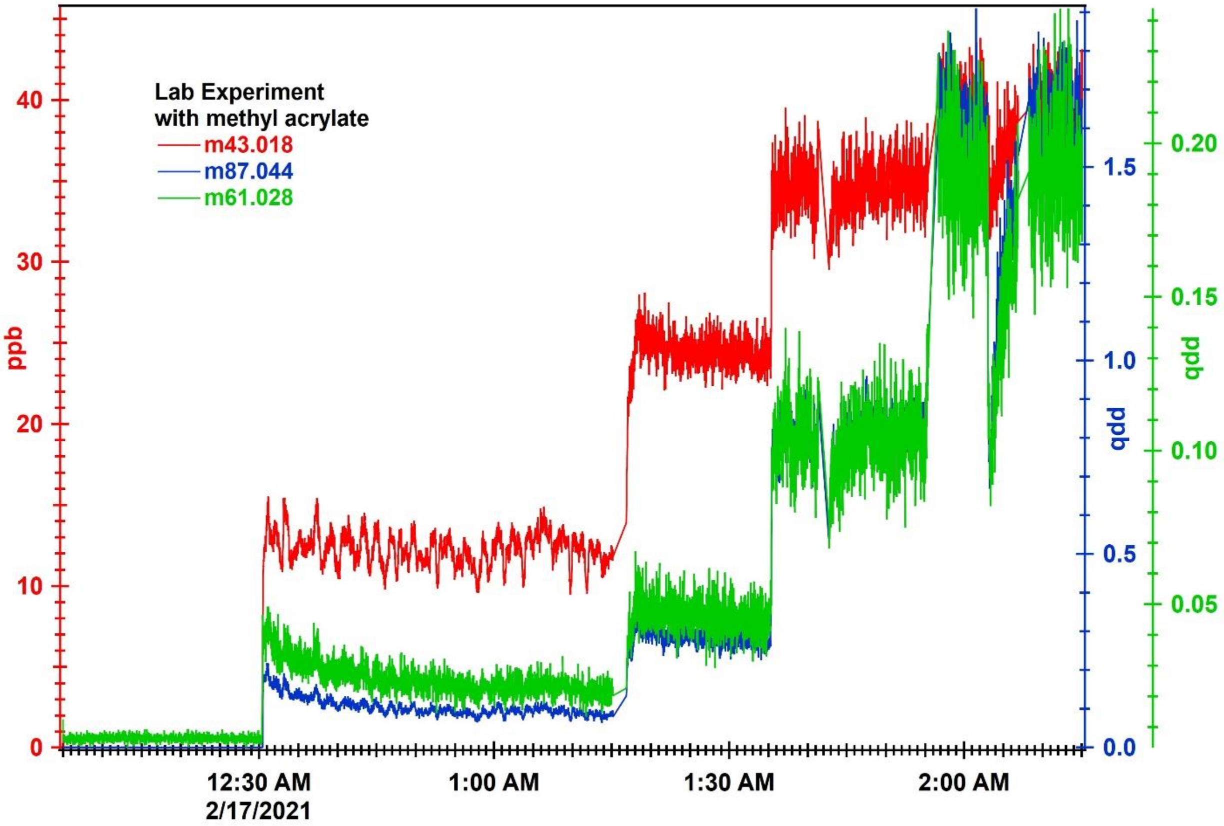


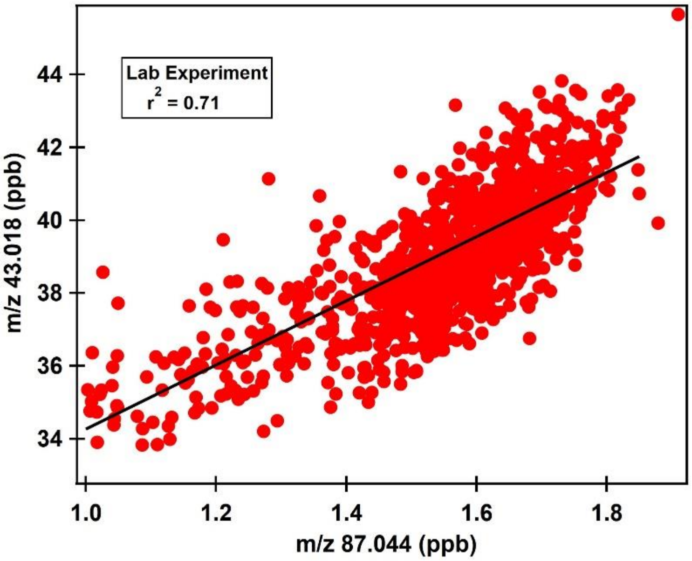


Lab Experiments with other possible contributing VOCs:

Previous studies have reported that m/z 87.044 signal can also be due to VOCs like 2,3-butadione and methyl acrylate (Müller et al., 2016;Koss et al., 2018). These compounds are reported to be emitted from incomplete combustion/biomass burning sources. We have carried out lab experiments with 2,3-butanedione and methyl acrylate standards to observe whether we observe any changes in the signal at m/z 43.018 when we introduce these two standards. We observed the similar response like vinyl acetate when we introduced different concentrations of these two standards into the PTR-TOF1000 (figures for the methyl acrylate experiment is shown below).

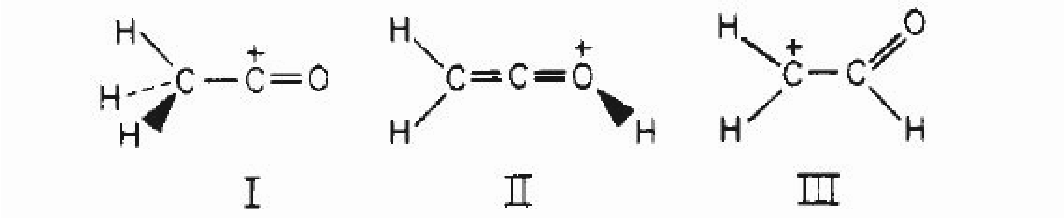
The strong correlations (e. g. $r^2 = 0.71$ for methyl acrylate) clearly indicate that 2,3-butanedione and methyl acrylate are also not contributing to the m/z 43.018 signals at Daesan.





Detection of ketene using PTR-TOF-MS:

Ketene has a proton affinity of 196 kCal/mol which is much higher than that of water (166 kCal/mol) and therefore, it is possible to detect protonated ketene using PTR-TOF-MS. The direct protonation of ketene can result in three different structural conformations and the most stable structure of protonated ketene is the acylium ion (Vogt et al., 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005) which is detected at m/z 43.018 using PTR-TOF-MS. The following are the three different possible conformations upon protonation of ketene and acylium ion (I) is the most stable structure as reported by several previous studies (Yarkony and Schaefer, 1975;Vogt et al., 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005).



Fragmentation of m/z 87.044 can also result in the formation of acylium ion at m/z 43.018 as we observed during our lab experiments and also mentioned by Prof. Wisthaler. However, during our field observations, we have not observed any correlation between m/z 43.018 and m/z 87.044 when we used the data for the plume episodes. Therefore, even we have detected the same acylium ion (at m/z 43.018) that can be formed from direct protonation of ketene as well as fragmentation of vinyl acetate, our results suggest that the origin of the acylium ion detected during our field campaign is the protonation of directly emitted ketene and not the fragmentation of vinyl acetate.

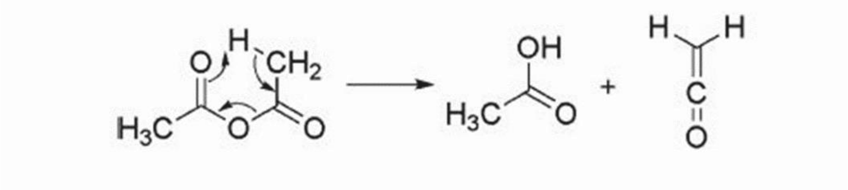
We have now added the following paragraph in the revised manuscript (P6 L180-202):

"Fragmentation of vinyl acetate (detected at m/z 87.044) could also potentially contribute to the signal at m/z 43.018. However, during our airborne measurements, m/z 87.044 did not show any high peaks that we observed in m/z 43.018 (attributed to ketene). In addition, no significant correlations were observed between m/z 43.018 and m/z 87.044 when data corresponding to the plume episodes were utilized. The signal-to-noise (S/N) ratio for m43.018 and m87.044 were 6 ppt and 2 ppt, respectively which indicates that the instrument sensitivity was good enough to observe the linearity between m43.018 and m87.044. This indicates that high peaks of m/z 43.018 cannot be attributed to the fragmentation of m/z 87.044 and the signal at m/z 43.018 had a different source. Previous studies have reported that m/z 87.044 signal can also be due to VOCs like 2,3-butadione and methyl acrylate (Müller et al., 2016;Koss et al., 2018). These compounds are reported to be emitted from incomplete combustion/biomass burning sources. We have carried out laboratory experiments with these two VOC standards and found that similar to vinyl acetate, these two VOCs were unlikely to be contributing to the m/z 43.018 peaks observed during our airborne measurements over Daesan. Ketene has a proton affinity of 196 kCal/mol which is much higher than that of water (166 kCal/mol) and therefore, it is possible to detect protonated

ketene using PTR-TOF-MS. The direct protonation of ketene can result in three different structural conformations and the most stable structure of protonated ketene is the acylium ion (Vogt et al., 1978;Nobes et al., 1983;Leung-Toung et al., 1989;Prakash et al., 2005) which is detected at m/z 43.018 using PTR-TOF-MS. Therefore, even we have detected the same acylium ion (at m/z 43.018) that can be formed from direct protonation of ketene as well as fragmentation of vinyl acetate/methyl acrylate/2,3-butanedione, our results suggest that the origin of the acylium ion detected during our field campaign is the protonation of directly emitted ketene and not the fragmentation of vinyl acetate."

Potential sources of ketene in the atmosphere:

Pyrolysis of acetic anhydride was reported to be a potential source of ketene in the atmosphere and follows the chemical mechanism shown below (Atkinson et al., 2016):



Louie et al. (2015) previously reported that pyrolysis of cellulose and lignins, which are the principal components of plants, produces various organic compounds, which, upon further pyrolysis, generate ketene as a major byproduct. Pyrolysis of acetone can also produce ketene (Brown et al., 1989) while Kahan et al. (2013) reported that pyrolysis of furan at 295 K could also be a potential source of ketene.

We have now added the following sentence in the revised manuscript (P2 L59-60):

"Pyrolysis of acetic anhydride is also reported to be a potential source of ketene in the atmosphere (Atkinson et al., 2016)."

Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to ketene, the possibility of the contribution from vinyl acetate cannot be ruled out completely and therefore, further studies focusing on this aspect needs to be carried out. Since the rate coefficient of vinyl acetate with OH radical is 2.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate was found to be ~ 20-25% less than that of ketene. Following table shows a comparison of the estimated OH reactivity and O_3 production potential for both ketene (already shown in Table 2b of the original manuscript) and vinyl acetate:

Research Flights	OH reactivity (s^{-1})*		O_3 production potential (ppb h^{-1})*	
	Ketene	Vinyl acetate	Ketene	Vinyl acetate
29 May	5.42 (33.76)	4.01 (24.96)	4.84 (30.10)	3.58 (22.28)

1 June	7.75 (51.24)	5.73 (37.88)	6.91 (45.70)	5.11 (33.82)
23 October	7.35 (33.33)	5.44 (24.64)	6.56 (29.80)	4.85 (22.00)
28 October	5.28 (15.74)	3.90 (11.64)	4.71 (14.00)	3.48 (10.39)
29 October	3.79 (14.77)	2.80 (10.92)	3.38 (13.20)	2.50 (9.75)
30 October	3.33 (19.71)	2.47 (14.57)	2.98 (17.60)	2.20 (13.01)
31 October	4.56 (8.09)	3.37 (5.98)	4.07 (7.22)	3.01 (5.34)

***** values in the parenthesis corresponds to the maximum OH reactivity and O_3 production potential, respectively.

We have included the following sentences as a short paragraph in the Conclusions section (P11-12 L382-389 of the revised manuscript):

“Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to ketene, the possibility of the contribution from vinyl acetate cannot be ruled out completely and therefore, further studies focusing on this aspect needs to be carried out. Since the rate coefficient of vinyl acetate with OH radical is 2.5×10^{-11} cm^{3} molecule^{-1} s^{-1} (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate can be ~ 20-25% less than that of ketene. Since ketene as well as vinyl acetate can significantly contribute to the OH reactivity and O_3 production, it is important to explore these new and understudied oxygenated VOCs and their impact on secondary pollutants formation.”

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Atkinson, S. J., Noble-Eddy, R., and Masters, S. L.: Gas-Phase Structures of Ketene and Acetic Acid from Acetic Anhydride Using Very-High-Temperature Gas Electron Diffraction, The Journal of Physical Chemistry A, 120, 2041-2048, 10.1021/acs.jpca.6b00704, 2016.

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Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J., and Smurthwaite, P. I.: Kinetics and mechanisms of the reactions of OH with some oxygenated compounds of importance in tropospheric chemistry, International Journal of Chemical Kinetics, 26, 113-130, https://doi.org/10.1002/kin.550260112, 1994.

Vogt, J., Williamson, A. D., and Beauchamp, J. L.: Properties and reactions of ketene in the gas phase by ion cyclotron resonance spectroscopy and photoionization mass spectrometry. Proton affinity, site specificity of protonation, and heat of formation of ketene, Journal of the American Chemical Society, 100, 3478-3483, 10.1021/ja00479a032, 1978.

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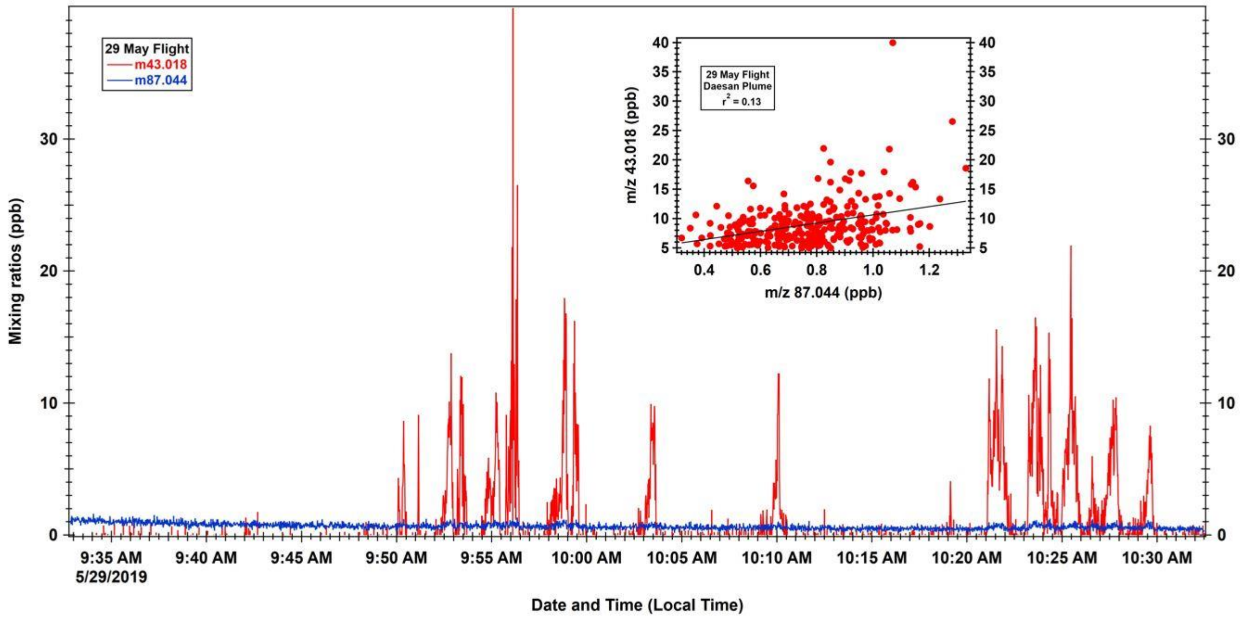
Reviewer #2:

Sarkar et al. used a PTR-TOF-MS to measure VOCs from the downwind plume of a petrochemical facility in South Korea. They found the signal m/z 43 was high and assigned it to ketene. Using these measurements, they further investigated the environmental implications. The conclusions in this manuscript can only be correct, given the ketene measurement was correct. However, as pointed by Prof. Armin Wisthaler and another reviewer, ketene measurement could be significantly biased. Actually, it might be another species, vinyl acetate, based on measurements in the similar region by Prof. Armin Wisthaler. I strongly agree with Prof. Armin Wisthaler's judgement, as it is well known that m/z 43 or CH_3CO^+ can be fragmented from a number of compounds, including acetic acid, ethyl acetate. I would recommend the authors consider the suggestion of Prof. Armin Wisthaler. Even the authors would change the topic from ketene to vinyl acetate, I would also like to see detailed measurements of vinyl acetate by PTR-TOF-MS.

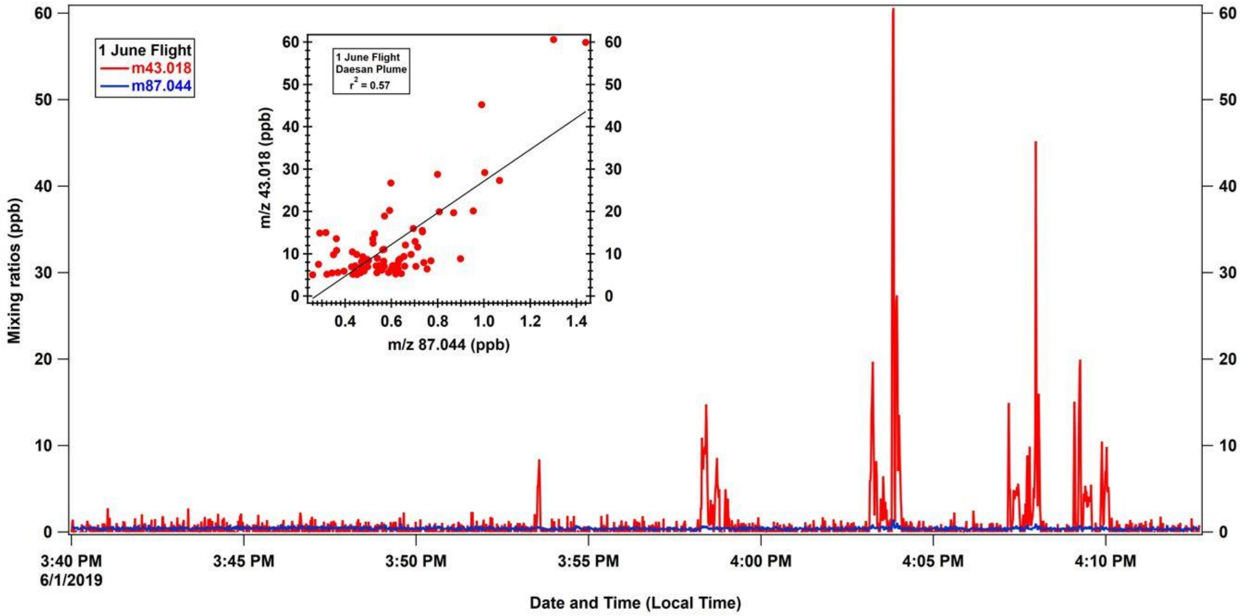
We have shown the laboratory experimental results as well as the comparison with our airborne measurement results and correlations while replying to Prof. Wisthaler (and Reviewer #1) which reads as follows:

We have not observed any high peaks similar to the m/z 43.018 (attributed to ketene) in the timeseries of m87.044 signal. Following figures show the timeseries of m/z 87.044 and m/z 43.018 (ketene) and their correlation plots for the plume episodes (in the inset) during all the flights.

29 May Morning Flight:



1 June Afternoon Flight:



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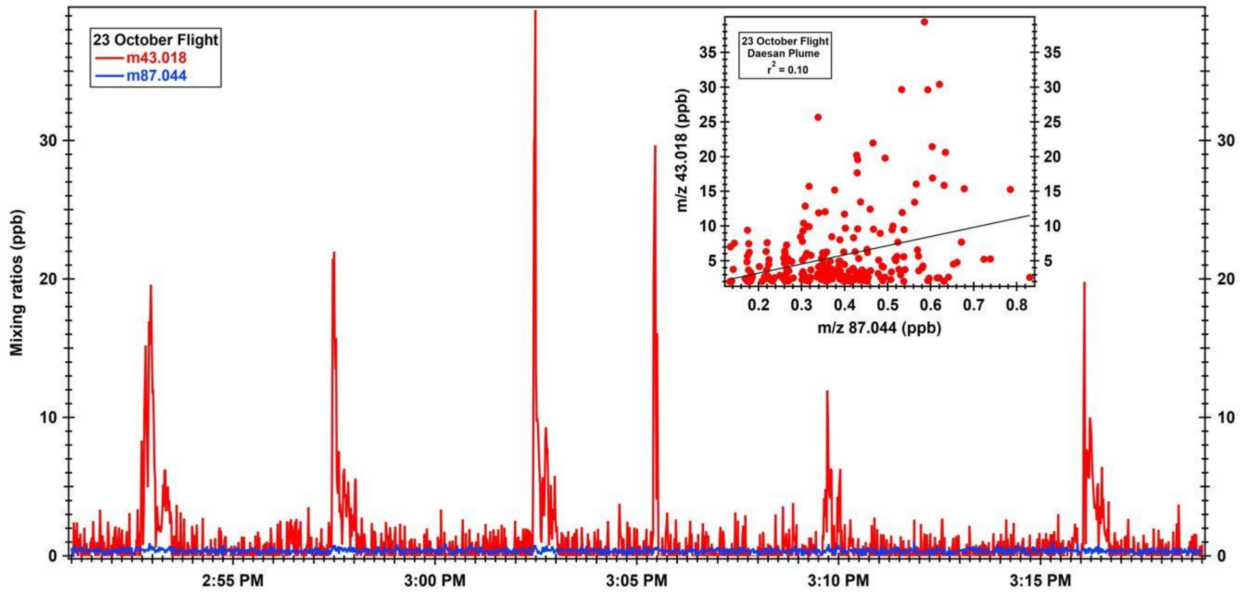
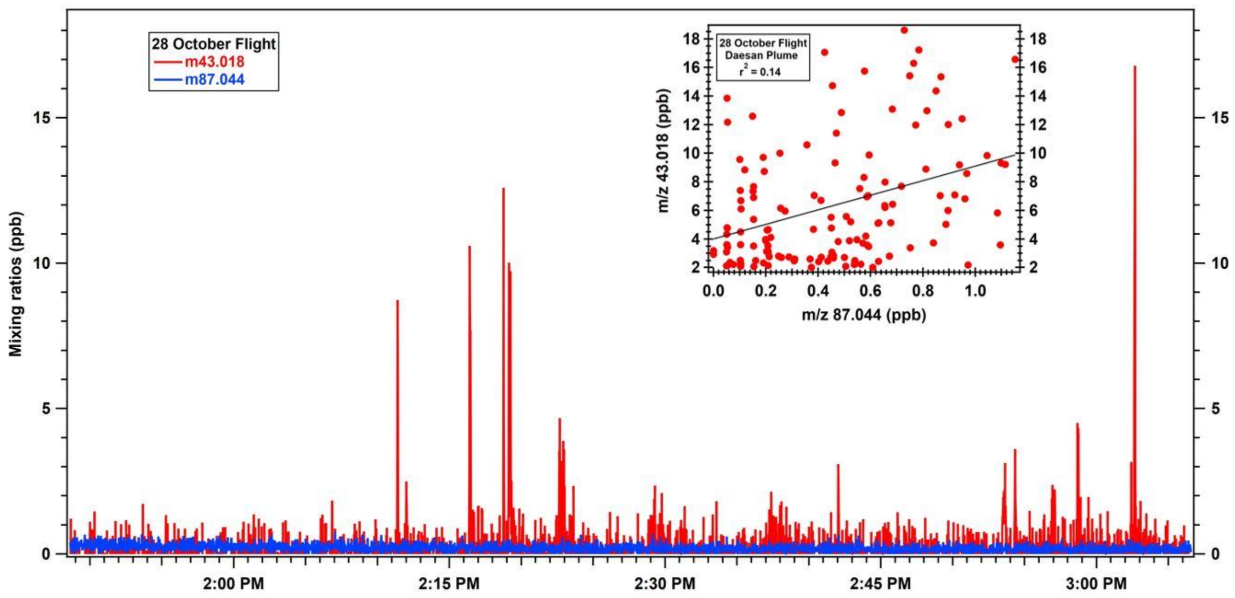
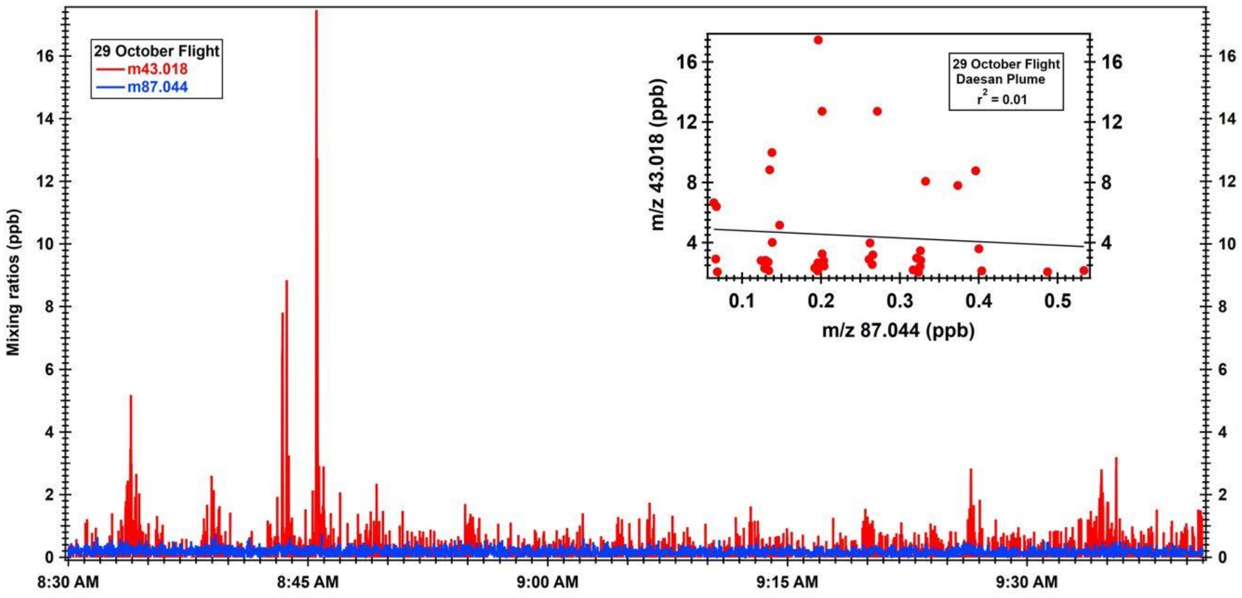


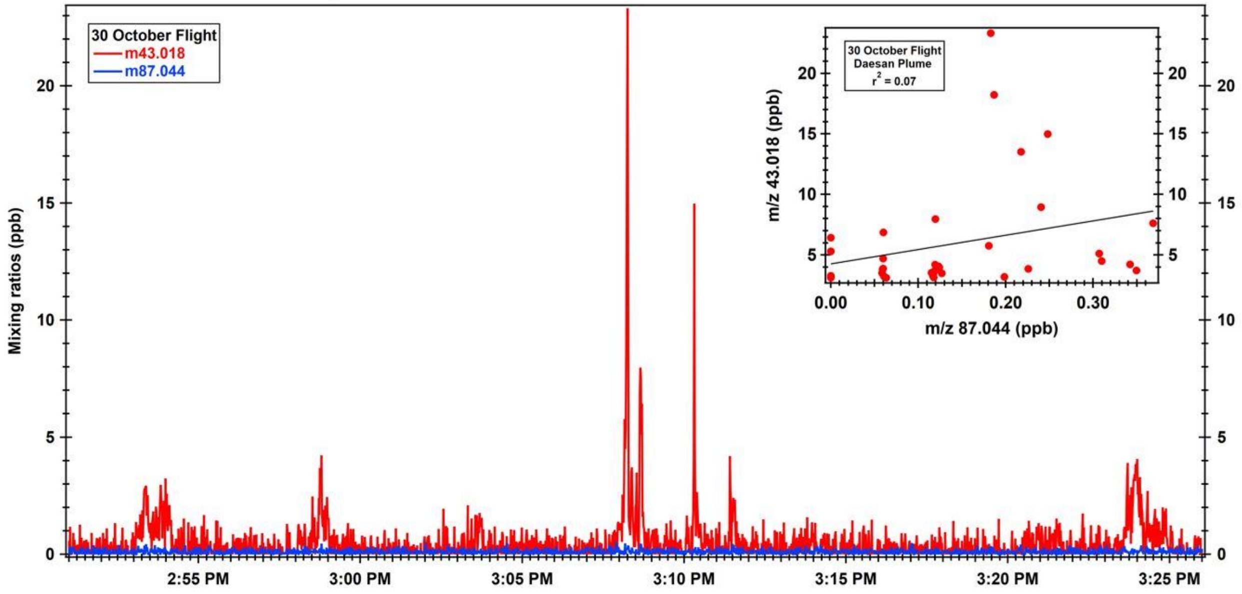
28 October Afternoon Flight:



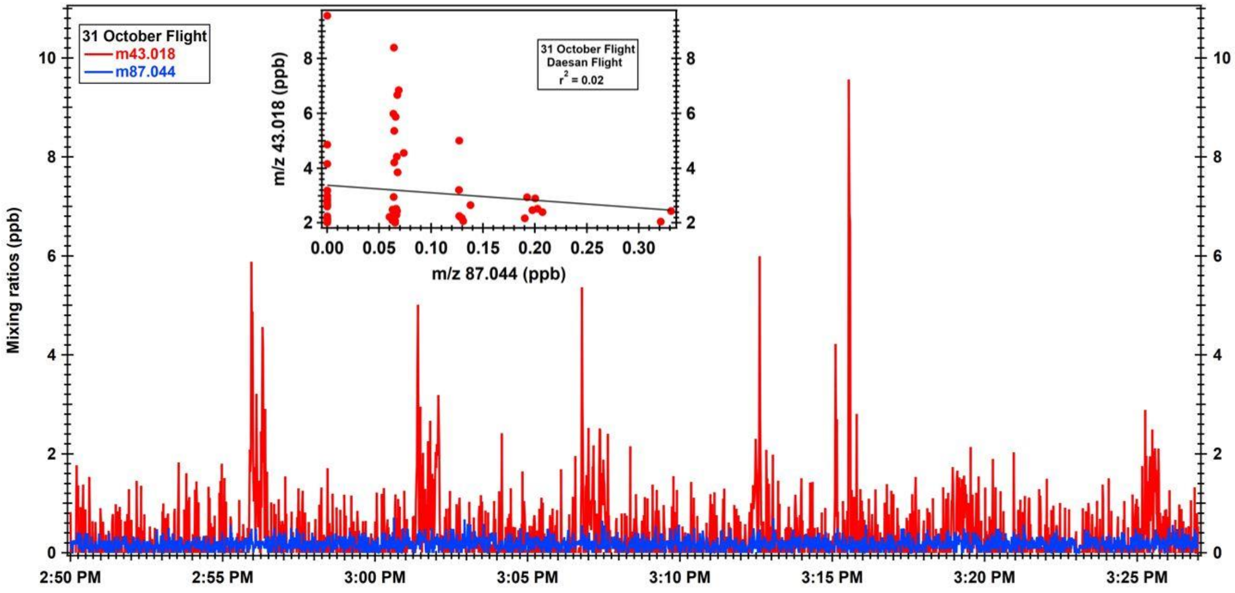
29 October Morning Flight:



30 October Afternoon Flight:



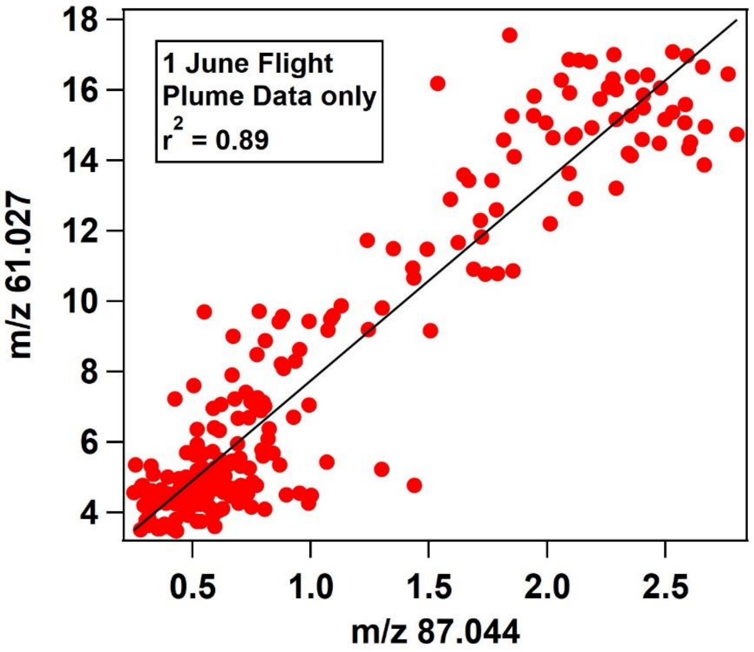
31 October Afternoon Flight:



As we can see from the timeseries plots during all the flights, m/z 87.044 did not show any high peaks that we observed in the case of m/z 43.018 (attributed to ketene). In addition, no significant correlations were observed (Figures in the inset) between m/z 43.018 and m/z 87.044 when data corresponding to the plume episodes were utilized. This indicates that high peaks of m/z 43.018 cannot be attributed to the fragmentation of m/z 87.044 and the signal at m/z 43.018 had a different source.

During the plume episodes at Daesan, the concentrations of vinyl acetate (m/z 87.044), which is an acetate ester, showed excellent correlations with the concentrations of m/z 61.027 (acetic acid

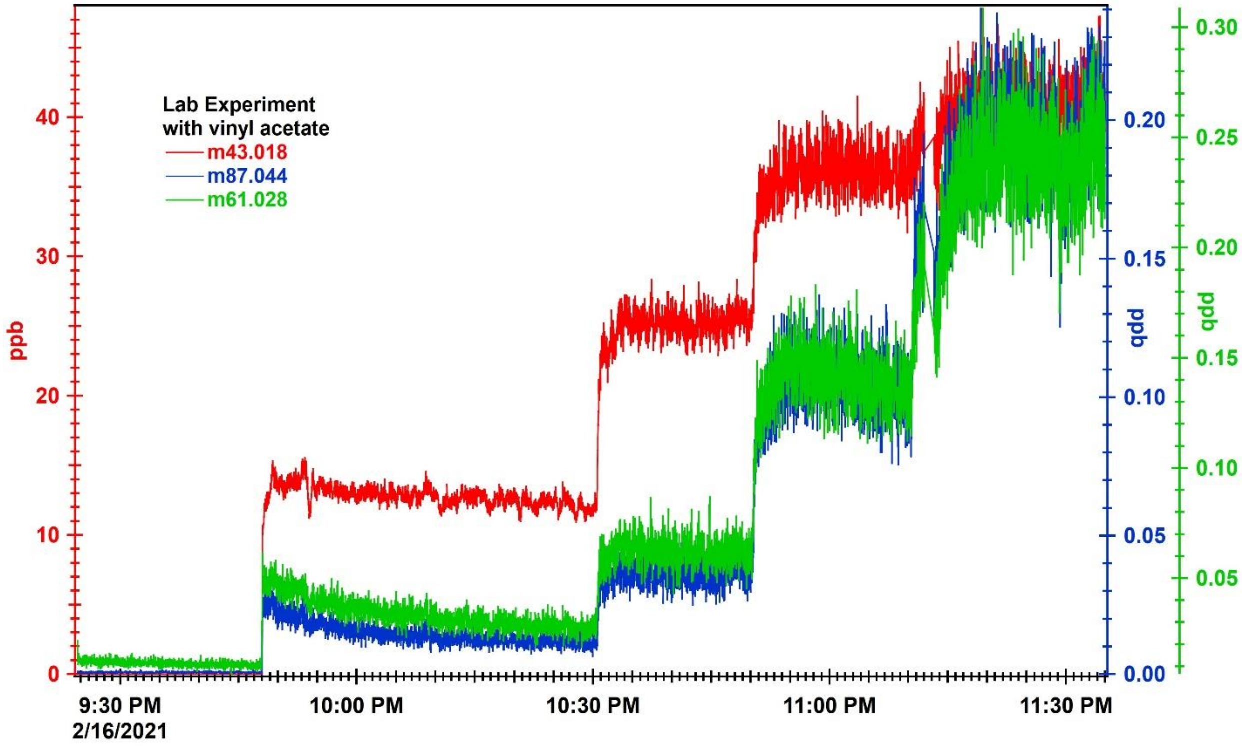
and glycolaldehyde, as mentioned in the original manuscript; P5 L66-67) as shown in the following figure. The excellent correlation (r^2 ~ 0.9) between m/z 87.044 and m/z 61.027 for the plume episodes during 1 June flight indicates that vinyl acetate and acetic acid had similar sources in Daesan. We have already corrected the ketene signal at m/z 43.018 for the contribution of acetic acid and glycolaldehyde which is mentioned in the original manuscript (P6, L177-178).

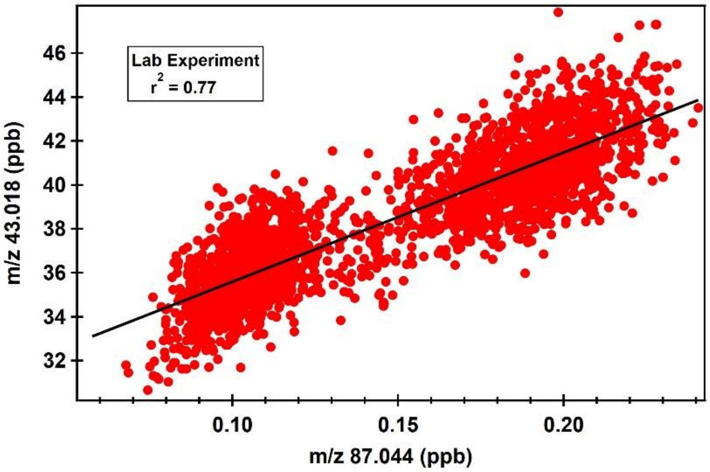


This further indicates that m/z 43.018 (ketene) has a direct emission source at Daesan and it does not originate from the fragmentation of vinyl acetate (m/z 87.044) within the PTR-TOF-MS.

Lab Experiments with vinyl acetate:

We have also carried out laboratory experiments by introducing different known concentrations of vinyl acetate standard into the PTR-TOF-MS (PTR-TOF1000) and observed that the signals at m/z 87.044 (vinyl acetate) correlates strongly with m/z 43.018 (acylium ion) as well as m/z 61.028 (acetic acid and glycolaldehyde). The timeseries of the experiment and the correlation plot (r^2 for the correlation ~ 0.77) between m/z 43.018 and m/z 87.044 are shown in the figures bellow. We have purposefully selected the data for higher concentration steps for the correlation analysis to be consistent with the high concentrations of m/z 43.018 that we measured in the field. This observation is similar to the laboratory observation mentioned by Prof. Wisthaler. If the m/z 43.018 signals were originated from the fragmentation of m/z 87.044, we would have observed similar correlations during our airborne measurements over Daesan. However, since we have not observed any such correlation in our field observations (as shown earlier), we believe the signal at m/z 43.018 does not originate from the fragmentation of vinyl acetate.





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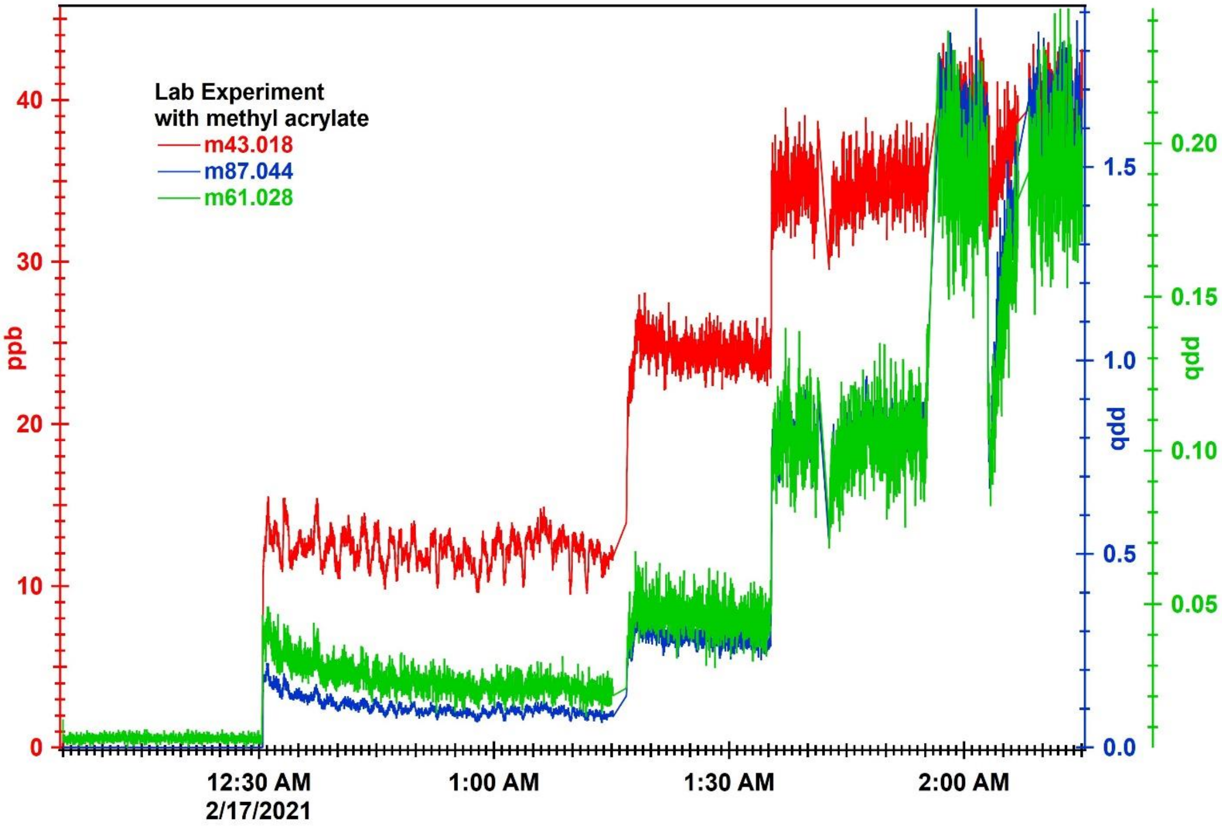
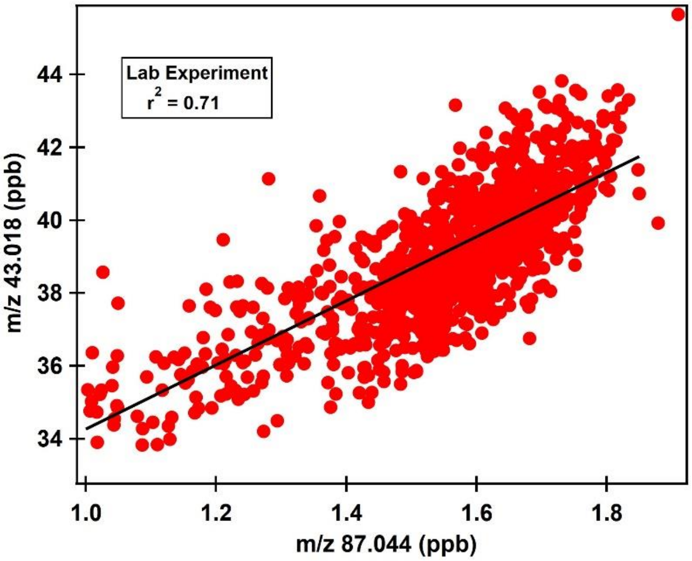
Previous studies have reported that m/z 87.044 signal can also be due to VOCs like 2,3-butadione and methyl acrylate (Müller et al., 2016;Koss et al., 2018). These compounds are reported to be emitted from incomplete combustion/biomass burning sources. We have carried out lab experiments with 2,3-butanedione and methyl acrylate standards to observe whether we observe any changes in the signal at m/z 43.018 when we introduce these two standards. We observed the similar response like vinyl acetate when we introduced different concentrations of these two standards into the PTR-TOF1000 (figures for the methyl acrylate experiment is shown below).

The strong correlations (e. g. $r^2 = 0.71$ for methyl acrylate) clearly indicate that 2,3-butanedione and methyl acrylate are also not contributing to the m/z 43.018 signals at Daesan.





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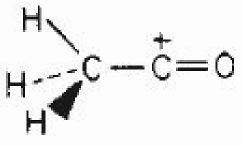
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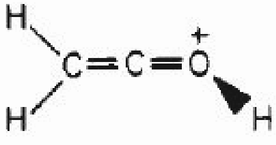
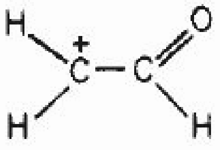

II


III

Fragmentation of m/z 87.044 can also result in the formation of acylium ion at m/z 43.018 as we observed during our lab experiments and also mentioned by Prof. Wisthaler. However, during our field observations, we have not observed any correlation between m/z 43.018 and m/z 87.044 when we used the data for the plume episodes. Therefore, even we have detected the same acylium ion (at m/z 43.018) that can be formed from direct protonation of ketene as well as fragmentation of vinyl acetate, our results suggest that the origin of the acylium ion detected during our field campaign is the protonation of directly emitted ketene and not the fragmentation of vinyl acetate.

We have now added the following paragraph in the revised manuscript (P6 L180-202):

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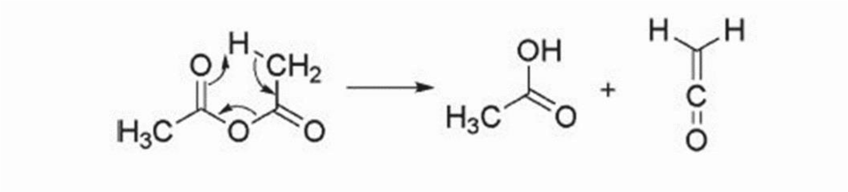

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We have now added the following sentence in the revised manuscript (P2 L59-60):

"Pyrolysis of acetic anhydride is also reported to be a potential source of ketene in the atmosphere (Atkinson et al., 2016)."

Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to ketene, the possibility of the contribution from vinyl acetate cannot be ruled out completely and therefore, further studies focusing on this aspect needs to be carried out. Since the rate coefficient of vinyl acetate with OH radical is 2.5×10^{-11} cm^3 molecule^{-1} s^{-1} (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate was found to be ~ 20-25% less than that of ketene. Following table shows a comparison of the estimated OH reactivity and O_3 production potential for both ketene (already shown in Table 2b of the original manuscript) and vinyl acetate:

Research Flights	OH reactivity (s^{-1})*		O_3 production potential (ppb h^{-1})*	
	Ketene	Vinyl acetate	Ketene	Vinyl acetate
29 May	5.42 (33.76)	4.01 (24.96)	4.84 (30.10)	3.58 (22.28)

1 June	7.75 (51.24)	5.73 (37.88)	6.91 (45.70)	5.11 (33.82)
23 October	7.35 (33.33)	5.44 (24.64)	6.56 (29.80)	4.85 (22.00)
28 October	5.28 (15.74)	3.90 (11.64)	4.71 (14.00)	3.48 (10.39)
29 October	3.79 (14.77)	2.80 (10.92)	3.38 (13.20)	2.50 (9.75)
30 October	3.33 (19.71)	2.47 (14.57)	2.98 (17.60)	2.20 (13.01)
31 October	4.56 (8.09)	3.37 (5.98)	4.07 (7.22)	3.01 (5.34)

***** values in the parenthesis corresponds to the maximum OH reactivity and O_3 production potential, respectively.

We have included the following sentences as a short paragraph in the Conclusions section (P11-12 L382-389 of the revised manuscript):

"Although based on our observation, we strongly believe that the m/z 43.018 signal corresponds to ketene, the possibility of the contribution from vinyl acetate cannot be ruled out completely and therefore, further studies focusing on this aspect needs to be carried out. Since the rate coefficient of vinyl acetate with OH radical is 2.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1} (Saunders et al., 1994), the estimated OH reactivity and O_3 production potential for vinyl acetate can be ~ 20-25% less than that of ketene. Since ketene as well as vinyl acetate can significantly contribute to the OH reactivity and O_3 production, it is important to explore these new and understudied oxygenated VOCs and their impact on secondary pollutants formation."

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