

Interactive comment on “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” by Yan Ma et al.

Anonymous Referee #1

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Ma et al. "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"

* General comments

Manuscript amt-2016-194 by Ma et al. presents recent measurements of air pollutants in the Yangtze-River-Delta (YRD) region of China over a two week period. During westerly winds the measurement site is closely downwind of an industrial area. Focus is the description of a (newly built?) PTR-ID-CIMS and the demonstration of its capabil-

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ity to quantify high ambient concentrations of formaldehyde (HCHO) and other VOCs. The instrument is described in detail. The instrument's performance might likely suffice – albeit with high LOD and poor time resolution – to identify heavy HCHO pollution events. By means of multiple-linear regression the authors show that 52% of the variability of HCHO can be explained by linear combination of measured concentrations of O₃, CO, benzene and toluene. From this analysis they conclude that HCHO at the measurement site is largely primarily emitted, which is an interesting result.

The manuscript is well structured, easily comprehensible and well written. The characterization of the performance of the instrument needs to be more detailed (humidity dependence of background and LOD, uncertainty of quantification (precision and accuracy) bases on a range of humidities expected in the ambient sample) and fairly compared to other instruments and to characterizations of similar methods in the literature (e.g. as published in AMT). The statements drawn from the method comparison (PTR vs DNPH) need to be statistically substantiated.

Even though the performance of this PTR instrument with regards to HCHO might not exceed those presented in the literature the authors are encouraged to present their instrument characterization in a quantitatively comparable way (and actually make the comparison). Based on a more thorough characterization they should be able to demonstrate that this instrument is suitable for the quantitative characterization of pollution episodes – the ambient trace gas data they present are in itself a valuable contribution.

* Specific comments

- Introduction:

In the light of this manuscript focusing on a measurement technique for HCHO the introduction of and performance comparison with alternative methods (or identical methods but different instruments) is too superficial. E.g. Vlansenko et al. (2010) and Warneke et al. (2011) detail the performance of their PTR-MS approach to which this instrument

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could be compared. New LIF instruments (e.g. Cazorla et al. 2015) outperform instruments based on Hantzsch process, CI-MS, or DNPH cartridges regarding the detection limit on short very short sampling periods (e.g. 10Hz). The performance of the method presented in this manuscript should be quantitatively compared.

- Experimental Methods:

L132: "The site was fairly away from local highways...". According to openstreetmap highway G40 passes only a few km to the west of NUIST campus, and G205 is even closer (depending on the exact location of the measurement), which does not seem to be reflected by the text.

L173+: Backgrounds. The authors state that m33 signals are the sum of protonated methanol and 16O17O+ as well as O2H+. They conclude that zeroing by means of redirecting the sample gas through a catalytical converter produces differential signals ($m33_{\text{ambient}} - m33_{\text{cc}}$) that are directly related to the density of protonated methanol and thus to the methanol sample concentration. This is only true if the other contributing m33 ion counts do not get altered by the zeroing procedure (e.g. by slightly changing humidity). The authors either need to demonstrate that the background contributors do not change due to the zeroing procedure or at least that humidity (thus m39/m21) in the drift tube does not change. This should be in the data. More importantly – since this manuscript focuses on HCHO – a similar demonstration needs to be presented for m31. A very strong humidity dependence of the m31 background signal is expected (see Fig 3c in Warneke et al., 2011).

L197+: The QMS was set to sample for 2s at each of the 40+ mass channels, but then there are 2s in between the sampling of consecutive mass channels – does the quadrupole filter / HF generator really take 2s to tune from one channel to the next? Please, comment on this.

L251+: The use of N2 for dry calibrations will change ion mobilities and KE compared to air and thus will not produce comparable results.

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L270+: Calculating empirical standard deviations on sample sizes of $N=3$ may cause considerable uncertainties. What was the (apparent) calibration-to-calibration LOD variability?

L272+: Calibrations under conditions that are otherwise identical to those encountered during ambient measurements are part of the quantification process. Apart from the above mentioned problems with changing buffer gas compositions (N2 vs air) sensitivities of HCHO under completely dry conditions are much higher than under typical ambient conditions (see Fig 5 in Vlasenko et al. 2010 or Fig 3b in Warneke et al. 2011). A precision determined under dry conditions is meaningless for the performance of the instrument under ambient sampling conditions. Please, evaluate the precision based on the calibrations under varying humidity conditions and compare them with performance characterizations in the literature.

L287+: Please, substantiate (data or literature) that varying O3 concentrations (0-140ppbv; Fig 5) in a complex mix of organic trace gases and aerosol flowing through a potassium iodide cartridge does not produce considerable carbonyl interferences. Results and Discussion:

L313+: This reviewer cannot discern wind conditions from the quiver plot in Fig 5. Please, replace the representation in a more suitable way (e.g. wind speed and direction time series).

L328+: "In addition, all heavy pollution episodes... were associated with easterly wind or nearly calm conditions". Please, find a way of presenting the data so that the readers can convince themselves of this finding. I suggest a rose-plot of HCHO mixing ratio distributions separated into e.g. 30deg wind sectors. Calm conditions (e.g. $u < 0.1$ m/s) could be treated separately if needed. The same for CO, aromatics and O3.

L335: Temporal variations of HCHO: The apparent proximity to significant point sources of pollutants leads to the expectation of strong variabilities of these pollutants. The limited duty cycle of the VOC measurements ($\sim 2\text{s}/180\text{s}$) make it likely

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that the measurement does not sufficiently capture these variabilities. The observed covariances of HCHO with other VOCs are likely underestimated due to the lags time between the sequentially measured mass channels because these time lags may be large compared to the characteristic time scale of the VOC variabilities. This is detrimental to the multi-linear regression. Please, discuss how an improved measurement scheme (better duty cycle) and/or different mass spec technology (e.g. TOF-MS) would affect the multi-linear regression analysis as well as the LOD.

L342+: HCHO comparison: How was the linear fit calculated? A fair comparison between two methods should use orthogonal distance regression (ODR) rather than least square regression (LSR). The former appoints measurement uncertainties to the two datasets according to their performance tests (or a priori knowledge), the latter implicitly assumes that data plotted on the y-axis has uncertainties and the data plotted on the x-axis is precise.

L348: Calculate confidence intervals for the fit parameters to test whether the slope, which differs from 1, and the bias are truly accounted for by the combined measurement uncertainties. If, under the consideration of the quantified measurement uncertainties, the slope and/or the bias are significantly different from 1 and 0, respectively, one must assume a systematic discrepancy. We won't know until the analysis is done (with measurement uncertainties quantified under ambient conditions; see comment to L272+ above).

L381+: "...the background level of HCHO was constrained to 1ppbv to represent the regional conditions." It is rather arbitrary to pick a background level from measurements performed 4 years earlier in a different season and at a different location. Did an unconstrained background level cause any of the parameters to turn negative? If so then non-negative matrix factorization might help to find the best solution. Or one could run a series of multiple-linear regressions over a range of (constrained) background levels and find the background level that maximizes R². A different background level might result in a linear combination that explains more than 52% of the HCHO variabil-

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ity. However, insufficient capturing of the concentration variabilities due to limited duty cycle and insufficient capturing of covariances due to lag-times (see L335: Temporal variations of HCHO, above) as well as additional variability of HCHO may strongly limit the percentage of explained variability of HCHO. The source-apportionment needs to be discussed in this light.

L394+: The linear regression between measured and modelled HCHO variability (also presented in (Fig 8) needs statistical treatment to allow for a quantitatively substantiated statement that measured and modelled HCHO variability agree reasonably (see comment L348 above).

Fig 3: The fit curve of the water vapor concentration dependency of the HCHO sensitivity does not show a theoretically expected 4-5 fold change of the sensitivity (compare to Fig 5 in Vlasenko et al. 2010). A too narrow humidity range in the test might partly be the reason that the 'true shape' is not captured by the fit. Please, comment on this. In any case, extrapolation of the humidity dependence of the HCHO sensitivity beyond the tested humidity range is not permissible and might limit the applicability of the calibrations to the ambient data set.

Fig 5: Replace the quiver plot in the top panel by time series of wind speed and direction. Add vertical grid lines to improve comparability of the time series. Potentially add a rose-plot of HCHO sector distributions (as separate figure)

Fig 6: Plot also 1:1 line and confidence ranges of the linear fit to test slope and bias for statistical significance.

Fig 8: Plot also 1:1 line and confidence ranges of the linear fit to test slope and bias for statistical significance.

Technical comments L127: Please, add coordinates of the sampling location. Reproduce with permission or refer explicitly to Figure 1 in Zheng et al. (2015 a). L331: "...calm with light easterly wind." Was it calm (i.e. no wind) or were their light easterly

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winds?

Vlasenko, A., Macdonald, A. M., Sjostedt, S. J., and Abbatt, J. P. D.: Formaldehyde measurements by Proton transfer reaction – Mass Spectrometry (PTR-MS): correction for humidity effects, *Atmos. Meas. Tech.*, 3, 1055-1062, doi:10.5194/amt-3-1055-2010, 2010.

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