# Field tests of a new WS-CRDS based, closed-path analyzer for simultaneous eddy covariance flux measurements of $CO_2$ and methane



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## ΡΙСΛ R R O

#### **Abstract**

Recent world-wide attention to greenhouse gases is spawning a new wave of development of instrumentation intended for flux measurements – not only for  $CO_2$  and water vapor – but for methane as well. We report on recent field work conducted with a new Picarro closed-path analyzer, based on cavity ringdown spectroscopy, that simultaneously provides eddy covariance measurements of carbon dioxide and methane, both at a 10 Hz data rate. Field testing of an initial prototype analyzer had







previously been performed, and recommendations for design enhancements generated during that round of testing have been subsequently implemented in the new analyzer.

Both field testing campaigns were conducted at Oregon State University where the analyzer was compared to an AmeriFlux Portable Eddy Covariance System for measuring fluxes using conventional infrared open- and closed path  $CO_2$  and water vapor analyzers. Data comparing the performance of this new analyzer against the currently-used AmeriFlux instrumentation is presented. The long term stability of the Picarro system enables it to conduct both high-speed flux measurements as well as long-term background concentration measurements. The stability of the analyzer also reduces or eliminates the need for frequent calibration and the linearity of the analyzer allows calibrations – when they are needed – to be conducted with only two gas standards. Further, the ability to measure two greenhouse gases in the same instrument will enable more cost-effective expansion of AmeriFlux sites to include both  $CO_2$  and methane measurements.

#### Instrumentation

A 10 Hz eddy-covariance flux analyzer which simultaneously measures  $CO_2$  and  $CH_4$  was developed by Picarro and evaluated against an open-path, NDIR-based  $CO_2$  analyzer (LI-COR LI-7500). For  $CH_4$  however, no instruments were available for comparison with the 10 Hz  $CH_4$  measurements made with the Picarro. The Picarro analyzer is based on the existing WS-CRDS technology (described below) but has enhanced speed, enabling its application to high-speed eddy-covariance measurements.

Light intensity as a function of time in a WS-CRDS system with and without a sample having resonant absorbance. This demonstrates how optical loss (or absorption by the gas) is rendered into a time measurement (left). By using a patented wavelength monitor, this measurement is continuously repeated at a number of well-controlled points in wavelength (right). The concentration is determined by a multi-parameter fit to this lineshape and is proportional to the gas concentration.

### Field Measurements of CO<sub>2</sub> & CH<sub>4</sub> Flux

Both the Picarro and LI-7500 analyzers were evaluated at the Marys River flux site (Oregon, US, mature Douglas-fir) subcanopy (4 m above ground for sonic, LI-7500, and Picarro sample inlet). The tube inlet length for the Picarro was ~10 m. Data from the Picarro was collected via its serial output by a Campbell Scientific CR1000 datalogger.

CO<sub>2</sub> Concentration Comparison: Picarro vs. LI-7500 CO<sub>2</sub> Fluxes Comparison: Picarro vs. LI-7500



*Figure 7.* Mean, bin-averaged cospectra of turbulent fluxes of  $CO_2$  from the two instruments, over period of 9 selected 30 min intervals (i.e. 4.5 h of measurements) along with sensible heat. Spectral densities were normalized by their covariance. The dashed line indicates the expected -4/3 power law of cospectral decay. Figure 8. Similar plot as in Figure 7: Cospectra from the Picarro analyzer for  $CH_4$  perturbations, over period of 9 selected 30 min intervals (i.e. 4.5 h of measurements) along with sensible heat.

#### Data Analysis

Analysis of both the powerspectra and of the cospectra of the observables during the measurement campaign was carried out (see Figures 3-8). These field results are also presented along with the theoretically-predicted characteristic features of atmospheric turbulence spectra. Overall, the observed discrepancies in the measurements between the analyzers (and deviation from ideal response) is attributable to differences in sample delivery (~10 m tubing length in the case of the Picarro). The loss in spectral energy at the highest frequencies arises through transport of the air sample through the tubing (in the case of the closed-path Picarro analyzer). This results in attenuation of the smallest eddy sizes and therefore highest frequency perturbations. In comparison with earlier testing of the analyzer at lower flow rates, the higher flow rate in this field trial has improved the results significantly. It is expected that shorter tubing would yield additional improvements.

In 2008, field testing had been carried out with a prototype 10 Hz Picarro analyzer, also evaluating it against incumbent NDIR-based analyzers. The results of that testing drove improvements to the design of the Picarro – represented in the data presented here. These improvements consisted essentially of increasing the flow through the instrument by using a higher-throughput pump (~4 Lpm vs ~11 Lpm in the current design) as well as making some slight modifications to the internal plumbing so as to maintain turbulent flow through the plumbing and measurement cavity.

Fast, interleaved  $CO_2$  and  $CH_4$  spectra atFast, dual-laser interleaved  $CO_2$  and  $CH_4$ 300 RingDowns per secondspectra at 300 RingDowns per second





#### Summary & Conclusions

Scatter plots show remarkable agreement between open-path LI-7500 and new Picarro analyzer. Magnitude of CO<sub>2</sub> fluxes observed by the Picarro is somewhat systematically smaller, but fluxes have not been corrected for high-frequency attenuation. The latter would result in a small decrease of fluxes. Calibrations of both compared instruments (offset and gain) agree well. Differences in slope (~ 1%) cannot explain observed small underestimation of CO<sub>2</sub> fluxes (refer to powerspectra & cospectra above).

- Mean CO<sub>2</sub> powerspectra agree well, but show small attenuation of high-frequency eddies with frequencies f >= 0.3 Hz. This is expected due to the 10 m sampling line and would be improved with shorter tubing.
- Cospectra also agree well, but show the same decrease in energy for small (high-frequency) eddies for  $f \ge 0.3$  Hz.

*Figure 1.* Typical data showing interleaved tuning of dual-laser system over  $CO_2$  and  $CH_4$  spectral lines used to measure concentration. Inset shows individual ring down measurements taken at specific locations along each peak, actively targeted by wavelength monitor control loop. *Figure 2.* Frequency of each laser as a function of time as each is tuned across the spectral lines in Figure 2. Rapid switching between lasers allows high-speed measurements while maintaining high measurement precision.



Figure 5. Mean, bin-averaged powerspectra of<br/>turbulent fluxes of  $CO_2$  from the two instruments,<br/>over period of 9 selected 30 min intervals (i.e. 4.5 h<br/>of measurements). Spectral densities were multiplied<br/>by natural frequency f and normalized by their<br/>variances to check for spectral power laws. One<br/>expects a -2/3 power law in the spectral decay of<br/>power-spectra. The attenuated high-frequency<br/>response of the Picarro analyzer is expected due to<br/>the long (~10 m) tubing length from the sampling<br/>point to the instrument.Figure 6. Simila<br/>from the Picarro<br/>period of 9 selected<br/>measurements)

*Figure 6.* Similar plot as in Figure 5: Powerspectra from the Picarro analyzer for  $CH_4$  perturbations, over period of 9 selected 30 min intervals (i.e. 4.5 h of

• No instrument artifacts could be observed in measured CO<sub>2</sub> perturbations and fluxes. There has been a significant improvement compared to the instrument evaluated in 2008. Evaluation of CH<sub>4</sub> performance needs to be conducted in a different environment with meaningful CH<sub>4</sub> dynamics – the CH<sub>4</sub> perturbations were too small in this location to provide good data for analysis. The time response of the instrument to both CO<sub>2</sub> and CH<sub>4</sub>, however, has been shown in previous testing to be essentially identical.

 No long-term drift of the mean concentrations of CO<sub>2</sub> or CH<sub>4</sub> was observable, and no repeated field calibrations were necessary.

• Spectrally-integrated statistical moments (mean, variance, etc.) agree very well over the entire measurement period when compared to the LI-7500.

 Precision of instrument (230 ppbv CO<sub>2</sub>, 1.2 ppbv CH<sub>4</sub> in 0.1 s) appears adequate for measuring fluxes from a wavelet analysis of magnitudes of concentration fluctuations.