

Fig. 7. Time series of H<sub>2</sub>O (red), HDO (blue), N<sub>2</sub>O (wine), and CH<sub>4</sub> (green) mixing ratios measured on the Rice University campus during February 1-8, 2016.

Although slightly higher H<sub>2</sub>O vapor concentrations were detected by our sensor system at some intervals during the sampling period, there is a good relationship ( $R^2 = 0.98$ ) between the calculated and measured concentration levels for this species shown in Fig. 8. The HDO/H<sub>2</sub>O ratio, which provides insight of the processes and dynamics of water vapor in the atmosphere, exhibited small variability during the monitoring period with levels between  $2.4 \times 10^{-4}$  and  $3.3 \times 10^{-4}$  and an average value of  $3 \times 10^{-4} \pm 1.9 \times 10^{-5}$ . This value indicates that the HDO mixing ratios are  $\sim 3000$  times smaller than H<sub>2</sub>O vapor mixing ratios, which is consistent with the expected abundance of this isotope [23]. In Fig. 7, the levels of N<sub>2</sub>O showed minor variability during the interval of monitoring, with mixing ratios ranging between 330 and 410 ppbv and an average mixing ratio of  $366 \pm 22$  ppbv. This value agrees with background levels reported previously for this gas species in the Houston area [2, 7]. The concentration of CH<sub>4</sub> ranged between 1.8 and 5.3 ppmv with an average of  $2.06 \pm 0.32$  ppmv, consistent with typical urban background levels previously observed for this gas species [24]. Large mixing ratios of CH<sub>4</sub>, with levels above 5 ppmv, were detected in the early morning of February 5, suggesting a CH<sub>4</sub> emission source close to the Rice Laser Science Group Laboratory during this period.

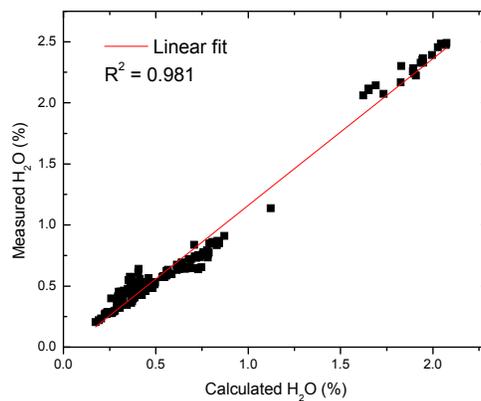


Fig. 8. Comparison of measured 1-hour averaged H<sub>2</sub>O vapor mixing ratios with levels calculated based on meteorological data collected at a TCEQ station located in the proximity of the Rice University campus (February 1-8, 2016).

Figure 9 shows the diurnal trends of the measured species during the sampling period. The mixing ratios of H<sub>2</sub>O and HDO exhibited large hourly variability mainly associated with unusually high levels of these species during the first ~24 h of sampling (February 1, and the early morning of February 2). As mentioned previously, these atypical mixing ratios were also observed in the H<sub>2</sub>O vapor levels calculated based on meteorological parameters. The average mixing ratios of H<sub>2</sub>O vapor and its heavier isotope followed a similar trend and showed higher levels during nighttime and expected decreased concentrations (associated with increases in ambient temperature) during the daytime. Although a side-by-side pattern can be noticed for the H<sub>2</sub>O and HDO hourly variation, the mixing ratios for the latter gas species exhibited a more pronounced pattern. The diurnal profile of N<sub>2</sub>O showed a minimum level in the morning hours (~8:00 CDT) with a slight increase in the mixing ratios during daytime. In general, the average concentration level of N<sub>2</sub>O exhibited a minor variation (ranging between ~360 and 370 ppbv) during a 24-h period. The diurnal trend of CH<sub>4</sub> mixing ratios showed a marked increase during the early morning hours with a subsequent decrease during the day and a minor secondary peak at ~21:00 CDT. The variability of the CH<sub>4</sub> levels from ~3:00 to 7:00 CDT (time interval of increased concentration for this species) was larger than that observed for periods where CH<sub>4</sub> mixing ratios exhibited similar levels to atmospheric background concentrations (~2 ppmv). The hourly profile for this gas species is consistent with previous reports of CH<sub>4</sub> mixing ratios trends at different urban locations [25, 26]. These results demonstrate the feasibility of the developed sensor system for continuous multi-gas species monitoring as well as its capability of simultaneously capturing distinctive atmospheric behavior and dynamics of H<sub>2</sub>O, HDO, N<sub>2</sub>O and CH<sub>4</sub>.

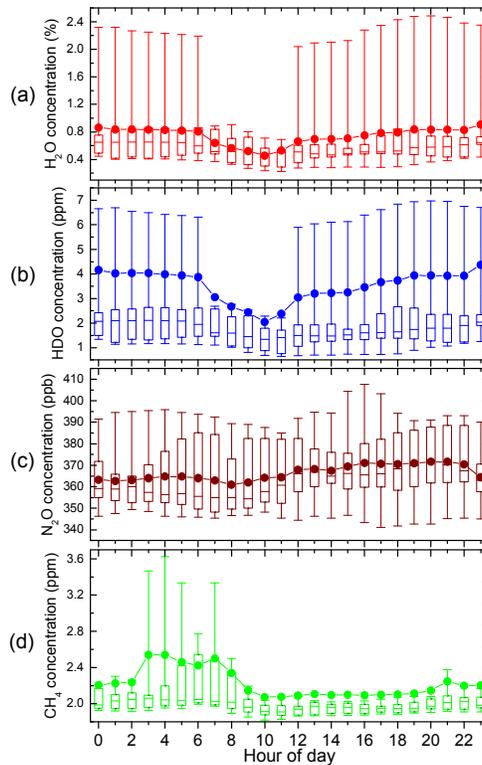


Fig. 9. Diurnal variations of atmospheric (a) H<sub>2</sub>O, (b) HDO, (c) N<sub>2</sub>O, and (d) CH<sub>4</sub> mixing ratios during the period of monitoring. Bottom whisker, bottom box line, top box line, and top whisker indicate 10th, 25th and 75th, 90th percentile, respectively. Line inside the box and solid circle represent the median and mean values respectively.

## 6. Conclusions

A CW EC-QCL based sensor system for simultaneous detection of atmospheric H<sub>2</sub>O, HDO, N<sub>2</sub>O, and CH<sub>4</sub> by using a compact MPGC with an effective optical path-length of 57.6 m was developed. The EC-QCL operates at ~7.8 μm in a mode-hop-free spectral range of 1225-1285 cm<sup>-1</sup>. The spectral tuning of the EC-QCL was calibrated by means of a Ge etalon with a free spectral range (FSR) of 0.0164cm<sup>-1</sup>. Four interference-free absorption lines were selected within the EC-QCL spectral region at a reduced pressure of 40Torr. A strategy of using 1f-normalized peak-to-peak values of WMS-2f was implemented to process the acquired spectral data. The noise level of the sensor system was evaluated using the Allan-Werle variance method with MDLs of 12.5 ppmv for H<sub>2</sub>O, 26.5 ppbv for HDO, 17.0 ppbv for N<sub>2</sub>O, and 24.0 ppbv for CH<sub>4</sub> at a 1-s integration time. Furthermore, MDLs of 1.77 ppmv for H<sub>2</sub>O, 3.92 ppbv for HDO, 1.43 ppbv for N<sub>2</sub>O, and 2.2 ppbv for CH<sub>4</sub> can be achieved with integration times at 50-s, 50-s, 100-s, and 129-s, respectively. The long-term stability of the four-gas sensor was verified by performing a one-week long ambient monitoring campaign on the Rice University campus. The H<sub>2</sub>O vapor concentration levels measured showed good agreement with the calculated concentration levels based on meteorological parameters from a nearby TCEQ station. The measurement results indicate that reported TDLAS based sensor system is able to perform the sensitive and precise detection of four non-CO<sub>2</sub> GHGs simultaneously.

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