ACCOUNTING FOR SPECTROSCOPIC EFFECTS IN EDDY COVARIANCE MEASUREMENTS OF METHANE FLUX

INTRODUCTION

- Eddy Covariance (EC) is one of the most accurate and direct methods to measure fluxes of H₂O, CO₂ and CH₄ (L., L., L.).
- Fluxes of CO₂ and H₂O are typically measured by EC using NDIR technology with compact low-power gas analyzers.
- CH₄ flux studies cannot utilize NDIR, so CH₄ gas analyzers use single-line or narrow-band laser spectroscopy.
- Like CO₂ and H₂O, the CH₄ density changes due to the flux itself, but also due to the air density changes related to temperature (T), water vapor (Q), and pressure (P).
- CH₄, however, is measured by single-line or narrow-band lasers, and is also influenced by T, Q, and P, affecting spectroscopic properties of the absorption line.

Here we propose a new concept to account for spectroscopic effects in the same way as Webb et al. (1980) accounted for respective density effects.

- The proposed concept is tested on a low-power open-path high-speed gas analyzer, the LI-7100 (LI-COR, Lincoln, NE, USA [4,5,7]).

DERIVATION OF TOTAL EFFECTS

- In simple terms, if it is known that spectroscopic effect of T is 30% of the density effect, one can correct both effects by multiplying thermal expansion term in WPL by 1.3.
- Or, if it is known that spectroscopic effect of Q is 40% of the density effect of Q, one can correct for both effects by multiplying dilution term in WPL by 1.4.
- Over wide range of conditions, the relationships between spectroscopic and density effects for T and Q are complex, because at each point they depend on P.
- However, one can derive a simple relatively simple equation for actual flux F_C:

\[ F_C = \frac{w \cdot q}{\rho} \cdot \frac{1 + \mu \cdot \rho_{g} - \mu \cdot \rho_{g}^{2}}{2} \]

Where: w - vertical wind speed, q - density at the measurement site, \( \rho_{g} \) - gas density, \( \mu \) - ratio of mol. masses of air to water vapor density; and T – air temperature in K; P – constant pressure.

These derivations are made from the first principles and do not rely on empirical details of spectroscopic properties.

DENSITY EFFECTS

- When EC flux is computed, the fast changes in gas density are correlated with the fast changes in vertical wind speed.
- Measured changes in gas density happen due to gas flux itself, due to thermal expansion and contraction of the air, vertical wind dilution, and pressure-related expansion and contraction.
- These processes are described by the Ideal Gas Law and by the Law of Partial Pressures, and often are called density effects.
- The gas flux is usually corrected for the density effects using widely-used Webb-Parman-Leuning terms (5). 

SPECTROSCOPIC EFFECTS

- When gas density is measured by laser spectroscopy, there are also spectroscopic effects affecting measured values, in addition to the density effects.
- Spectroscopic effects are related to the changes in shape of the absorption line due to the changes in gas T, Q, and P (4,8).
- Effects are individual for each specific absorption line, highly dependent on measurement technique, and known from spectroscopy laws and HITRAN(2).
- Spectroscopic influence measured gas density depending on fluctuations in T, Q, and P.

VALIDATION

- The proposed concept was tested at the field experimental site of the University of Nebraska-Lincoln, with multi-year history of chamber-based CH₄ fluxes ranging from -0.12 to 0.13 mg m⁻² h⁻¹ (10).

SUMMARY AND CONCLUSIONS

- Reliable relationships were established between density effects and spectroscopic effects based on the first principles of Ideal Gas Law, Partial Pressures Law, spectroscopy laws and HITRAN.
- Spectroscopic effects were incorporated into WPL density terms, originally developed to compensate for the density effects.
- Results were field-validated for cold and warm periods versus chamber measurements over a “zero-flux” experimental site.
- The proposed approach allows the use of cost-effective low-power single-gas analyzers in EC flux measurements without the need for fast T, H₂O, and P measurements inside the sampling cell.

REFERENCES AND RESOURCES