

Progress on direct air/sea CO₂ flux observations: results from DYNAMO2011 and TORERO2012

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Outline

- Overview of new analyzers
- Results from field deployments
- Discuss the most significant errors resulting from instrumental and meteorological causes to address them
- Recommendations

Overview of Instrumental Methods

Cavity Ring-Down Spectrometers / Picarro

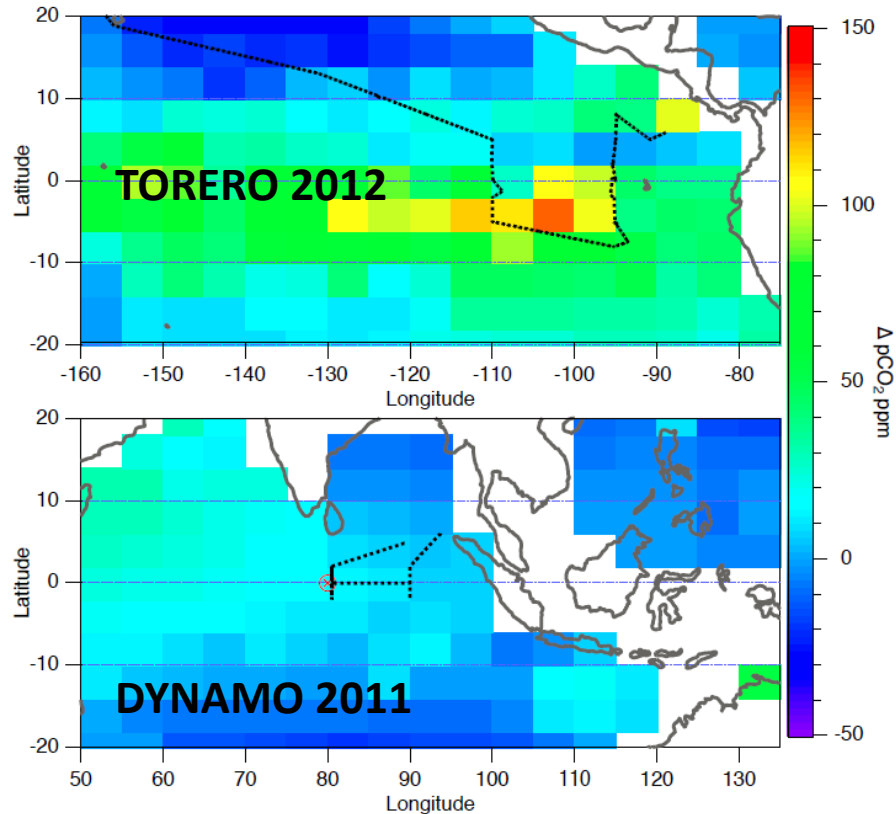


- reduction in decay time when absorbing molecules are introduced is proportional to absorbance.
- absorption peak \rightarrow peak height \rightarrow gas concentration
- cavity temperature and pressure carefully controlled
- correction for line broadening is also necessary



- broadband light + chopper wheel to sequentially measure infrared absorption at narrow bands corresponding to CO₂, H₂O
- Compensation for zero-drift and cross-sensitivity + Band-broadening correction
- measure optical cell temperature and pressure
- motion related interference
- water vapor interference on CO₂ measurements

Overview of Field deployments



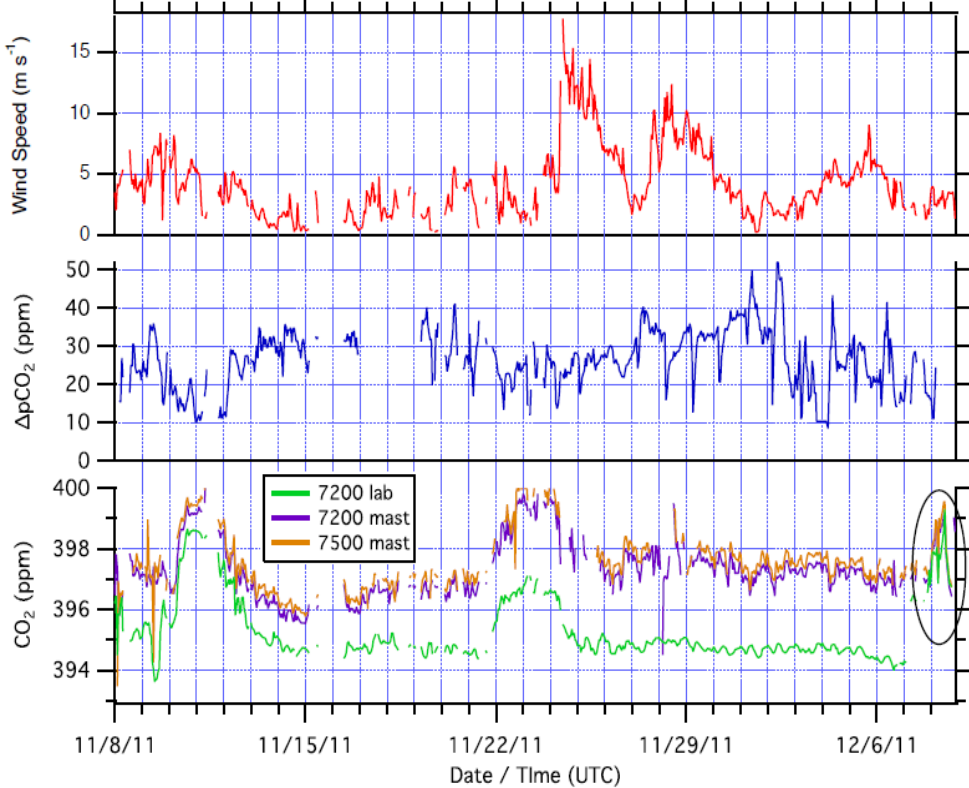
DYNAMO 2011 (R/V Revelle)

- August 2011 to February 2012
- Dynamics of the Madden-Julian Oscillation
- Three LI7500, two LI7200 and pCO₂
- 200-tube Nafion air dryer with sample air dew point to <-15 °C
- 30m, 40 Lmin⁻¹, 4Lmin⁻¹

TORERO 2012 (R/V Ka'imimoana)

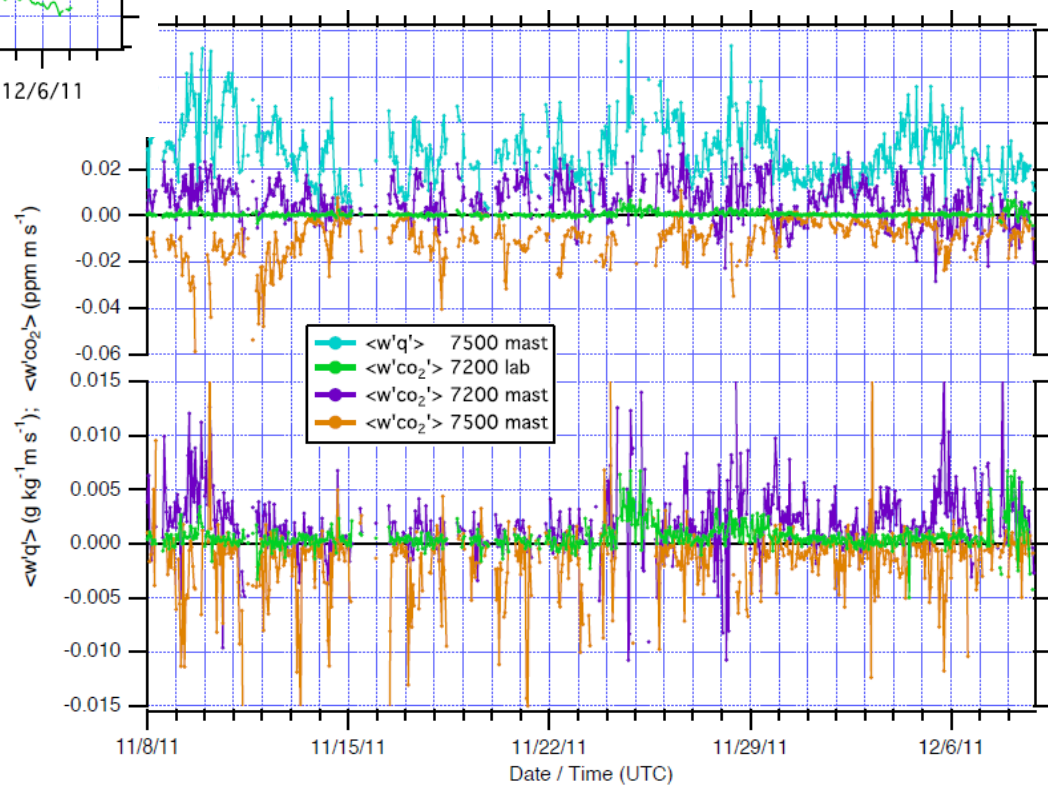
- 25-Jan-2012 to 27-Feb-2012
- distribution, reactivity and abundance of oxygenated organics and halogen radicals over the Eastern Pacific
- one CRDS fast CO₂ analyser (Picarro model G1301-f) with Nafion dryer
- 50m, 80 Lmin⁻¹, 5Lmin⁻¹



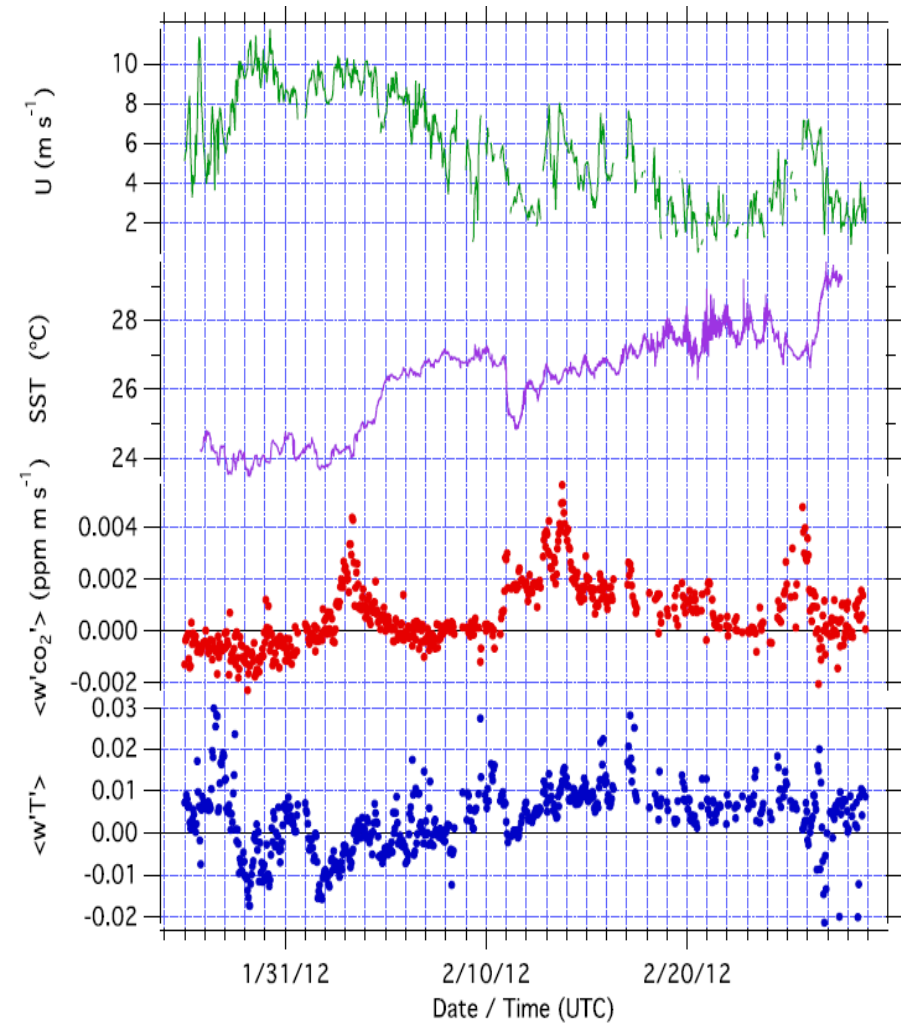


Results: Flux Observations - DYNAMO 2011

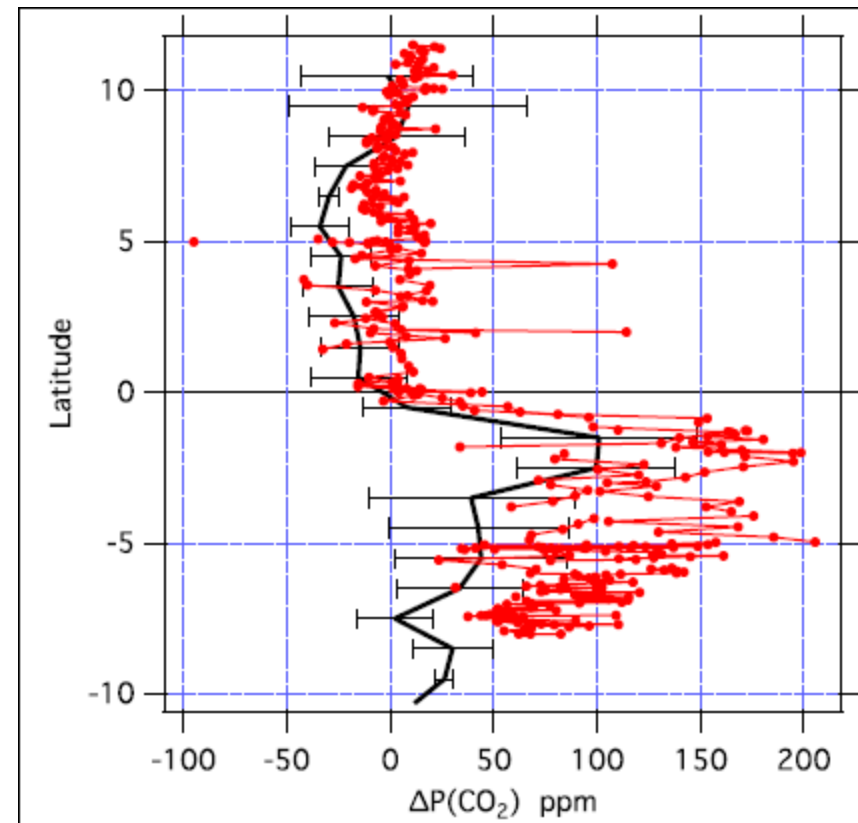
We can measure a zero flux!



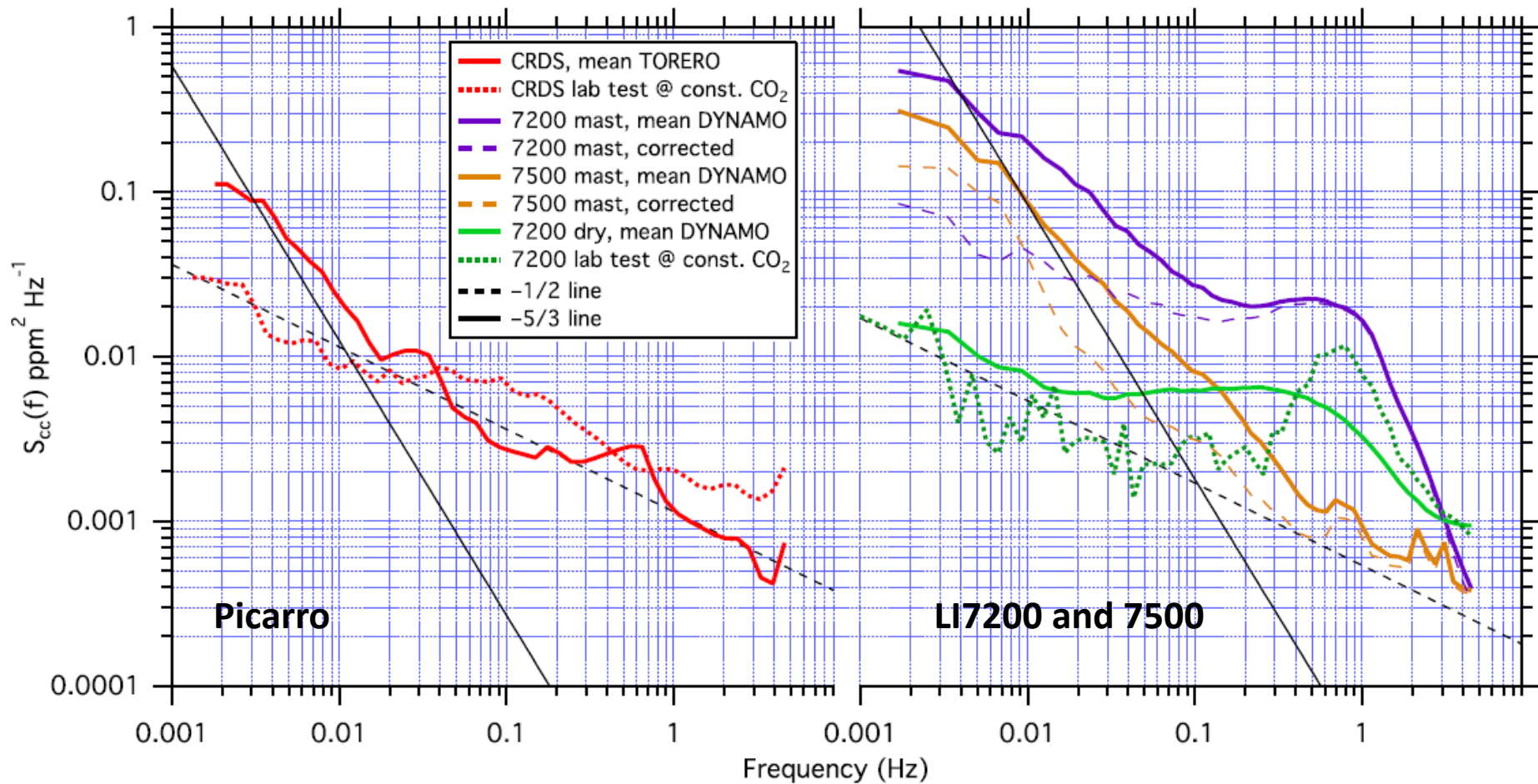
Results: Flux Observations - TORERO 2012



$\Delta p\text{CO}_2$ computed from the CRDS flux data compares favourably with January-February mean $\Delta p\text{CO}_2$ from equatorial cruise data in the region

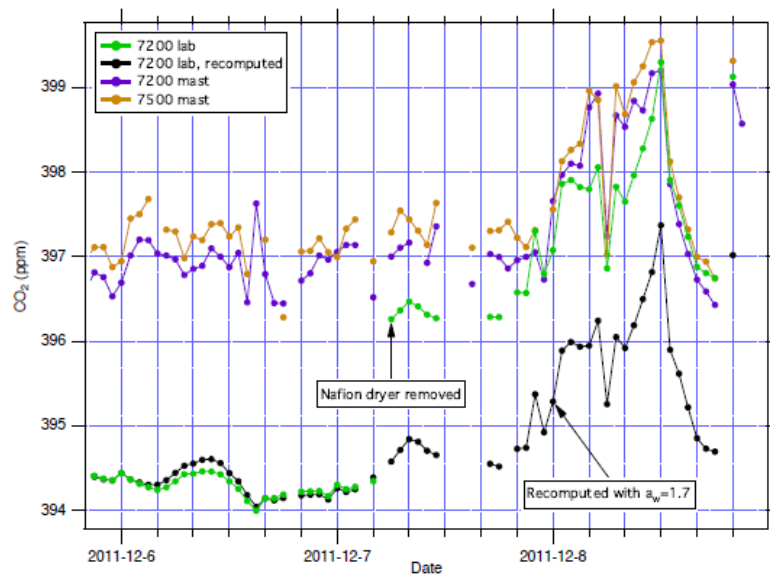
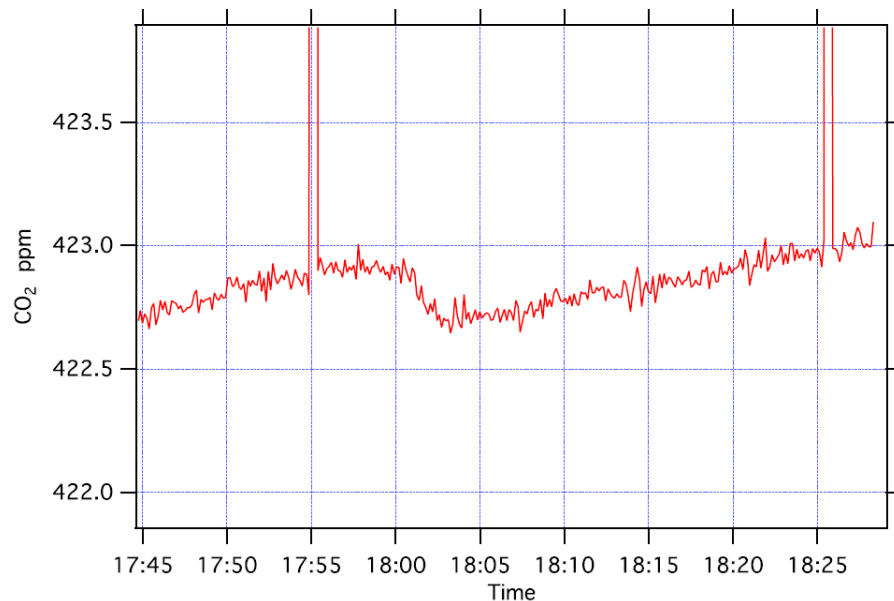
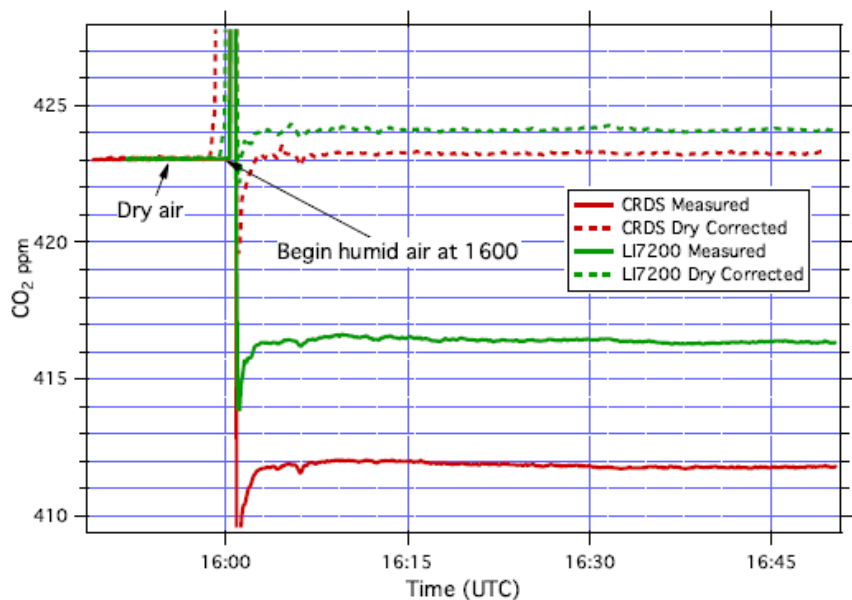


Noise Characteristics



Interferences and Corrections

Water Vapour Cross-Sensitivity



Interferences and Corrections

Water Vapour Cross-Sensitivity

$$c = c_m - \mu_0 q$$

$$\overline{w'c'} = \overline{w'c'_m} - \mu_0 \overline{w'q'}$$

	Base Case	Median $F_{CO_2} \pm 1\sigma$	(ppm m s ⁻¹)
		PKT ^a	Cross-correlation ^b
LI7200 lab ^c	0.00047±0.00049	–	–
LI7200 mast ^d	0.00663±0.00396	0.00061±0.01423	0.00122±0.00155
LI7500 mast ^e	-0.00678±0.00314	-0.00254±0.00467	-0.00081±0.00222

^a Prytherch et al. (2010a)

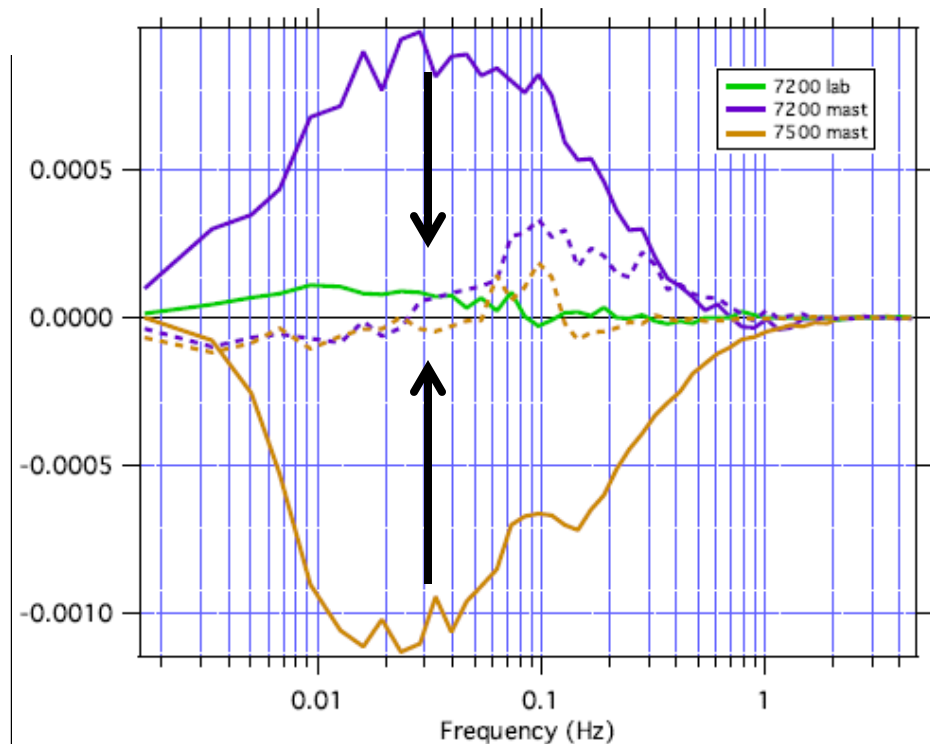
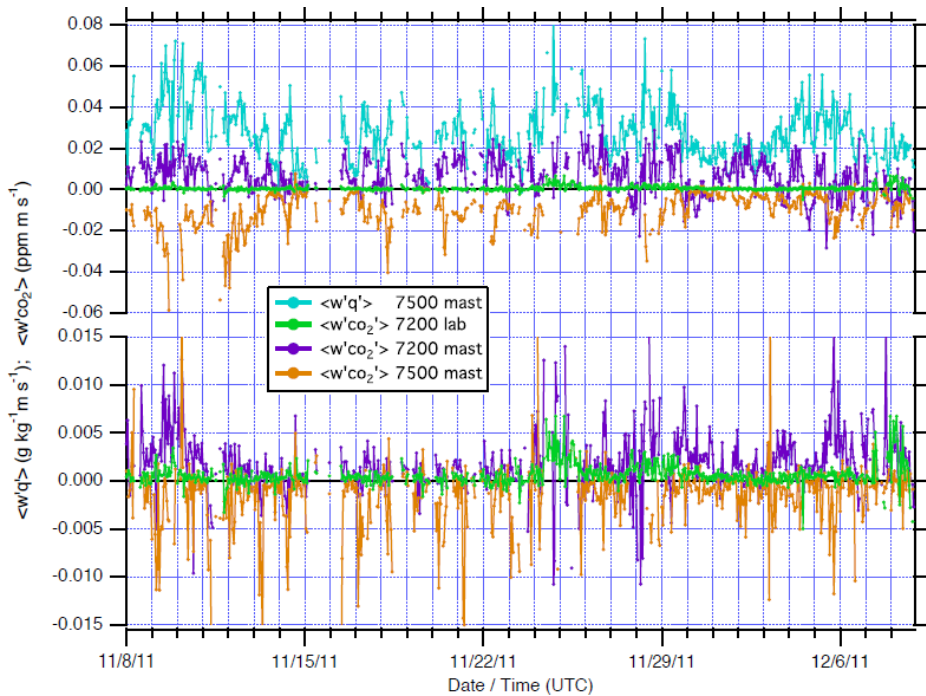
^b Edson et al. (2011)

^c dry-air data, WPL and dilution corrections not required

^d computed from “dry” mole fraction output. No WPL/dilution correction

^e WPL and dilution corrected

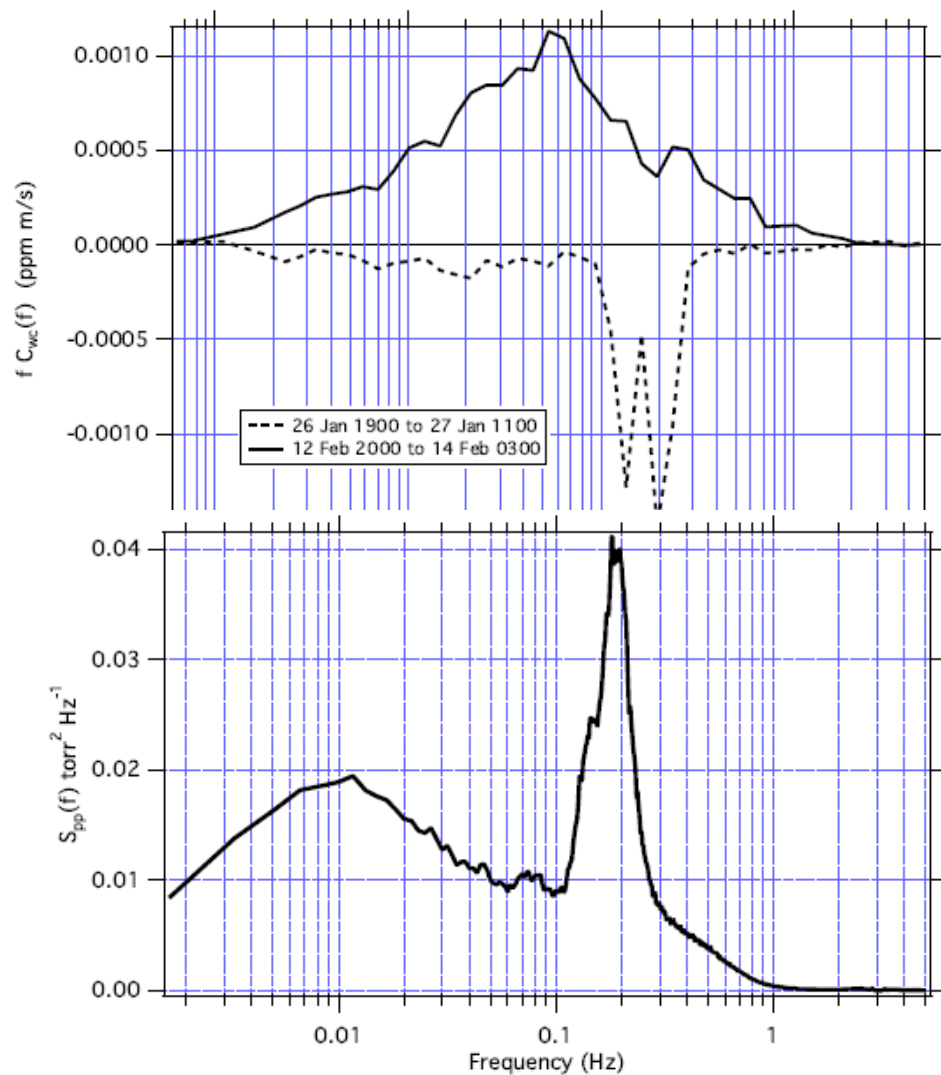
- The PKT method (Prytherch et al., 2010a)
- cross-correlation method (Edson et al., 2011)



Interferences and Corrections

Motion Related Effects for CO_2 Analysers

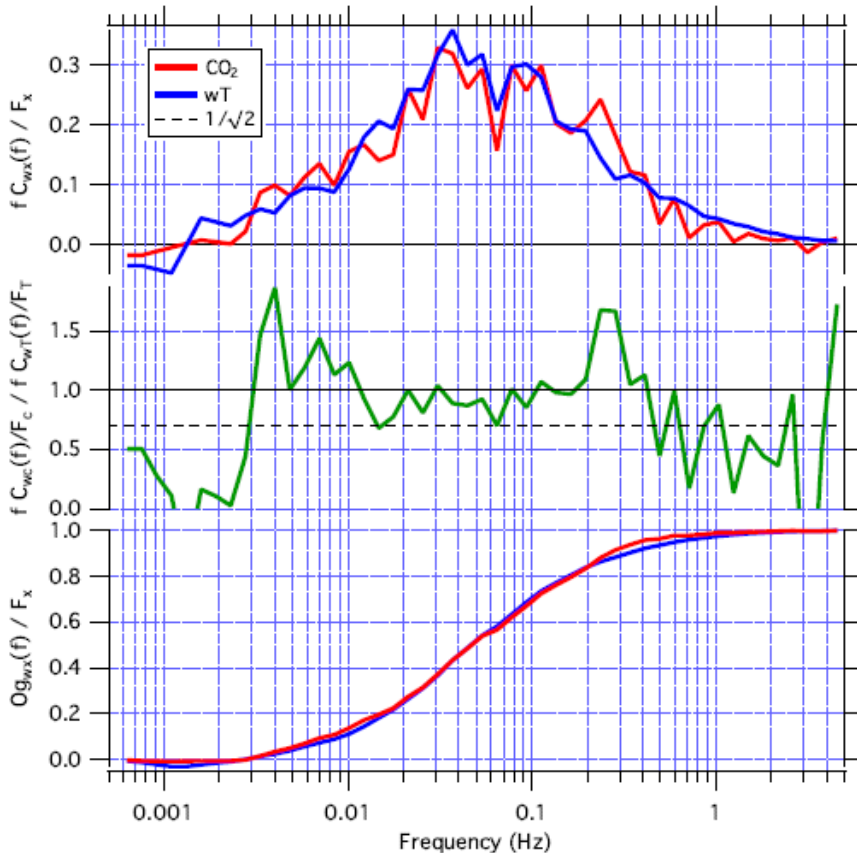
- motion decorrelation applied to DYNAMO dataset $\rightarrow c = c_m - \mu_0 q$



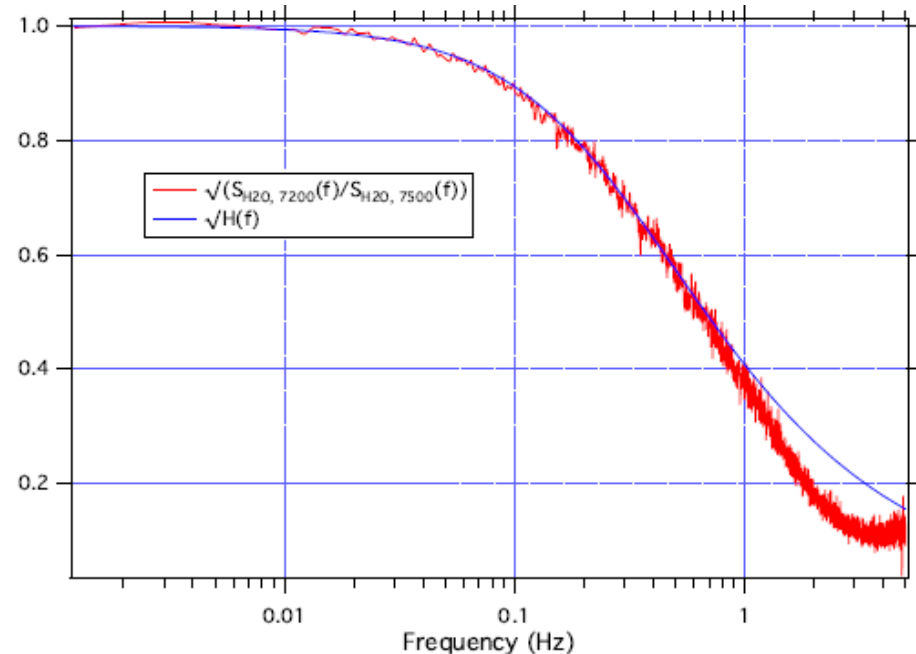
Interferences and Corrections

Spectral attenuation

- additional low-pass filtering effects from tubing in closed-path systems
- 2 approaches:
 - transfer functions (empirical or puff)
 - spectral similarity methods with $w'T'$ or $w'q'$ for instance.



- DYNAMO and TORERO puff more liable measure of the attenuation correction.
- 6-7% correction for TORERO and DYNAMO



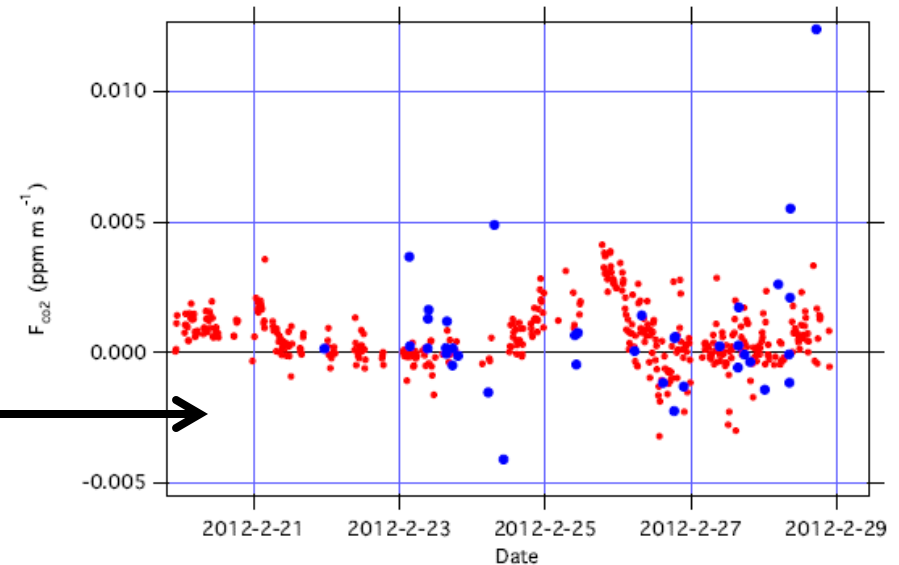
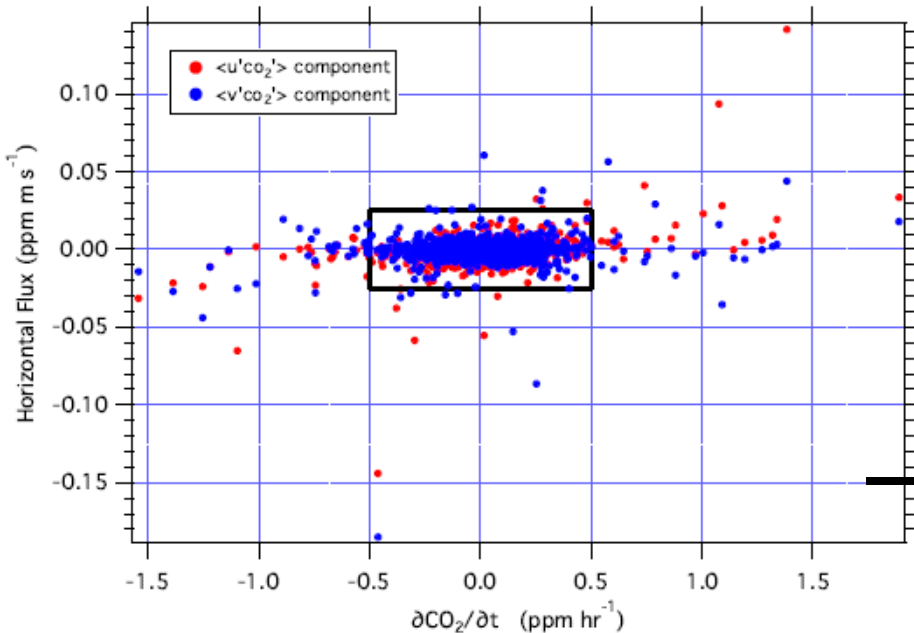
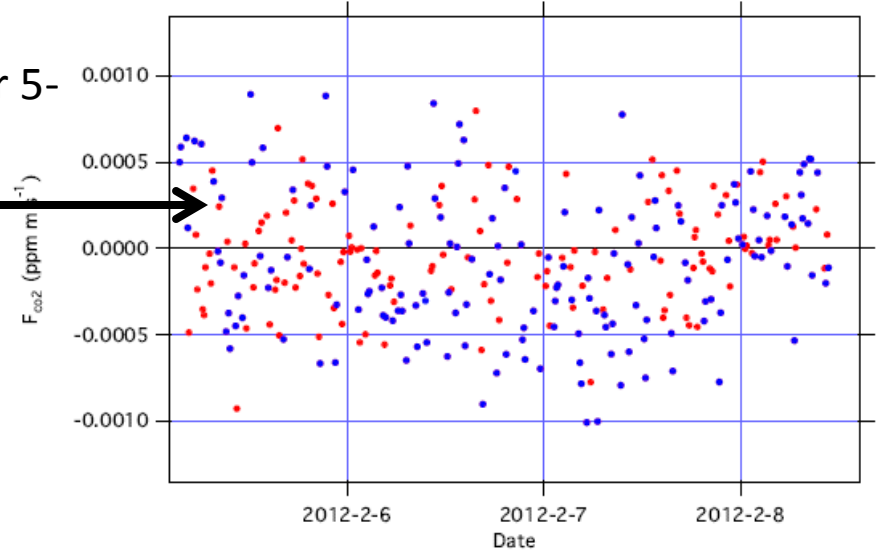
Interferences and Corrections

Stationarity, Homogeneity and Entrainment

- fractional difference in covariance flux over 5- and 30-minute timescales

$$RN_{cov} = \left| \frac{(\overline{w'x'})_5 - (\overline{w'x'})_{30}}{(\overline{w'x'})_{30}} \right| \leq 0.3$$

- $\partial CO_2/\partial t$, $u'co_2'$ and $v'co_2'$ were used to select for steady-state CO_2 conditions
- subjective



$\partial CO_2/\partial t < 0.5 \text{ ppm hr}^{-1} \rightarrow \sim .25\% \text{ of } CO_2 \text{ background concentration per } 60\text{km at } 8 \text{ m/s!}$

Summary and Recommendations

1. water vapour interference is the most significant factor limiting precision and accuracy for shipbased CO₂ flux studies
 - **DRY!** (computed corrections in the LI-COR algorithm appear to be insufficiently precise for measurements of air-sea gas transfer). Eliminates crosstalk and WPL correction uses altogether and a lot of uncertainty
2. At high flow rates, long sample lines do not significantly degrade flux measurements with closed-path analysers.
 - A variety of useful methods exist to determine frequency attenuation and lag time
 - In our case, hourly gas pulses at the sample inlet have proven most useful in our work
3. motion interference need to be carefully evaluated and corrected as possible
4. scalar stationarity for flux measurements of CO₂ and other trace gases is necessary.
 - Traditional stationarity tests are not always effective near the flux detection limit.
 - An examination of horizontal turbulent fluxes can help improve selectivity of the stationarity test.