Measuring surface ocean CO$_2$ partial pressure from autonomous platforms

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Mauna Loa monthly mean CO₂ – the “Keeling Curve“
Global Carbon Cycle – the most simple depiction...

600

~165*

2070

~118*

38000

*Period 1800-1994
Global Carbon Cycle – the slightly more complicated version...

- Fossil Fuel & Cement Land-Use
- Land Emissions Change sink
- Respiration & Fires
- Volcanism

- Plants & Soil
  - Fossil Organic Carbon: >6000 -220
  - Rock Carbonates
  - Geological Reservoirs

- Ocean
  - Units are Pg C for reservoirs and Pg C/yr for fluxes

- Atmosphere
  - [590 + 161]
  - 21.9
  - 20

- Weathering
  - 0.2
  - 0.4
  - 1.1

- River outgassing
  - 0.2

- River export
  - 1

- River fluxes
  - 1.1

- Weathering
  - 0.5
WANTED: $p\text{CO}_2$ climatology

Takahashi et al., 2008.
DSR II: in press.
Giant task behind a simple figure

Takahashi et al., 2008.
DSR II: in press.

Black: Takahashi et al. (2002) Climatology
Red: Added in Takahashi et al. (2008) Climatology
“Voluntary Observing Ships“

Global VOS network for $pCO_2$ measurements
1st Kiel VOS line: M/V Falstaff

- **M/V Falstaff**: Wallenius Lines, Stockholm/Sweden
- Established and operated under CAVASSOO in 2002-2003
- Re-activated under CarboOcean in April 2005
- Operation discontinued in summer 2006

- Continuous meas. with telemetry: $pCO_2\text{sea}$, $pCO_2\text{atm}$, $T$, $S$, $O_2$, chlorophyll (worldwide)
- Discrete meas.: DIC, TA, DOC/DON, POC/PON, nutrients, $\delta^{13}C$-DIC (only Atlantic)
2nd Kiel VOS line: M/V Atlantic Companion

- M/V Atlantic Companion: Atlantic Container Lines, NJ/USA
- Agreement with ACL settled in June 2005
- GO/Neill $pCO_2$ system installed in Jan. 2006
- In operation since Feb 2006 with trans-Atlantic crossings every 2.5 weeks

- Continuous meas. with telemetry: $pCO_2^{sea}$, $pCO_2^{atm}$, $T$, $S$, $O_2$, chlorophyll
- Discrete meas.: DIC, TA, DOC/DON, POC/PON, nutrients, $\delta^{13}C$-DIC
CARBOOCEAN, WP4, IFM-GEOMAR contribution
A seemingly simple measurement: take an equilibrator...
... and a $\text{CO}_2$ detector – and you are done!? 

But how good are the data? 
How can we assess the quality of the $p\text{CO}_2$ measurement? 
How do the data compare?
At-sea intercomparison of two $p\text{CO}_2$ systems in the North Sea (Sept. 1994)

Mean offset: $0.2 \pm 1.5 \mu\text{atm}$
International at-sea $pCO_2$ intercomparison during R/V Meteor Cruise 36/1 (June 1996)

The international at-sea intercomparison of $fCO_2$ systems during the R/V Meteor Cruise 36/1 in the North Atlantic Ocean

Ame Körtzinger a,b, Ludger Minton a, Douglas W.R. Wallace a, Kenneth M. Johnson a, Craig Neill c, Bronte Tilbrook d, Philip Towler d, Hisayuki Y. Inoue e, Masao Ishii e, Gary Shaffer f, Rodrigo F. Torres Saavedra g, Eiji Ohtaki h, Eiji Yamashita i, Alain Poisson j, Christian Brunet j, Bernard Schauer j, Catherine Goyet k, Greg Eisched k

Fig. 8. Results for June 14: seawater $fCO_2$ as measured by system “A”–“G” (underway) and “H” (discrete) or calculated from $A_T$ and $C_T$ measured on discrete samples (top panel), deviations of seawater $fCO_2$ from reference (11-min running mean of “D” and “E”, middle panel), and in situ surface temperature and salinity (bottom panel).
International at-sea $p$CO$_2$ intercomparison during R/V Meteor Cruise 36/1 (June 1996)


$x$CO$_2$ calibrations are typically not better than 1 ppmv

Fig. 3. Results from the check of the CO$_2$ calibration performance: shown are observed deviations from the concentrations of all NOAA-CMDL CO$_2$ standards measured as “unknowns”. See legend for details of the nominal concentrations used by each system for calibration. Also shown is the range of measured $x$CO$_2$ during the whole intercomparison.
Fig. 6. Results of atmospheric CO$_2$ measurements: deviation of the CO$_2$ mole fraction in dry air [xCO$_2$ (air)] as measured by laboratories “A”–“E” and “G” from a running mean of “D” and “E” for the period from June 7, 2230 UTC to June 17, 0630 UTC.
Temperature sensor are often not calibrated with adequate accuracy!

Fig. 4. Results of the check of the equilibrator temperature probes of systems “A”–“G”: shown are deviations of measured temperatures from the reference temperature, when equilibrator probe and reference probe were kept together in the same water bath until readings had become stable. Also shown are the linear correction lines that were applied to temperature readings of a given system.
A new commercial system that has learned from all these exercises ...

- Developed by Craig Neill at the University of Bergen/Norway
- First series of instruments produced at University of Bergen
- Production handed over to General Oceanics Inc., Miami/FL, U.S.A.
- First GO/Neill Model 8050 series delivered after further modification
- Instrument is being used on many VOS lines worldwide
... and allows us to do very nice measurements
How to do autonomous sub-surface $pCO_2$ measurements?

- SAMI-$pCO_2$ Sensor (spectrophotometric system with pH dye)
- Developed by Mike DeGrandpre, Univ. of Missoula/MT, U.S.A.
- Produced by Sunburst Sensors LLC, Missoula/MT, U.S.A.

$$pH = pK_s + \log \frac{[\text{Ind}^{2-}]}{[\text{HInd}^-]}$$

$$\frac{[\text{Ind}^{2-}]}{[\text{HInd}^-]} = \frac{E_{620}^0}{E_{434}^0 - E_{HInd}^{620}} \cdot \frac{E_{434}^{620} - E_{HInd}^{434}}{E_{Ind}^{434} - E_{HInd}^{434}}$$
Another instrument for doing great measurements* 


*if it works...
Another instrument for doing great measurements*

Can we go even smaller and more robust with sub-surface $pCO_2$ measurements?

- NDIR-based $pCO_2$ sensors
- Membrane-separated headspace
- Commercially available (e.g. Pro Oceanus, Halifax/Canada; Contros GmbH, Kiel/Germany)
- First tests on autonomous profiling floats
How can we fight the old biofouling problem?
What is the long-term goal for CO$_2$ sensors – the oxygen example
High-tech platforms not to be missed by the CO$_2$ community

ARGO

3110 Active Floats

- Dissolved Oxygen, Chlorophyll Fluorescence, Turbidity (7)
- Standard Argo: Pressure, Temperature, Salinity (3110)
- Dissolved Oxygen (126)
- Ice Detection (98)

February 2008
High-tech platforms not to be missed by the CO$_2$ community