Responses to Community' Comments on Manuscript EGUSPHERE- 2024-1325

(Molecular and seasonal characteristics of organic vapors in urban Beijing: insights from Vocus-PTR measurements)

Thanks for the comments. We have addressed them in the following paragraphs and made the corresponding changes in the revised manuscript. The comments are shown in blue italic text, followed by our responses. Changes in the revised manuscript are highlighted and presented as "quoted underlined text" in our responses.

1. In Figure S3, the transmission efficiency of C8 aromatics (C8H11+) is greater than 1. Does the authors have any explanation for this?

Response: We have modified the method of determining the sensitivity and recalculate the transmission efficiency.

Firstly, we used more compounds to determine the linearity. As mentioned in Table S2, we used 2 cylinders of calibration gas to calibrate the Vocus-PTR during different observation periods. Although the sensitivities of calibration gases varied across different observation periods, the relative sensitivities to toluene were comparable. We plot the sensitivities of the 2 cylinders of calibration gas together in Figure R1a. The y axis is the normalized sensitivity to toluene, and the x axis is their corresponding k_{PTR}. The black squares represent calibration gases from cylinder 1, and the black dots represent calibration gases from cylinder 2.

Then, we refitted the linearity using $C_7H_9^+$, $C_8H_{11}^+$, $C_9H_{13}^+$, $C_{10}H_9^+$, and $C_5H_9O_2^+$, with the result of the linear fit shown by the black line in the figure. The equation is y = 0.43x+0.23 with an R^2 of 0.87. Note that the sensitivity of toluene needs to be multiplied when using the equation. The species with gray labels have lower sensitivities due to the influence of transmission, so it is necessary to correct for the transmission efficiency.

Thirdly, we calculated the transmission efficiency based on these calibration gases, except for $C_5H_9^+$, $C_{10}H_{17}^+$ and $C_{11}H_{11}^+$, as shown in Figure R1b. The cut off is around 40, we have added this information in the main text. We revised this part in the main text.

For the new transmission efficiency, the average transmission efficiency of C8-C10 aromatics is slightly above 1, but this is reasonable within the margin of error.

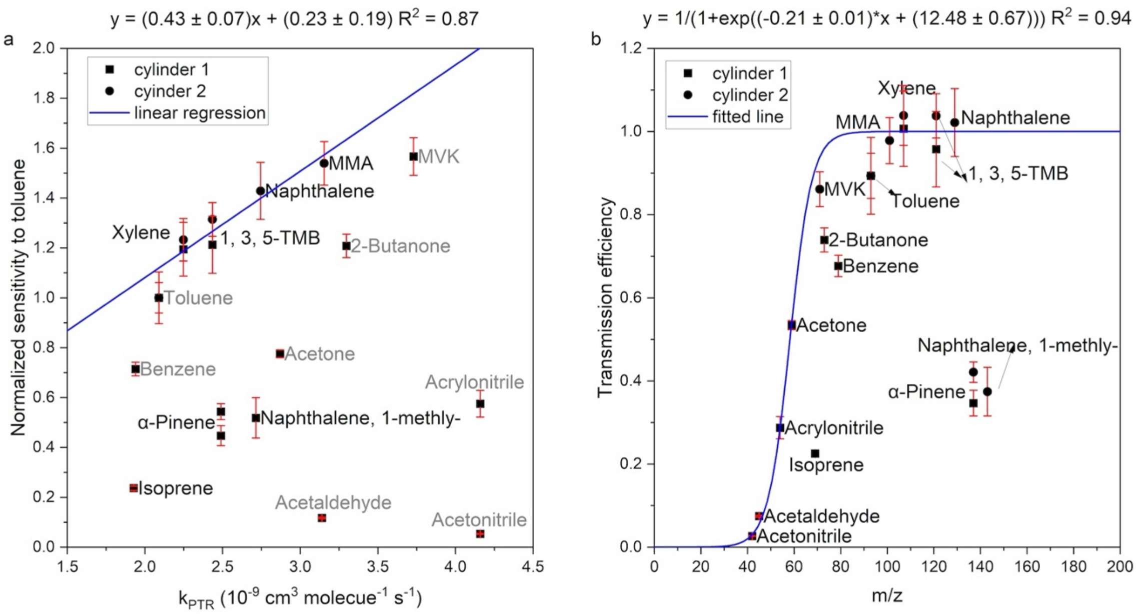

Figure R1 (also shown as Figure S3 in the supporting information). Calibration results of mixed calibration gases. (a) The scatter plot of the sensitivities of mixed calibration gases and their k_{PTR}. The blue line is the linear fitting of $C_7H_9^+$, $C_8H_{11}^+$, $C_9H_{13}^+$, $C_{10}H_9^+$, and $C_5H_9O_2^+$, respectively. The error bar refers to standard deviation. The sensitivities of species with gray labels are affected by transmission. (b) The transmission efficiency of mixed calibration gases. The blue line is the fitted transmission efficiency curve based on that of mixed calibration gases. The error bar refers to standard deviation.

[Line 200 to 216] Figure S3a shows the measured sensitivities of mixed calibration gases and their corresponding k_{PTR} values. The linear regression between kPTR and sensitivities was obtained based on sensitivities of $C_7H_9^+$, $C_8H_{11}^+$, $C_9H_{13}^+$, $C_{10}H_9^+$, and $C_5H_9O_2^+$ with an R^2 of 0.87. Sensitivities of other ions in mixed calibration gases may be influenced by transmission (ions labeled as gray) and fragmentation ($C_5H_9^+$, $C_{10}H_{17}^+$ and $C_{11}H_{11}^+$). The transmission efficiency of mixed calibration gases was calculated using sensitivities of mixed calibration gases, as shown in Figure S3b. The transmission efficiency of mixed calibration gases aligns well with the fitted transmission efficiency curve, except for $C_5H_9^+$, $C_{10}H_{17}^+$ and $C_{11}H_{11}^+$, which potentially experience fragmentation (fragmentation of measured ions are discussed below). For organic vapors without standards, their theoretical k_{PTR} were used to constrain sensitivities, while for organic vapors with no theoretical k_{PTR}, an average k_{PTR} of known species, 2.5×10-9 cm^3 $molecule^{-1}$ s^{-1} was used to constrain their sensitivities. The theoretical k_{PTR} of organic vapors are from previous studies (Zhao and Zhang, 2004; Cappellin et al., 2012; Sekimoto et al., 2017).

2. What were the Limit of detection (LoD) values of the VOCs containing more than 6 oxygen atoms?

Response: We calculated the 1 min LODs for both calibrated and uncalibrated compounds using zero-gas background measurements taken every 2 hours during the observation periods (as shown in Figure R2). The LODs were calculated as 3 times the standard deviation of the zero-gas background divided by the obtained sensitivity. Very few formulae of VOCs containing more than 6 oxygen atoms were detected in this study, and we group them together with VOCs containing 6 oxygen atoms. The LODs for VOCs containing 6 or more oxygens is 0.06 ± 0.04 ppt.

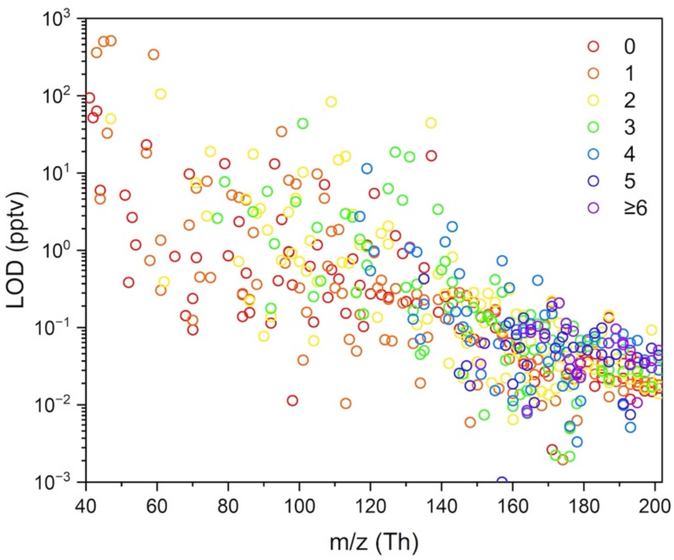

Figure R2 (also shown as Figure S4 in the supplementary). Average limits of detection (1 min) for detected compounds. Different colors refer to different oxygen number of compounds, as labelled in legend.