

Fig. 7. Time series of H₂O (red), HDO (blue), N₂O (wine), and CH₄ (green) mixing ratios measured on the Rice University campus during February 1-8, 2016.

Although slightly higher H₂O 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/H₂O 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 2.4×10^{-4} and 3.3×10^{-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 ~ 3000 times smaller than H₂O vapor mixing ratios, which is consistent with the expected abundance of this isotope [23]. In Fig. 7, the levels of N₂O showed minor variability during the interval of monitoring, with mixing ratios ranging between 330 and 410 ppbv and an average mixing ratio of 366 ± 22 ppbv. This value agrees with background levels reported previously for this gas species in the Houston area [2, 7]. The concentration of CH₄ ranged between 1.8 and 5.3 ppmv with an average of 2.06 ± 0.32 ppmv, consistent with typical urban background levels previously observed for this gas species [24]. Large mixing ratios of CH₄, with levels above 5 ppmv, were detected in the early morning of February 5, suggesting a CH₄ emission source close to the Rice Laser Science Group Laboratory during this period.

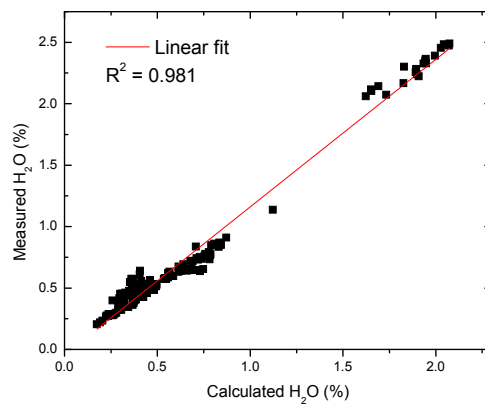


Fig. 8. Comparison of measured 1-hour averaged H₂O vapor mixing ratios with levels calculated based on meteorological data collected at a TCEQ station located in the proximity of the Rice University campus (February 1-8, 2016).

Figure 9 shows the diurnal trends of the measured species during the sampling period. The mixing ratios of H₂O 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 H₂O vapor levels calculated based on meteorological parameters. The average mixing ratios of H₂O 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 H₂O and HDO hourly variation, the mixing ratios for the latter gas species exhibited a more pronounced pattern. The diurnal profile of N₂O 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 N₂O exhibited a minor variation (ranging between ~360 and 370 ppbv) during a 24-h period. The diurnal trend of CH₄ 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 CH₄ levels from ~3:00 to 7:00 CDT (time interval of increased concentration for this species) was larger than that observed for periods where CH₄ mixing ratios exhibited similar levels to atmospheric background concentrations (~2 ppmv). The hourly profile for this gas species is consistent with previous reports of CH₄ 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 H₂O, HDO, N₂O and CH₄.

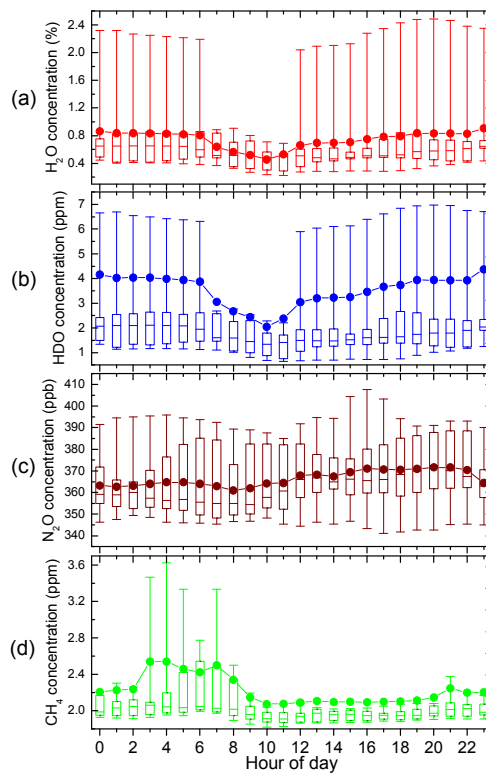


Fig. 9. Diurnal variations of atmospheric (a) H₂O, (b) HDO, (c) N₂O, and (d) CH₄ mixing ratios during the period of monitoring. Bottom whisker, bottom box line, top box line, and top whisker indicate 10th, 25th and 75th, 90th percentile, respectively. Line inside the box and solid circle represent the median and mean values respectively.

6. Conclusions

A CW EC-QCL based sensor system for simultaneous detection of atmospheric H₂O, HDO, N₂O, and CH₄ 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⁻¹. The spectral tuning of the EC-QCL was calibrated by means of a Ge etalon with a free spectral range (FSR) of 0.0164cm⁻¹. 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 H₂O, 26.5 ppbv for HDO, 17.0 ppbv for N₂O, and 24.0 ppbv for CH₄ at a 1-s integration time. Furthermore, MDLs of 1.77 ppmv for H₂O, 3.92 ppbv for HDO, 1.43 ppbv for N₂O, and 2.2 ppbv for CH₄ 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 H₂O 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-CO₂ GHGs simultaneously.

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