

Quantum Cascade Laser Based Sensor for In Situ and Real Time Atmospheric Trace Gases Measurements

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Abstract—In this paper, we report on the development of a field-deployable instrument based on a continuous wave distributed feed-back (DFB) QCL operating at 4.56 μm for simultaneous, in situ detection of atmospheric trace gases N_2O and CO with high sensitivity, precision and temporal response. Long-term lab and field performance will be presented.

I. INTRODUCTION

Quantum cascade lasers (QCLs) are relatively new sources of mid-infrared radiation (between 2.5 and 25 μm), and are well suited to the application of in-field sensing, being robust, compact, wavelength-versatile, as well as with narrow line width and low power consumption. All that makes laser absorption spectroscopy based on these QCL lasers has become one of the most popular technologies for quantitative chemical detection in a variety of fields including atmospheric monitoring, industrial process control, security or bio-medical studies.

In the present study, measurements of atmospheric carbon monoxide and nitrous oxide at a rural site were performed using a novel continuous-wave (CW) room temperature (RT) QCL based sensor [1] during the summer 2011 PARADE field campaign at Taunus Observatory, a low elevation mountain site in south-western Germany. The sampling was done at a high frequency (1 Hz) for approximate one month, to provide insights into short-term variability and diurnal cycles. Ancillary measurements of nitrogen oxides (NO and NO_2), O_3 and meteorological parameters enabled us to study the oxidative chemistry of the troposphere and the air mass origin at the measurement site.

II. RESULTS AND DISCUSSION

Fig. 1(a-f) presents the linear regression of 6 typical plumes sampled over the measurement period indicates that the $[\text{CO}]/[\text{NO}_x]$ ratio ranges from 3.33 to 14.98 ppbv/ppbv, which is consistent with emission ratios measured by Backer et al. in Germany [31], who reported $[\text{CO}]/[\text{NO}_x]$ ratios between 0.63 and 38.33 for vehicles with different fuel types, and mean values of 3.05 and 5.56 for car and truck, respectively. Evidently, each plume shows a very high correlation between CO and NO_x concentrations with R^2 ranging from 0.77 to 0.90. The observed difference in the emission ratios for individual plume is likely associated with many factors such as engine/catalyst age and type, engine state, fuel type, plume age and environment conditions. The tight correlation between CO and NO_x concentrations indicate that, despite the clearer environment, these high correlated plumes observed on the measurement site are potentially due to nearby common sources, or the transport of polluted air from anthropogenic sources, for instance, the influence of pollution plumes from Frankfurt city and the Rhine-Main area. By referring to the

meteorological data and O_3 concentrations, we found that the plume with the highest emission ratio of 14.98 (Fig. 1(c)) was due to the vehicular emissions (relatively fresh air masses) advected to the site from up-wind motorways, as mentioned before. While other plumes mainly attributed to the influence of aged air masses from Frankfurt city (Fig. 1(a) and (d)) and the Rhine-Main area (Fig. 1(b), (e) and (f)). From the point of view of emission ratios, it is difficult to define the difference of air masses from these two locations. However, the results indicate that air masses from Frankfurt region were normally observed at afternoon and midnight, while those from the Rhine-Main area were observed at morning hours at the sampling site.

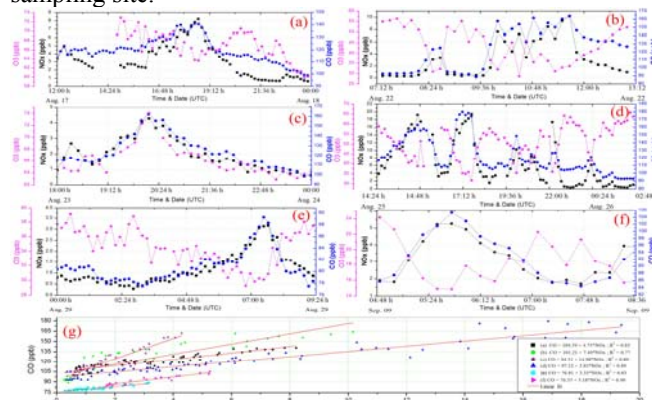


Fig. 1. Time series plots of CO, NO_x and O_3 for some typical plumes observed over the measurement period (panel a-f), and scatter plots of CO versus NO_x (panel g). Linear regression fitting parameters are listed in the box (details see text).

III. SUMMARY

The results showed apparent diurnal variations. Strong correlations between CO and NO_x indicate vehicular emissions are the major contributors to the notable CO plumes observed at the sampling site. Combination of local meteorological situation and backward trajectories analyses suggested that the high CO plumes were associated with anthropogenically polluted air masses by atmospheric transport from nearby cities, such as Frankfurt and the Rhine-Main area. We also characterized oxidant production of ozone, which is consistent with other observations.

REFERENCES

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