“Detection of formaldehyde emissions from an industrial zone in the Yangtze-River-Delta region of China using a proton transfer reaction ion-drift chemical ionization mass spectrometer” (AMT-2016-194) by Yan Ma et al..

Reply to the Comments by the Reviewer #2:

We are grateful to the reviewer for the helpful suggestions that have improved the manuscript substantially. Below we have included the review comments in italic followed by our responses. The manuscript has been revised accordingly.

1) “A major issue is the selection of the tracer species benzene and toluene. I understand that those are species nicely measured by the PTR-ID-CIMS, but these species are known to have a wide range of emission sources and are not as unambiguously related to specific sources as would be CO for combustion processes. The relatively low R2 value of 0.52 for the multiple linear regressions fit seems to reflect this.”

Response: We understand the reviewer’s concern. Indeed, benzene and toluene can be emitted into the atmosphere by many sources, including automobile exhausts and industrial-related processes. However, the industrial zone in Nanjing is a rather intensive point source in a regional scale as indicated by Fig. 1 of Zheng et al. (2015). The cluster of petrochemical facilities in the industrial zone is considered one of the largest in China. Benzene and toluene are both raw materials and distilled products in these facilities. These industry-related emissions are much stronger than automobile emissions. In addition, no clear rush hour peaks were found in the time series of benzene and toluene during pollution days. In addition, the observed benzene to toluene ratio of 1.7±1.0, significantly higher than 0.5, an indicator of automobile emissions (Hoque et al., 2008). Under this special circumstance, we choose benzene and toluene as the tracer species. This issue has been discussed in the manuscript section 3.4.

2) “If there is primarily emitted HCHO, which I think there is, then it would best show up at night under conditions where the measurements site is located downwind the potential emission sources, i.e. meteorological and day vs. nighttime screening is needed. In case there would not be enough data available to do this analysis, at least one case study describing such a situation should be shown. After adding this additional analysis and addressing the comments listed below, I would recommend the publication of this manuscript in AMT.”

Response: As suggested by the reviewer, we have included a case study of April 18, 2015. From 10:00 AM of April 18, there was a persistent easterly wind with wind speed varying within a few meters per second. Meanwhile significant increase of HCHO was observed at the site. Especially, after 19:00 HCHO apparently anti-correlated with wind speed. At ~23:00 wind direction suddenly switched to westerly wind and wind speed increased to 3~5 m s⁻¹. HCHO was found suddenly decreased to ~2 ppbv. Evidently, this pattern of HCHO on April 18 can only be explained by primary sources other than automobile emissions. In addition, we have added several rose-plots into the manuscript to show that VOC plumes were mostly
associated with easterly winds.

**Figure 8.** Time series of wind direction (WD) and wind speed (WS) (Panel a), m/z 37/19 ratio and RH (Panel b), O₃ and CO (Panel c), m/z 79 and m/z 93 (Panel d), and m/z 31 signal (Panel e) on April 18, 2015. The dips in panel d and e are the periods when background checks were made.

3) L71-72: It should be clarified whether this statement about a threshold of 100 ppbv HCHO for allergic reaction is of relevance in outdoor air pollution. Also, what exposure time is the basis for this value?

Response: This statement is based on exposure experiments conducted by the Agency for Toxic Substances and Disease Registry. No specific exposure time is reported. We have revised the statement as (L73):

“During exposure tests, breathing in as low as 100 ppbv HCHO may cause allergic reactions in certain population ([http://www.atsdr.cdc.gov/toxfaqs/tfacts111.pdf](http://www.atsdr.cdc.gov/toxfaqs/tfacts111.pdf), accessed October 2016).”

4) L80-85: There is a non-negligible difference of HCHO emissions between light-duty and heavy-duty diesel vehicles. This should be mentioned. It could be of relevance with regard to different composition of the traffic fleet, in particular in industrial zones, where heavy-duty vehicles are likely present. In this context I recommend the authors to address findings in a recent paper by Rappenglück et al., which also compares some traffic emissions models. Here there are also HCHO/CO emission ratios listed which could be helpful for the authors’ data interpretation (Rappenglück et al.: Radical Precursors and Related Species from Traffic as Observed and Modeled at an Urban Highway Junction, J. Air Waste Man. Assoc., 63:11, 1270-1286, doi: 10.1080/10962247.2013.822438, 2013)

Response: We agree with the reviewer that the findings of Rappenglück et al. (2013) are very important for evaluating HCHO emissions from automobiles. Although heavy-duty diesel
vehicles were present in the studied area, their contribution to HCHO emission inventory may be substantially less than that of industrial activities due to their relative small populations. We have inserted the following sentences into L88:

“A recent study by Rappenglück et al. (2013) suggests that currently available mobile emission models (e.g. MOBILE6 and MOVES) may significantly underestimate the HCHO emissions from vehicles and there is a non-negligible difference of HCHO emissions between light-duty and heavy-duty diesel vehicles.”

5) L187-188: Is this statement about potential future application of the instrument of relevance for this paper?
Response: Yes, this is a future application of the PTR-ID-CIMS. The purpose of this statement was to address the advantages of the PTR-ID-CIMS design, which may enable the PTR-ID-CIMS not only to do VOC measurements but also to be modified for other applications.

6) L193-195: This statement is not completely correct, as the authors cannot exclude that other sources than industry sources might have impacted their measurement site.
Response: We have modified the sentence as (L207):

“In this work, we focus on the measurement and analysis of VOC emissions in the YRD region using the PTR-ID-CIMS, especially from industry-related sources.”

7) L201: Is this statement about on-going activities of relevance for this paper?
Response: We agree with the reviewer this sentence has little relevance for this paper and we have deleted the sentence from the manuscript.

8) L223-224: What is the standard deviation of each set of calibration? What is uncertainty of the fit in Fig. 3?
Response: The calibration results in Fig. 3 were based on calibrations conducted during the field measurement period and thus were used for humidity correction. To fully characterize the PTR-ID-CIMS performance, we have conducted laboratory HCHO calibrations under various RH conditions. Figure 5 shows the calibration results with RH ranging from 1.0% to 81.5%. The variations of the instrument sensitivity (NCPS per ppbv) ranged from a few percent to 17%. We have inserted the following sentences into the manuscript (L304):

“To fully characterize the humidity effects on its performance, the PTR-ID-CIMS was also calibrated under various relative humidity conditions (1.0%, 17.5%, 29.0%, 47.0%, 62.5% and 81.5%) using pure air as the carrier gas. The relative humidity of the VOC standards was achieved by passing the carrier gas through a water bubbler similar as the one used in Zheng et al. (2015). The results are shown in Fig. 5. Based on three times the standard deviation of the background signals, the PTR-ID-CIMS detection limit (DL) of HCHO varied from 0.9 ppbv for dry condition to 2.4 ppbv for 81.5% RH at room temperature. The variations of the instrument sensitivity (NCPS per ppbv) ranged from a few percent to 17%. We also
determined the calibration-to-calibration DL variation at different RH levels to be less than 16% for RH < 81.5%. Therefore, the instrument precision for HCHO measurements was estimated to be < 18%, including the 1% uncertainty associated with the HCHO standard concentrations.”

9) L244-245: What were the mixing ratios of the VOC target compounds in the VOC standard?
Response: The mixing ratios of the VOC target compounds in the VOC standard are on the order of a few hundreds of ppbv with an uncertainty of < 5%, e.g. the mixing ratios of benzene and toluene were 208 and 157 ppbv, respectively. The following sentence has been included into L278:

“The mixing ratios of the target VOCs inside the cylinder are on the order of a few hundreds of ppbv with an uncertainty of < 5%, e.g., the mixing ratios of benzene and toluene were 208 ppbv and 157 ppbv, respectively.”

10) L251-252: Why do the authors make calibrations under dry conditions, if the real ambient sample would not be dry?
Response: We agree with the reviewer that completely dry condition will not be encountered in this work. However, in order to fully characterize the performance of the PTR-ID-CIMS, it is necessary to perform calibrations under various humidity conditions, including dry conditions. We have inserted the following sentences into the manuscript (L304):

“To fully characterize the humidity effects on its performance, the PTR-ID-CIMS was also calibrated under various relative humidity conditions (1.0%, 17.5%, 29.0%, 47.0%, 62.5% and 81.5%) using pure air as the carrier gas. The relative humidity of the VOC standards was achieved by passing the carrier gas through a water bubbler similar to the one used in Zheng et al. (2015). The results are shown in Fig. 5. Based on three times the standard deviation of the background signals, the PTR-ID-CIMS detection limit (DL) of HCHO varied from 0.9 ppbv for dry condition to 2.4 ppbv for 81.5% RH at room temperature. The variations of the instrument sensitivity (NCPS per ppbv) ranged from a few percent to 17%. We also determined the calibration-to-calibration DL variation at different RH levels to be less than 16% for RH < 81.5%. Therefore, the instrument precision for HCHO measurements was estimated to be < 18%, including the 1% uncertainty associated with the HCHO standard concentrations.”

11) L268-280: The calibrations for HCHO, benzene and toluene were mostly done in mixing ratios ranges significantly higher than those observed in ambient air. How do the authors know that this calibration would still be valid for the lowest dynamic range of the instrument?
Response: Ideally, we want to calibrate the PTR-ID-CIMS with VOC standards coving the ambient concentration range. The concentrations of VOC standards ranged from a few ppbv to a couple dozens of ppbv covering ~1 dynamic range, which in fact overlapped with the ambient VOC level observed in this work, especially in the case of aromatics. Since the
sensitivity of PTR-ID-CIMS to HCHO was relatively lower than to aromatics, we applied higher HCHO standard concentrations, which were commonly used in other works (Vlasenko et al., 2010; Warneke et al., 2011). Theoretically, the instrument response to VOCs will hold linearity when the VOC concentration decreases, since the reagent ion (H$_3$O$^+$) concentration will still be several orders of magnitude higher than product ions. However, when VOC concentration increases to a certain level, depletion of H$_3$O$^+$ due to ion-molecular reactions cannot be ignored and the linearity will not hold anymore. Therefore, within the VOC concentrations encountered in this work, we were confident the PTR-ID-CIMS will response to the VOCs linearly.

12) L272-276: Does the uncertainty value stated by the author include the uncertainty of the VOC standard and its dilution? Does it also include the uncertainty arising from the humidity effect?
Response: We determined the HCHO standard concentration by DNPH cartridge measurements and three independent measurements agreed with each other within 1% (see section 2.4). Benzene and toluene standards concentration were taken as that given by the manufacturer with an uncertainty of < 5%. The humidity effects were further investigated by performing laboratory calibrations under various humidity conditions. The uncertainties associated with VOCs standard concentration have been accounted for in the reported uncertainty values (see response to comment 13). We have inserted the following sentences into the manuscript (L304):

“To fully characterize the humidity effects on its performance, the PTR-ID-CIMS was also calibrated under various relative humidity conditions (1.0%, 17.5%, 29.0%, 47.0%, 62.5% and 81.5%) using pure air as the carrier gas. The relative humidity of the VOC standards was achieved by passing the carrier gas through a water bubbler similar to the one used in Zheng et al. (2015). The results are shown in Fig. 5. Based on three times the standard deviation of the background signals, the PTR-ID-CIMS detection limit (DL) of HCHO varied from 0.9 ppbv for dry condition to 2.4 ppbv for 81.5% RH at room temperature. The variations of the instrument sensitivity (NCPS per ppbv) ranged from a few percent to 17%. We also determined the calibration-to-calibration DL variation at different RH levels to be less than 16% for RH < 81.5%. Therefore, the instrument precision for HCHO measurements was estimated to be < 18%, including the 1% uncertainty associated with the HCHO standard concentrations.”

13) L277-280: What was the uncertainty of the benzene and toluene measurements?
Response: Based on laboratory calibrations with RH ranging from 1% to 81%, we found benzene and toluene calibrations showed no humidity effects and the variation of instrument sensitivities (NCPS per ppbv) to benzene and toluene were respectively less than 3.7% and 6.0%. Given the 5% uncertainty associated with the VOC standard concentration, we conclude the uncertainties of the benzene and toluene measurements were less than 8.7% and 11.0%. We have inserted the following statement into the manuscript (L322):

“In a similarly way as the case of HCHO, we determined the uncertainties of benzene and
toluene measurements were less than 8.7% and 11.0% (including the 5% uncertainty associated with the VOC standard concentration) in this work.”

14) L326-327: The authors should include quantitative statements about the individual correlation among the different species.
Response: Although all these air pollutants were found within the plumes arrived at the site, during the entire measurement period, the overall correlation coefficients ($R^2$) among individual species were found ranging from 0.2 ~ 0.4, with the best correlation observed between benzene and HCHO. However, much better correlation among individual species can be found within individual plumes. We have included the following statement in L366:

“On the other hand, positive correlations ($R^2 = 0.2~0.4$) were found among HCHO, aromatics, and CO and significantly better correlations ($R^2 = 0.4~0.6$) among individual species could be found within individual plumes, which strongly suggest that primary emissions were responsible for the observed high concentrations of HCHO.”

15) L340-341: I think any solar radiation would support secondary HCHO formation. It is not restricted to "subtropical" solar radiation. Also why would the solar radiation in Tijuana be stronger than in Nanjing, if both locations are about the same latitude?
Response: We have included the solar radiation data in Fig.5. Evidently, HCHO plumes do not correlate with solar radiation very well. The reviewer is right that Nanjing and Tijuana have similar latitudes, but the Cal-Mex occurred in May and June 2010 while this study occurred in April 2010. We revised this sentence as (L406):

“Assisted by the stronger subtropical solar radiation in May/June 2010 during Cal-Mex than in April 2015 during this study, stronger solar radiation can result more HCHO formation from VOC oxidation in Tijuana.”

16) L346-351: As the sampling time for DNPH cartridges varied from 0.6~2 hours the authors want to include the standard deviation of the PTR-ID-CIMS measurements during these time frames in Figure 6.
Response: As suggested by the reviewer, error bars of one standard deviation of PTR-ID-CIMS data points were added to Fig. 9.

Figure 9. Linear correlation between PTR-ID-CIMS and DNPH measurements of HCHO.
The blue trace represents the 1:1 guideline. The black solid line is the linear fit based on orthogonal distance regression. The dashed line and the dot-dashed line denote the 95% confidence interval band and the 95% prediction band, respectively. The error bars indicate one standard deviation of PTR-ID-CIMS data within the corresponding DNPH sample collection time.

17) L361: What do the authors mean by "In fact many flares could be visually identified within the industrial zone" while the authors mention a bit further down: "However, due to the complexity and limited accessibility of the industrial activities, pinpoint the individual emission source of HCHO was virtually impractical in this study. Further detailed investigations within the industrial zone are needed to fully comprehend industrial VOCs emissions" (L408-411)? Isn't this a contradiction?
Response: The purpose of the second statement was to point out that in the industrial zone there might be other primary sources of HCHO, which cannot be easily identified as flares and thus have not been fully characterized. We have revised the statement as (L544):

“The relatively weak correlation of $R^2 = 0.52$ was most likely due to the complexity of petrochemical industry. Many organic synthesis processes may also lead to HCHO emissions. These tracers used in this work may not represent all processes that contributed to HCHO emissions. More studies are needed to further investigate the potential primary sources of HCHO in the industrial zone and to fully characterize industrial VOCs emissions.”

18) L364-367: Actually there are wide ranges of benzene/toluene ratios observed in traffic emissions. Hoque et al (2008) themselves mention benzene/toluene ratio ranges from various cities from 0.1-0.5. It is known that those ranges depend on traffic fleet composition (e.g. gasoline vs diesel driven engines). The authors should report the typical traffic fleet benzene/toluene ratio for Nanjing and based on this reference discuss the observed deviations and define their origins.
Response: To our best knowledge, there have been no roadside measurements or tunnel studies conducted in Nanjing. Therefore, we cannot obtain the benzene/toluene ratio for Nanjing. However, in this work the benzene/toluene ratio within CO plumes were determined to be 1.7±1.0, significantly higher than literature values. On the other hand, it is well known that both benzene and toluene are widely used in petrochemical industry. Especially, benzene is the basic material for many chemical syntheses. Therefore, we concluded that these primary HCHO measured in this work were emitted from processes relevant to petrochemical industry.

19) L367-372: This is confusing. Why can benzene and toluene be used as tracers for petrochemical industry, when they are also emitted in combustion processes as CO?
Response: Indeed, benzene, toluene and CO can all be found in vehicle exhausts. However, the benzene/toluene ratio within CO plumes (1.7±1.0) were significantly higher than the signature ratios obtained for various vehicles. Moreover, the cluster of petrochemical facilities in Nanjing was considered one of the largest in China and benzene and toluene are mass-produced and utilized in these petrochemical facilities. Therefore, most of the benzene
and toluene observed in this work were not likely co-emitted with CO by vehicles. Accordingly, we choose CO as tracers of combustion-related sources and benzene and toluene as tracers of petrochemical processes that may also lead to formaldehyde emissions. We have revised the manuscript as (L481):

“Although it is well known that HCHO and CO were present in vehicle exhaust, the benzene to toluene ratio within CO plumes were determined to be $1.7 \pm 1.0$ and significantly higher than 0.5, an indicator of automobile emissions (Hoque et al., 2008), suggesting that these air masses were not dominated by vehicle exhaust and thus most of the benzene and toluene observed in this work were not likely co-emitted by vehicle exhausts.”

20) L372-373: "...O3 was mostly from secondary formation.... What other sources for O3 exist?
Response: We have removed “mostly” from the sentence.

21) L395-396: The authors report a correlation of $R^2=0.52$, which is actually significantly lower than mentioned in other publications using other tracers. Do the authors have a suggestion why this is the case?
Response: We think this relatively weak correlation of $R^2 = 0.52$ was most likely due to the unknown complexity of petrochemical industry. Many organic synthesis reactions may also lead to HCHO emissions. The tracers used in this work may not represent all the processes that contributed to HCHO emissions. More studies are needed to further investigate the potential primary sources of HCHO in the industrial zone. We have included the following statement in the manuscript (L544):

“The relatively weak correlation of $R^2 = 0.52$ was most likely due to the complexity of petrochemical industry. Many organic synthesis processes may also lead to HCHO emissions. These tracers used in this work may not represent all processes that contributed to HCHO emissions. More studies are needed to further investigate the potential primary sources of HCHO in the industrial zone and to fully characterize industrial VOCs emissions.”

22) L396-403: How do the authors know that the relative contributions to the observed HCHO listed for CO, benzene, and toluene come from industrial sources exclusively?
Response: We agree with the reviewer that we cannot exclude the other possible primary HCHO sources, such as vehicles exhausts. However, given the magnitude of industrial activities within the studied area, we concluded that industrial activities were the dominant HCHO sources. In theory, CO and aromatics also represented industry related vehicle emissions in this work, which may account for a significant portion of the vehicle fleet emission in the studied area. However, we cannot specify the portion of vehicles emission based on the available tracers. We have included the following statement in the manuscript (L539):

“In theory, CO and aromatics also represented industry related vehicle emissions in this work, which may account for a significant portion of the vehicle fleet emission in the studied area.
To specify the portion of vehicles emission cannot be achieved by the current available tracers."

23) L407: What are "irrelevant air pollutants"?
Response: We agree with the reviewer this statement is not necessarily true. We have revised it as (L542):

“The positive correlations between HCHO and these aforementioned air pollutants established a statistical link between HCHO and industrial activities.”

24) L423-425: What were the R2 values for the individual correlations of CO, benzene, and toluene with HCHO within plumes?
Response: We found that the individual correlations ($R^2$) of CO, benzene, and toluene with HCHO within plumes varied from 0.4 to 0.6, indicating that these air pollutants were not necessarily co-emitted from a single source. From the case study of April 18, it is evident that all these air pollutants are found substantially elevated in the plume but present different variation profiles with periods significantly longer than the measurement duty-cycle (~3 min). These fine structures in pollutant time-series indicate that these species were originated from the area but might be associated with different industrial activities. The following statement has been included in L424:

“It is evident that all air pollutants shown in Fig. 8 were substantially elevated in the plume but present different variation profiles with periods significantly longer than the measurement duty-cycle (~3 min). These fine structures in pollutant time-series indicate that these species were originated from the same area but might be associated with different industrial activities.”

Figure 8. Time series of wind direction (WD) and wind speed (WS) (Panel a), m/z 37/19 ratio and RH (Panel b), $O_3$ and CO (Panel c), m/z 79 and m/z 93 (Panel d), and m/z 31 signal (Panel e) on April 18, 2015. The dips in panel d and e are the periods when background...
checks were made.

25) L430-431: How high were the benzene/toluene ratios?
Response: During the field measurements, benzene to toluene ratio was determined to be $1.7 \pm 1.0$, which was substantially higher than literature values obtained from vehicle emissions. We have revised the sentence as (L481):

“Although it is well known that HCHO and CO were present in vehicle exhaust, the benzene to toluene ratio within CO plumes were determined to be $1.7 \pm 1.0$ and significantly higher than 0.5, an indicator of automobile emissions (Hoque et al., 2008), suggesting that these air masses were not dominated by vehicle exhaust and thus most of the benzene and toluene observed in this work were not likely co-emitted by vehicle exhausts.”

26) Figure 5: - radiation time series should be included. What is the background value for CO? It looks like around 1 ppm. Is this true?
Response: The radiation time series has been included in Fig. 6. Background CO concentration in China is significantly higher than that observed in the United States. Chan and Yao (2008) have summarized CO observation from 1999 to 2005 in Guangdong China. Figure 7c in Chan and Yao (2008) clearly shows that CO varies around 2 mg m$^{-3}$, corresponding to $\sim 1.6$ ppmv in mixing ratios.

![Figure 6](image_url)

**Figure 6.** Time series of meteorological parameters (wind, RH, T, and solar radiation) (Panel a, b and c), trace gases (O$_3$ and CO) (Panel d), benzene (C$_6$H$_6$) and toluene (C$_7$H$_8$) (Panel e), and HCHO (Panel f). The black dots in Panel e are DNPH cartridge measurements of HCHO.
References:


