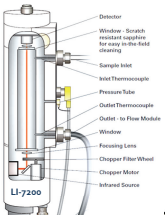
MEASURING CO_2 AND H_2O FLUXES FROM FAST MIXING RATIO WITHOUT A NEED FOR DENSITY CORRECTIONS

G. Burba*[1], A. Schmidt[2], R. Scott[3], T. Nakai[4], J. Kathilankal[1], G. Fratini[1], C. Hanson[2]; B. Law[2], D. McDermitt[1], and R. Eckles[1]

[1]LI-COR Biosciences, Lincoln, NE (*george.burba@licor.com); [2]College of Forestry, Oregon State University, Corvallis, OR; [3]ARS-USDA, Tucson, AZ; [4]University of Alaska, Fairbanks, AK

INTRODUCTION

- New fast CO_2/H_2O analyzer, the LI-7200, is made for low power operation when used with short intake tube of 1.5 m or less [1]



- Two fast air temperatures and one air pressure are measured in the cell synchronously with CO_2/ H_2O
- This provides the ability to compute fast mixing ratio (MR), or dry mole fraction, on-the-fly [2]
- MR can be used for Eddy Covariance flux calculations without the need for Webb-Pearman-Leuning density terms [2, 3, 4, 5, 6]
- This approach may offer substantial advantages in terms of reduced flux uncertainties and minimum detectable flux
- In order to use mixing ratio from LI-7200 to compute fluxes, field data should be examined to verify the following:
  - **(i) Density-based fluxes from LI-7200 match the standards**
  - **(ii) Mixing ratio-based fluxes match density-based fluxes**

FIELD EXPERIMENTS

Comparison of MR-based to density-based flux calculations was made in 9 field experiments covering wide range of conditions [2]:

6 experiments from AmeriFlux Roving Station using LI-7200
1 experiment from UAF site in Alaska (AK)
1 experiment from USDA site in Arizona (AZ-2)
1 experiment from LI-COR field test facility in Nebraska (NE)

Site	Location	Coordinates	Elevation m	Ecosystem	Canopy ht m	Inst. ht m	Average T C	Measurement start	Measurement end
AK	Alaska	65 07 31 N; 147 29 17 W	210	burned forest	0.5	2.5	12.2	6-Aug	14-Sep
AZ-1	Arizona	31 54 30 N; 110 10 22 W	991	shrubland	0.7	3.6	28.3	5-Jul	14-Jul
AZ-2	Arizona	31 82 14 N; 110 86 61 W	1116	savanna	2.5	6.4	24.7	14-Apr	29-Jul
CA-1	California	33 22 38 N; 116 37 22 W	1429	shrubland	0.7	3.0	17.8	26-May	3-Jun
CA-2	California	37 04 04 N; 119 11 40 W	2020	forest	30	48	21.1	14-Jul	21-Jul
NE	Nebraska	40 51 22 N; 96 39 17W	350	ryegrass*	0.1	2.6	17.6	15-Sep	12-Nov
NM-1	New Mexico	34 21 27 N; 106 41 00 W	1590	grassland	0.3	2.9	23.7	27-Jun	5-Jul
NM-2	New Mexico	34 20 06 N; 104 44 39 W	1593	shrubland	0.6	2.8	28.0	18-Jun	25-Jun
OR	Oregon	44 38 05 N; 123 12 05 W	70	ag. grassland	0.05	3.0	7.9	5-Mar	22-Mar

** data from 2009; the rest in the table are from 2010*

CONCEPT OF MR & WPL

Fundamentally, fluxes can be computed from a covariance between vertical wind speed and mixing ratio after [2, 3, 4, 5, 6]:

$$Fc = \overline{w\rho s} \approx \bar{\rho}_d \overline{w's'} \quad (1)$$

However, traditional flux calculations usually use density measurements which are native to the gas analyzers:

$$Fc_o \approx \overline{w'q_c'} \quad (2)$$

and then apply density corrections after Webb et al. [3]:

$$Fc = Fc_o + \mu \frac{E}{\rho_d} \frac{q_c}{1+\mu \frac{\rho_v}{\rho_d}} + \frac{H}{\rho C_p} \frac{q_c}{T_a} + 0 \quad (3)$$

Dilution Term: E is computed from water vapor density measured in the cell simultaneously with CO2

Thermal Expansion Term: H in the LI-7200 cell is below 10% of ambient due to 1 m intake; remainder can be computed from in-cell fast temperatures

Pressure Expansion Term: It is usually neglected, but may be important, and can be computed from fast measurements inside the LI-7200 cell [6]

Fc – final corrected flux; w - vertical wind speed; ρ – total air density; S – wet mole fraction; ρ_d – dry air density; s – mixing ratio (dry mole fraction); Fc_o– uncorrected flux; q_c – gas density; E – evapotranspiration; H – sensible heat flux; ρ_v – H_2O vapor density; C_p – specific heat; T_a– air temperature in K; μ– ratio of mol. masses of air to water

MR can be computed in LI-7200 on-the-fly from density, using instantaneous water mole fraction (X_w), two temperatures (T) and a pressure (P) measured in the cell, and a gas constant (R):

$$S = q_c \frac{RT}{P} \quad => \quad s = \frac{S}{(1-X_w)} = q_c \frac{RT}{P(1-X_w)} \quad (4)$$

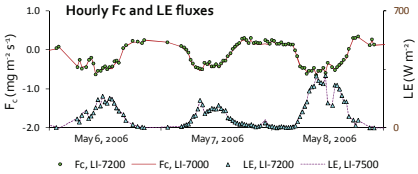
So, fluxes from LI-7200 could be computed both in traditional manner from density (Eq. 3), and from mixing ratio (Eq. 1)

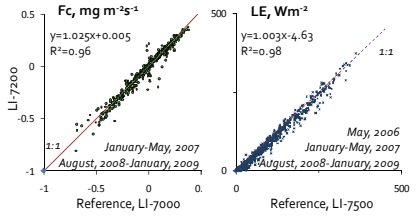
Fast MR has been used before with conventional closed-path analyzers, without fast T and P, because Ta was attenuated in the long intake tube, P' was small, and water vapor was measured

However, in the enclosed LI-7200, when used with short tube, most but not all of the fast fluctuations in Ta are attenuated, so calculating flux via MR from such instrument requires validation

DENSITY-BASED FLUXES

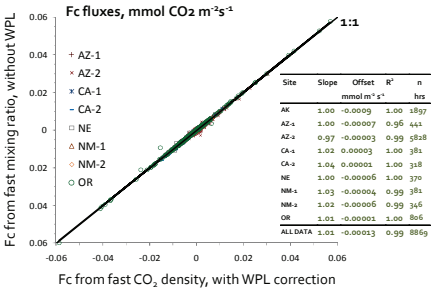
- Traditional density-based fluxes from LI-7200 were compared to the standards in field experiments over ryegrass in Nebraska and over a wetland in Florida [1]
- The open-path LI-7500 was chosen as a standard for water vapor flux (LE) because it does not attenuate water vapor in the intake tube
- The closed-path LI-7000 was chosen as a standard for CO2 flux (Fc) because it is not subject to surface heating effect in extremely cold conditions
- Hourly CO_2 and H_2O fluxes were within 2.5% of the standards (LI-7000 and LI-7500, respectively) in all experiments
- Observed 2.5% difference was not statistically significant, for P<0.05
- The field data confirmed good performance of LI-7200 in terms of the traditional density-based flux calculations and WPL correction



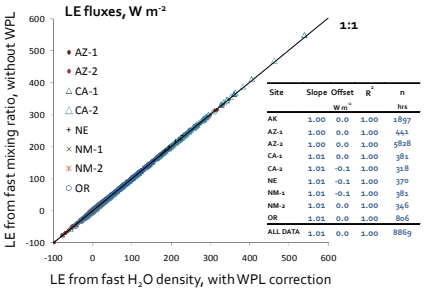


MIXING RATIO-BASED FLUXES

- Mixing ratio-based fluxes without WPL are plotted below vs. traditional density-based fluxes of Fc and LE for all 9 field deployments
- Mixing ratio-based CO2 flux was within 0%-4% of the density based flux at all sites
- The site with largest difference of 4%, CA-2, had measurement height 7-18 times taller than the any other site, highest LE flux affecting WPL terms, and least number of available data hours
- Water vapor fluxes were within 1% at all 9 sites, with 1% of LE leading to 2-5% of improvement in the energy budget closure



Site	Slope	Offset mmol m^{-2} s^{-1}	R^2	n hrs
AK	1.00	-0.0009	1.00	1897
AZ-1	1.00	-0.00007	0.96	441
AZ-2	0.97	-0.00003	0.99	5828
CA-1	1.02	0.00003	1.00	381
CA-2	1.04	0.00001	1.00	318
NE	1.00	-0.00006	1.00	370
NM-1	1.03	-0.00004	0.99	381
NM-2	1.02	-0.00006	0.99	346
OR	1.01	-0.00001	1.00	806
ALL DATA	1.01	-0.00013	0.99	8869



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SUMMARY

- New enclosed gas analyzer LI-7200 can use short intake tube, because fast T and P are measured in the cell with CO_2 and H_2O
- LI-7200 outputs fast gas density and MR at the same time
- This provides opportunity to compare MR-based fluxes without WPL correction with traditional density-based fluxes with WPL
- Traditional density-based fluxes from LI-7200, on-the-fly MR calculations, and resulting MR-based fluxes were examined:
  - **(i) The density-based fluxes from LI-7200 compared well with open-path and closed-path standards**
  - **(iii) MR-based fluxes and density-based fluxes matched well in all 9 experiments over wide range of conditions**
- The ability to compute MR-based fluxes is important for gas flux measurements, because elimination of density corrections can increase flux data quality and temporal resolution, and may help to reduce the magnitude of minimum detectable flux

REFERENCES

[1] Burba G, D McDermitt, D Anderson, M Furtaw, and R Eckles, 2010. Novel design of an enclosed CO2/H2O gas analyzer for Eddy Covariance flux measurements. Tellus B. Chemical and Physical Meteorology, 62(5): 743-748

[2] Burba G, A Schmidt, R Scott, T Nakai, J Kathilankal, G Fratini, C Hanson, B Law, D McDermitt, R Eckles, M Furtaw, and M Velgersdyk, 2011. Calculating CO2 and H2O eddy covariance fluxes from an enclosed gas analyzer using an instantaneous mixing ratio. Global Change Biology, *Submitted*

[3] Webb E, G Pearman, and R Leuning, 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. *Quart. J. Roy. Meteorol. Soc.*, 106: 85-100

[4] Leuning R, 2004. Measurements of trace gas fluxes in the atmosphere using eddy covariance: WPL correction revisited. In: Handbook of Micrometeorology (eds X. Lee, W. J. Massman and B. Law). Kluwer Academic Publishers, Dordrecht, Boston, London, 119–332.

[5] Lee X, W Massman, and B Law, Eds, 2004.Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis. Springer-Verlag, Berlin, Germany. 250pp.

[6] Nakai T, H Iwata, and Y Harazono, 2011. Importance of mixing ratio for a long-term CO2 flux measurement with a closed-path system. Tellus B, 63(3): 302-308

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