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Atmospheric Measurement Techniques Discussions

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 #2

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This is an interesting paper about the application of a PTIR-ID-CIMS in an air quality application, here in looking into HCHO emissions from an industrial zone in Nanjing, China. Overall, the paper shows some valuable material and associated discussion. A major issue is the selection of the tracer species benzene and toluene. I understand that those are species nicely measured by the PTIR-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. Bearing this in mind it appears necessary to perform a more stringent data screening. 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.

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?

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 Rappengluck 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 (Rappengluck 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)

L187-188: Is this statement about potential future application of the instrument of relevance for this paper?

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.

L201: Is this statement about on-going activities of relevance for this paper?

L223-224: What is the standard deviation of each set of calibration? What is the

uncertainty of the fit in Fig. 3?

L244-245: What were the mixing ratios of the VOC target compounds in the VOC standard?

L251-252: Why do the authors make calibrations under dry conditions, if the real ambient sample would not be dry?

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?

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?

L277-280: What was the uncertainty of the benzene and toluene measurements?

L326-327: The authors should include quantitative statements about the individual correlation among the different species.

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?

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 PTIR-ID-CIMS measurements during these time frames in Figure 6.

L361: What do the authors mean by "In fact many flares could be virtually 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 de-

tailed investigations within the industrial zone are needed to fully comprehend industrial VOCs emissions" (L408-411)? Isn't this a contradiction?

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.

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?

L372-373: "..O3 was mostly from secondary formation..". What other sources for O3 exist?

L395-396: The authors report a correlation of R2=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?

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?

L407: What are "irrelevant air pollutants"?

L423-425: What were the R2 values for the individual correlations of CO, benzene, and toluene with HCHO within plumes?

L430-431: How high were the benzene/toluene ratios?

Figure 5: - radiation time series should be included.

- What is the background value for CO? It looks like around 1 ppm. Is this true?

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