



Accounting for spectroscopic effects in eddy covariance calculations of methane flux

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Closed-path and open-path designs of high-speed gas analyzers are widely used in Eddy Covariance research to quantify CO₂ and H₂O fluxes. Typically such devices use NDIR technology due to combination of good performance, low cost, field robustness, low maintenance and power demands. Recently, new analyzers were developed to measure fluxes of gases beyond CO₂ and H₂O using laser spectroscopy. The new way of measuring gas concentrations may also bring a need for a new additional correction to the flux values.

Traditionally, when Eddy Covariance flux is computed, the fast changes in gas density are correlated with fast changes in vertical wind speed. Measured changes in gas density happen due to gas flux, thermal expansion and contraction of the sampled gas, water vapor dilution, and pressure-related expansion and contraction. These are standard processes described by Ideal Gas Law and by Law of Partial Pressures, and often are called *density effects*. The gas flux is usually corrected for these density effects using Webb-Pearman-Leuning correction [1].

When gas density is measured by the means of laser spectroscopy, there are also *spectroscopic effects* affecting measured gas density depending on fluctuations in temperature (T), water vapor (q) and pressure (P), in addition to the density effects. The spectroscopic effects are related to changes in the shape of the absorption line due to changes in gas T, q, and P. These effects are individual for each specific absorption line [2], and the method for compensating these effects are also highly dependent on the measurement technique. Depending on the absorption line probed, spectroscopic effects may add or subtract from density effects, or may have a positive slope with T and negative with P, or vice versa.

For closed-path gas analyzers, the majority of density effects and spectroscopic effects could be reduced or eliminated, when: (i) intake tube is very long, (ii) air sample is dry, and (iii) pressure fluctuations are very small. This way fast fluctuations in T are attenuated, fast fluctuations in q are removed entirely, and fast fluctuations in P are neglected. While minimizing uncertainty related to density and spectroscopic effects, use of long intake tubes and drying air sample also lead to significant increase in power demand, and to increased uncertainties due to excess attenuation of the fluctuations of the gas of interest in the drier.

Not drying air sample leads to the need for applying density correction for dilution, and spectroscopic corrections for gas absorption due to fast fluctuations in water vapor pressure. For both of these corrections water vapor should be measured accurately at hi-speed inside the closed-path device, which increases measurement costs.

In addition, such closed-path analyzers have to work under significantly reduced pressures, and require powerful pumps and grid power (600-1500 Watts). Power and labor demands may be reasons why these instruments are often deployed at locations with good infrastructure and grid power, and not where the gas of interest is produced.

Alternatively, open-path design can offer very low-power (e.g. 5-10 Watts) solution permitting solar-powered deployments. It is cost-effective permitting an addition of a single new gas measurement to the present array of CO₂ and H₂O measurements. Measurements are truly in-situ avoiding attenuation of gas fluctuations in the intake tube. These features enable long-term deployment of permanent, portable or mobile open-path flux stations at remote locations with high production of the gas of interest. However, in the case of the open-path analyzers, both density effects and spectroscopic effects cannot be designed out or neglected.

Here we propose a new way to account for spectroscopic effects due to fast fluctuations in air T, q, and P in the same manner as Webb et al. [1] proposed a way of accounting for respective density effects. Since both density effects and spectroscopic effects are known from Gas Laws and HITRAN [2] respectively they could be incorporated into WPL correction [2]. We use an example of the fast open-path methane gas analyzer, LI-7700 [3], yet the proposed approach would also apply to any closed-path design where fluctuations in T, q, and P are not fully eliminated.

References:

- [1] Webb, E. K., Pearman, G. I., and R. Leuning, 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. *Quart. J. R. Met. Soc.*, 106: 85-100
- [2] Rothman, L.S., Gordon, I.E., Barbe A., Benner, D.C., Bernath, P.F., et al., 2009. The HITRAN 2008 molecular spectroscopic database. *Journal of Quantitative Spectroscopy Radiative Transfer* 110: 533–572
- [3] McDermitt, D., G. Burba, L. Xu, T. Anderson, A. Komissarov, J. Schedlbauer, D. Zona , W. Oechel, S. Oberbauer, G. Starr, and S. Hastings, 2010. A new low-power, open path instrument for measuring methane flux by Eddy Covariance. *Applied Physics B: Lasers and Optics*. In print.