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Atmospheric Measurement Techniques Discussions

Interactive comment on "Understanding the ability of low-cost MOx sensors to quantify ambient VOCs" *by* Ashley M. Collier-Oxandale et al.

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COMMENT: "This manuscript presents a field evaluation of two different metal oxide (MOx) sensors for volatile organic compound (VOC) detection, comparing the sensor signals with speciated VOC measurements from a proton-transfer mass spectrometer (PTR-MS). Measurements were made for approximately 3 weeks as part of a larger air quality study at the Platteville Atmospheric Observatory, Colorado, which is in close proximity to extensive oil and gas activity. The analysis is detailed and well written, and the work is a good addition to the available literature on these devices."

RESPONSE: The authors appreciate the overview provided by the reviewer and would like to thank the reviewer for their insightful comments, which helped to strengthen this

work.

COMMENT: "My main comment on the work is how applicable the conclusions are to more typical environments. The proximity to large emissions of VOCs from oil and gas activity makes for a very favorable environment for the MOx sensors being evaluated, due to the elevated VOC mixing ratios and the large dynamic range observed. The authors suggest that these technologies could be used more widely for monitoring public health exposure, however, even in polluted urban environments mixing ratios of VOCs can be at least an order of magnitude lower than observed in this study. For example, Warneke et al. (2013) show benzene data from Los Angeles, from both ground and airborne measurement platforms, where all measurements are below the suggested 0.5 ppb lower limit for data exclusion proposed by the authors in Section 3.1.4. It would be very useful for the reader if the authors commented more on this and repeated some of the comparisons with the PTR-MS for only data in a range that would be comparable with a more typical urban environment."

RESPONSE: The authors agree with the reviewer that this is an important point. To address this comment, a discussion of the potential for elevated levels of VOCs in oil and gas production areas and how this may compare to typical urban areas has been added to Section 2.1. Additional discussion of sensor performance considering the levels of VOCs observed in this study as compared to what might be seen in other environments has also been added to Section 3.1.4. As per the reviewer's suggestion, the authors also ran the regression analysis for Models 1 and 2 for benzene, utilizing only values under 0.75 ppbV. The resulting figures are available in the Supplemental Materials (Supplemental Figure S3, also attached here as Fig. 1) and a comment regarding this additional analysis has been added to the text. Essentially, correlation to the reference data remains high – suggesting that it may be possible to train models for lower detection limits. However, it's also possible that the benzene signal is being enhanced by the other well-correlated aromatics that the sensors seem well-suited to detect. Further study will be necessary to confirm whether lower detection limits are

possible to achieve in field settings.

COMMENT: “Page 9 lines 15:23: What was the motivation behind choosing ppbC instead of ppbV for the summed compound comparisons? In theory which unit gives better agreement should depend on the mechanism of the sensor interaction with the compounds. Unless the sensor converts a fixed fraction of a VOC to CO2 and H2O does the use of ppbC not weight the signal from the larger compounds more than the smaller ones? The authors should comment on this, as if the use of ppbV instead of ppbC changes the agreement shown in Figures 2-5 it would suggest something about the sensor sensitivities to different VOCs in the groupings.”

RESPONSE: This is an important observation and was a point of discussion among the authors as well. The authors chose to use ppbC, as opposed to ppbV, as it seemed like the more appropriate way to sum the VOC signals because it does take in to account the differences in individual VOC compound sizes. Given the sensor operating principles (i.e., a chemical reaction on the sensor surface), we would expect the extent of the sensor response to vary based on the size as well as the make-up of the VOC compound. When we fit to a summed ppbC signal, we are fitting to a signal that incorporates some of these important differences. Furthermore, the authors did begin by summing the ppbV values for each VOC species and running the same analysis. The result was no change for the BTEX summed signal – likely due to the fact that these signals were all highly correlated, so the magnitude of the signal changed but not the overall trends. There was, however, a slight improvement for Model 1 for the summed VOC signal when the ppbC values were used as opposed to the ppbV values. This improvement was likely due to the ppbC sum being weighted for the larger BTEX compounds. This signal placed a smaller emphasis on the oxygenated VOC compounds, which as suggested by the results presented in Figure 9, the sensor may be less well-suited to predict. The authors have added further rationale for this choice to Section 2.4 in the hopes of clarifying this decision for readers.

COMMENT: “Table 3: More details required on why the models used were chosen.

Was the formulation of these models informed by experiments or are they the best performing from a larger selection of randomly selected models?”

RESPONSE: A brief explanation has been added to Section 2.4 in an attempt to clarify why these models were selected. The reasoning was to begin with models typically used to calibrate low-cost air quality sensors, as this is a more preliminary look at VOC sensors in the field. Additional predictors were added to attempt to address issues with the models (e.g., patterns in the residuals). These added predictors were found through trial and error.

COMMENT: “Figures 2-5: Although the bootstrapping shown in Fig. 9 illustrates well the sensitivity of the model performance to the choice of training and test data, a statement in Sect. 3.1 on how sensitive model performance is to the choice of training data would be informative.”

RESPONSE: When this same analysis was run displaying the model performance results for the training data rather than that testing data, it produced similar trends. The main difference was improvements to the performance statistics (i.e., a higher R-squared and a lower RMSE values). While the authors agree that model performance with respect to training data is an important consideration, we are not sure this study provides the best dataset to examine this issue, given the relatively short length of the deployment (e.g., it does not span any seasonal changes) and that there are no periods where the site was obviously subject to a distinctly different mixture of VOCs, thus we have not added any figures at this point. That being said, the authors would be happy to add the results of this analysis with respect to different selections of training data to either the main paper or the appendix if it would be valuable to readers.

COMMENT: “Page 11 line 11: Proton-transfer within the PTR-MS is also a chemical reaction. The slower time response could be due to a slower surface reaction on the MOx sensor but more likely due to the diffusion control of gas sampled to the sensor surface.”

RESPONSE: The authors agree that diffusion is an important factor in the sensor's exposure and response to the target pollutants and the statement has been reworded to highlight it's role.

COMMENT: "Figure 7: The authors should explain the reason for the choice of values held constant (0.75 and 0.05 ppb for benzene, 19 and 38 ppb for summed aromatics, and 2.5 and 3 ppm for methane). The authors need to explain the reasoning behind choosing these values and the effect it has on the conclusions of this section of the paper."

RESPONSE: In order to address this comment an explanation as to why the 75th and 95th percentile values were chosen has been added to the text prior to Figure 7. Then, following Figure 7, the discussion of the results depicted was expanded to examine the implications of these results for sensor use. In short, the reason for this selection was based on the assumption that a well-suited use of low-cost VOC sensors, at least for now, is for the detection of relatively large enhancements above background or typical levels. The results of the analysis depicted in Figure 7 have implications for use of sensors for in particular applications.

COMMENT: "SI: SI plots require more descriptive captions."

RESPONSE: The authors have expanded the descriptions in the captions for all the plots in the Supplemental, in an effort the clarify these additional materials.

References Warneke, C., et al. (2013), Photochemical aging of volatile organic compounds in the Los Angeles basin: Weekday-weekend effect, J. Geophys. Res. Atmos., 118, 5018–5028, doi:10.1002/jgrd.50423.

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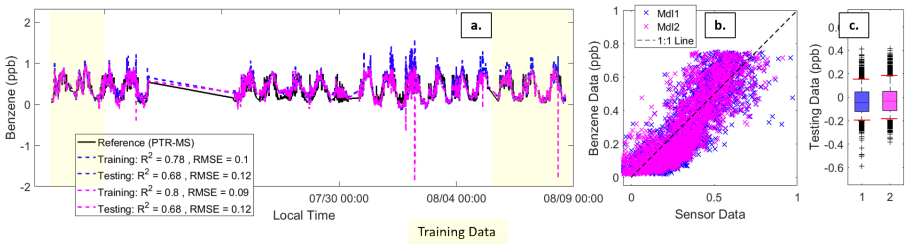

Fig. 1.