



# ACCOUNTING FOR SPECTROSCOPIC EFFECTS IN EDDY COVARIANCE MEASUREMENTS OF METHANE FLUX

G. Burba\*, T. Anderson, D. McDermitt, A. Komissarov, L. Xu, B. Rtnsche, D. Allyn, and K. Ediger  
LL-COR, Biosciences, Lincoln, NE, USA, \*george.burba@llcor.com

## INTRODUCTION

- Eddy Covariance (EC) is one of the most accurate and direct methods to measure fluxes of H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> [1,2,3]
- Fluxes of CO<sub>2</sub> and H<sub>2</sub>O are typically measured by EC using NDIR technology with compact low-power gas analyzers
- CH<sub>4</sub> flux studies cannot utilize NDIR, so CH<sub>4</sub> gas analyzers use single-line or narrow-band laser spectroscopy
- Like CO<sub>2</sub> and H<sub>2</sub>O, the CH<sub>4</sub> 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)
- CH<sub>4</sub> 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. (1989) accounted for respective density effects
- The proposed concept is tested on a low-power open-path high-speed gas analyzer, the LI-7700 (LI-COR, Lincoln, NE, USA [4,5,7])



## 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, water vapor 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-Pearman-Leuning terms [6]:

$$F_c = w'q_c + \mu \frac{q_m}{q_d} w'q_c + (1 + \mu\sigma) \frac{q_m}{T} w'T'$$

Raw Flux Covariance:  $F_c$  - flux corrected for vertical wind speed,  $w'$  - vertical wind speed,  $q_c$  - gas density,  $\mu$  - ratio of mol. masses of air to water,  $q_m$  - dry air density,  $q_d$  - dry air density,  $T'$  - air temperature anomaly

Water Dilution Term:  $\mu \frac{q_m}{q_d} w'q_c$  - computed from any fast measured density, at standard air density, at standard air density

Thermal Expansion Term:  $(1 + \mu\sigma) \frac{q_m}{T} w'T'$  - computed from any fast measured density, at standard air density, at standard air density

## FULL EQUATION

- To compute correct CH<sub>4</sub> flux, the raw flux covariance should be corrected for both density effects and spectroscopic effects
- Using physical relationships described before, the standard WPL equation correcting for just density effects becomes the modified equation correcting for both density effects and spectroscopic effects:

$$F_c = w'q_c + \mu \frac{q_m}{q_d} w'q_c + (1 + \mu\sigma) \frac{q_m}{T} w'T'$$

$$F_c = A(w'q_c + \mu \frac{q_m}{q_d} w'q_c + B \mu \frac{q_m}{q_d} w'q_c + C(1 + \mu\sigma) \frac{q_m}{T} w'T')$$

- Please note that the only difference between the standard WPL equation and the modified equation correcting for both density effects and spectroscopic effects are the three multipliers: A, B and C [4, 5, 9]
- At normal conditions for LI-7700, the A ranges from 0.96 to 0.99, B ranges from 1.41 to 1.43, and C ranges from 1.32 to 1.34
- Multipliers A, B, C can be permanently programmed into flux processing code - please contact george.burba@llcor.com for the detailed algorithm

## 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 [7,8]
- Effects are individual for each specific absorption line, highly dependent on measurement technique, and known from spectroscopy laws and HITRAN [7]
- Spectroscopic effects influence measured gas density depending on fluctuations in T, Q and P

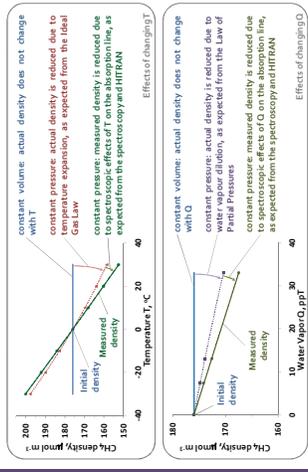
### KEY CONCEPT

Fast changes in T, Q, or P lead to:  
 (i) gas density effects as per Ideal Gas Law and Partial Pressures Law  
 (ii) spectroscopic effects as per spectroscopy laws and HITRAN

So, if one can establish relationships between density effects and spectroscopic effects of T, Q and P respectively, one can incorporate the spectroscopic effects into WPL terms [4,5,9].

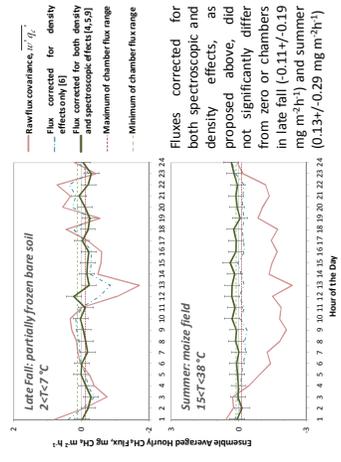
## RELATING DENSITY & SPECTROSCOPIC EFFECTS

- Depending on the absorption line probed, spectroscopic effects may add or subtract from density effects, or may differ for T, Q, and P
- Examples below are for T and Q effects for the specific case of LI-7700 for CH<sub>4</sub> density of 176  $\mu\text{mol m}^{-3}$  at initial conditions of 0°C and dry air



## FIELD VALIDATION

- The proposed concept was tested at the field experimental site of the University of Nebraska-Lincoln, with multi-year history of chamber-based CH<sub>4</sub> fluxes ranging from -0.12 to 0.13  $\text{mg m}^{-2} \text{h}^{-1}$  [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, H<sub>2</sub>O, and P measurements inside the sampling cell

## REFERENCES AND RESOURCES

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## 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 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 single relatively simple equation for actual flux  $F_c$ :

$$F_c = w'q_c + \mu \frac{q_m}{q_d} w'q_c + (1 + \mu\sigma) \frac{q_m}{T} w'T'$$

$$F_c = A(w'q_c + \mu \frac{q_m}{q_d} w'q_c + B \mu \frac{q_m}{q_d} w'q_c + C(1 + \mu\sigma) \frac{q_m}{T} w'T')$$

where:  $A = \frac{1}{1 + \mu\sigma \frac{q_m}{T} \frac{1}{w'T'}}$ ,  $B = \frac{1}{1 + \mu\sigma \frac{q_m}{T} \frac{1}{w'T'}}$ ,  $C = \frac{1}{1 + \mu\sigma \frac{q_m}{T} \frac{1}{w'T'}}$

- These derivations are made from the first principles and do not rely on empiricism: detailed description and step-by-step derivation is provided in [5, 9]