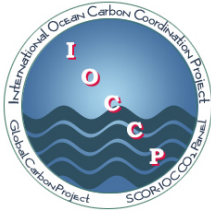


## Ocean Surface $p\text{CO}_2$ , Data Integration and Database Development



An international workshop co-sponsored by  
NIES, IOCCP, and PICES WG 17  
January 14-17, 2004 Tsukuba, Japan



Independent Administrative Institution

National Institute for Environmental Studies



### Working Group I Report: Results from the 2003 Intercomparison Experiment

**Experimental Set-up** – The pool was located at the National Research Institute of Fishery Engineering, Hazaki, Japan, and contained 170,000 liters of coastal seawater adjusted to a salinity of 33. The water was filtered several days before the start of the exercise. Temperatures ranged between 11.0 and 12.5 °C during the 4 days of the experiment.

**Groups and System Specifications** – see Appendix 3.

**General Procedure** – The intercomparison experiment was carried out over 5 days between March 10-14, 2003. The instruments were run during the night,  $x\text{CO}_2$  was calculated, and results were compiled by a data manager and compared and discussed in the afternoon. The  $p\text{CO}_2$  levels in the pool were adjusted using NaOH or HCl. NIES provided calibration gases with concentrations of: 271.33, 329.72, 390.11, and 449.85 ppm. In addition, NIES supplied dry air and  $\text{CO}_2$ -free gas, which was used as a reference gas.

#### March 8

Leak tests for standard calibration gases were carried out and data format was checked.

#### March 10-11 night-time run

The first test started 10 March at 20:00 with pool  $p\text{CO}_2$  at 280 ppm. The  $p\text{CO}_2$  was increased to 450 ppm at 02:00 on the 11<sup>th</sup>. At 08:00 on the 11<sup>th</sup>, data from all systems were recovered and  $x\text{CO}_2$  was calculated and compiled by the data manager.

#### March 11-12 night-time run

The second test started with a pool  $p\text{CO}_2$  of 450 ppm at 20:00 measured over 4 hours, then  $p\text{CO}_2$  was adjusted to 360 ppm at 00:00, and then to 270 ppm at 04:00 on the 12<sup>th</sup>. The 270 ppm was used to check the reproducibility of the first test.

#### March 12 daytime

Some groups checked possible contamination of  $\text{CO}_2$  through the equilibrator vent using dry ice and soda lime ( $\text{CO}_2$ -free air).

#### March 12-13 night-time run

The third test was carried out by adjusting the  $p\text{CO}_2$  in the pool to 270 ppm at 20:00 on the 12<sup>th</sup>, then to 360 ppm at 00:00 and to 450 ppm at 04:00.

#### March 13 daytime

Time response test was performed by alternating the water intake between the pool (around 450 ppm) and a smaller tank (500 L) with a different  $p\text{CO}_2$  (around 250 ppm).

### March 13-14 night-time run

Temperature dependence test was performed with constant  $p\text{CO}_2$  at approximately 400 ppm and the temperature was increased by  $1.5^\circ\text{C}$  in the pool water.

### March 14 daytime

Test for time response continued. The systems were packed and prepared for shipping.

### **Summary of Discussion of Results:**

1. Systems with small equilibrators must have accurate temperature measurement and correction. The underwater pump with 300 L/min flow rate gave a temperature increase of about  $0.05^\circ\text{C}$ . This implies that an onboard pump with a smaller flow rate will give a larger temperature increase (electric heating / water flow rate). Solutions: Thermal insulation, especially for small equilibrators; precise temperature correction; sea chest thermometer must be prior to the water pump.
2. Organic matter decomposition (from accumulation in the equilibrator) gives a positive bias. Solutions: If possible use an equilibrator design without filtration (large inlet or showerhead hole); clean equilibrator and filter unit frequently; use large water flow equilibrators since they experienced relatively small effects even with significant organic matter decomposition.
3. Re-supply air (circulating equilibrators) give positive bias at low  $p\text{CO}_2$  and negative bias at high  $p\text{CO}_2$ . Solutions: Minimize need for re-supply air; increase equilibrator efficiency; pre-equilibrate the re-supply air; place NDIR in the circulation loop so measured air is returned to equilibrator.
4. Equilibrator pressurization or depressurization (from changing water levels in the equilibrator, flow rate instabilities, etc) can be a major source of noise. Solutions: Precise measurement of equilibrator pressure so corrections can be applied; pump design and optimized alignment of the pump to minimize fluctuations.
5. Reactive equilibrators (membrane equilibration or chemistry sensors having reactive surfaces for  $\text{CO}_2$ ) may have a memory effect under conditions of large and rapid  $p\text{CO}_2$  change.
6. Temperature differences between the equilibrator air and standard gas temperatures can lead to error. Solutions: Circulation loop design (low enough flow rate to allow accurate temperature reading); thermal insulation of NDIR system enclosure and enough residence time.

### **Work Plan for Publications:**

The group will follow the outline of Meteor Intercomparison (NDP-067) publication except there will be no data associated with publication (technical report, not an NDP)

All agree to use the same A, B, C designations for systems as used in the NDP-067 report to facilitate comparisons between the 1996 and 2003 intercomparisons.

Timeline: The goal is to have first draft by mid April, with a final draft by June in time to make a presentation at the October PICES meeting.

Title: *International Indoor Seawater Pool pCO<sub>2</sub> Intercomparison – results and recommended practices*

OUTLINE

- I. Introduction [Nojiri]
- II. Description of Exercise [NIES]
  - a. Pool setup
    - i. Water issue (water source, circulation etc.)
    - ii. Temperature issues
    - iii. pCO<sub>2</sub> control
    - iv. Plumbing (pump, including order of systems?)
    - v. Ancillary measurements
    - vi. Separate experimental designs
  - b. Standard Gas
    - i. What they were and how calibrated
    - ii. Plumbing
  - c. Temperature sensors
    - i. NIES supplied sensors
    - ii. Comparison with individual sensors
    - iii. Comparison with pool sensors
  - d. Data handling
    - i. Individual group calculations
    - ii. combined calculations
    - iii. Use of NIES system as reference for comparison
- III. Methods and procedures (summary table and text on similarities and differences, statement on the differences in what the system types measure (xCO<sub>2</sub> vs. pCO<sub>2</sub>), references on individual published techniques can be included in appendix)
  - a. Shipboard type systems [Currie]
  - b. In situ type systems [DeGrandpre, Merlivat, Friederich]
- IV. Individual Results (each group summarize results and what they learned) [each individual group will contribute text]
  - i. Differences between this set-up and normal set-up
  - ii. Observed precision
  - iii. response experiment - observed response time
  - iv. dry ice/soda lime experiment - vent contamination
  - v. other individual experiments
  - vi. other issues that came up
  - b. NIES (short and long)
  - c. KEEC
  - d. NOAA
  - e. MBARI Underway (OM decomposition)
  - f. KOREA (calibration problems)
  - g. UEA (high standard deviation, calibration jumps in data)
  - h. NIWA (calibration)

- i. IFM (temperature gradient, system flooding)
- j. NRIFS (memory)
- k. MBARI mooring
- l. CARIOCA (OM decomposition)
- m. SAMI-CO<sub>2</sub>
- V. Overall results [Nojiri]
  - a. Summary of results with combined plots and tables
- VI. Recommended Practices
  - a. Design recommendations
    - i. Ship issues/water handling (location of intake, temperature contamination-insulating lines, equilibrators, cleaning of lines, etc.) [Kortzinger, Sabine]
    - ii. Electronics package/air handling (detectors, wet vs. dry measurements, pumps, valves, tubing, air filtering, flow rates, etc.) [Luger]
    - iii. Air measurements (why, issues, validity of using ship as a platform, wind direction filtering) [Nojiri]
    - iv. Initial Data handling (important parameters to log, useful ancillary measurements, etc.) [Friederich]
    - v. Calibration [Nojiri]
      - 1. standard gases
      - 2. temperature
      - 3. pressure
    - vi. QA/QC [Sabine]
      - 1. tests to evaluate system
      - 2. data checks
      - 3. intercomparison exercises
  - b. Potential errors to watch out for [NIES]
    - i. Temperature issues
    - ii. OM decomposition
    - iii. Re-supply air issues
    - iv. Equilibrator pressure issues
    - v. Memory
    - vi. Gas standard temp vs. sample temp
      - To Do by end of February:
      - DeGrandpre – send revised data to Nojiri
      - Friederich – send time response
      - Merlivat – send data file
      - UEA – Check data (additional despiking?)
      - Nojiri – send general data to all participants

### APPENDIX III: INTERCOMPARISON EXPERIMENT GROUPS AND SYSTEM SPECIFICATIONS

Group	AIST (K. Harada) / Kanso Company	NIES (Vi)	NOAA (C. Neill)	MBARI (G. Friederich)	Korea (Kang, Kim)	UEA (U. Schuster)	NIWA (K. Currie)	IfM Kiel (H. Lueger, K. Frils)
<b>Equilibrator Design</b>	Showerhead (MRI)	1. Mixer + long bubbler 2. Mixer + short bubbler	Showerhead  Recycling air	Liqui-cel (Polypropylene hydrostatic pressure "cell") Recycling air	Showerhead Flow through  Recycling air	Percolator (equilibrator filled with borosilic rashig rings)	Showerhead and bubbling  Flow through Recycling air	Laminar flow bubbler  Flow through Recycling air
<b>Detection</b>	NDIR Rosemount	NDIR LI-COR	NDIR LI-COR 6262 Stopped flow	NDIR LI-COR 6262	NDIR LI-COR 6252	NDIR LI-COR 7000	NDIR LI-COR 6251	NDIR LI-COR 6262
<b>Output</b>	ppm	mV	ppm	ppm	mV	ppm	mV	mV
<b>Measured Parameter</b>	xCO <sub>2</sub> (dry)	xCO <sub>2</sub> (dry)	xCO <sub>2</sub> (dry)	fCO <sub>2</sub> (wet)	xCO <sub>2</sub> (dry)	xCO <sub>2</sub> (dry) (fCO <sub>2</sub> at sea)	xCO <sub>2</sub> (dry)	xCO <sub>2</sub> (dry)
<b>Total Vol. (L) Water Vol.(L) Air Vol. (L)</b>					33 12 21			1
<b>Air Flow (mL/min) Experiment Normal</b>	600 600	350 350	80 80	300 / 750 ? 300	100 100	100 100	300 300	830 830
<b>Calibration Gases Experimental Normal</b>	4 (no 0) 4 (no 0)	4 + 0 gas 4 + 0 gas	4 4	3 (1,3,4) + soda lime 0; 3 + soda lime 0	3 + ref (1,3,4) 4 (incl. Ref and 1 working std)	4 (all std except 0); 2	4 std (3+0) nr 1,3,4; 2 std (0, 380 ppm)	4 std + 0 ref. 3 std + 0 ref.
<b>Calibration Frequency Experimental Normal</b>	Hourly 5 min / gas	Every 6 hours each std 10 s	Hourly 3 min / each;	Hourly each std 1 minute	4 hr and working std	Every 6 hours; Every 6 hours	Every 12 hours 5 min /	Hourly 2 min / each 6 s

		for 10 min use last 3 min for calibration	Hourly 3 min / each	use last 10 s; Hourly each std 1 minute use last 10 s	hourly; 6 hr and hourly working std		each ; Every 8 hours 5 min / each	average
<b>Analysis Cycle</b>	5 min air 4 times / hour 9 min SW/ twice / hour	10 min air 4hr SW	3 min / 30 min SW 3 min air once / hr			Experiment: 3 hours seawater, 20 min std. Normal: SW 30 min, air 10 min, 3 cycles, std 10 min.	Exp: SW 12 hr	Experiment: no air meas.  Normal: 6 min std, air 3 min, SW rest 51 min.
<b>Data Logging</b> Sample calibration		10 s 10 s		2 sec / avg 10 s 1 min	15 min / each std every 10 sec (exp) 2 sec norm	Every minute	Every 30 sec.	Every minute
<b>Dryers</b>	Permapure (©Nafion) Mg(CLO4)2 Coldtrap 5 °C.	Permapure (©Nafion) Mg(CLO4)2 Coldtrap	Permapure (©Nafion)	Mg(CLO4)2	Permapure (©Nafion)	Mg(CLO4)2 (only condensator at sea)	Permapure (©Nafion) Mg(CLO4)2	Mg(CLO4)2 Peltier Permapure (©Nafion) Silica gel for counter flow
<b>Temp reading</b> Experimental Normal	NIES	Thermistor Thermistor	NIES	NIES Pt100	NIES / Thermistor Thermistor	NIES Pt100 Sens 0.1 C	NIES T sensor (0.01C)	NIES Pt100
<b>Vented ?</b>	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes

## SENSOR SYSTEMS

Group	CNRS (T. Danguy, L. Beaumont)	NRIFS (T. Ono, K. Sasaki)	MBARI (G. Friederich)	SAMI (C. Beatty)
<b>Equilibrator</b>	Sensor Indicator methyl blue membrane	Sensor Goretex membrane	Equilibrator (copper tube with Teflon tube inside)	Silicon membrane Indicator Bromomethylblue (BTB) 434, 620, 740 nm
<b>Detection</b>	Spectrophotometer 2.6 mm path length 20 µL indicator (conc. $10^{-4}$ mol / kg, dissolved in synthetic seawater)	LI-COR 6262	LI-COR 800	Spectrophotometer Photodiode 1 cm path length 50 µL indicator (conc $10^{-5}$ mol/kg, dissolved in deionized water)
<b>Output</b>	fCO <sub>2</sub> (wet)		fCO <sub>2</sub> (wet)	
<b>Calibration</b>	Known xCO <sub>2</sub> gas bubble in SW at known P, S, T, for different T and get a calibration curve for different T. CMDL 1 std meas 2 <sup>nd</sup> std		Soda lime zero & atmosphere 3 of 2 <sup>nd</sup> std checked against primary CMDL standard before mooring set up	1600 ppm dry gas dilute to create calibration curve
<b>Measured Cycle</b>	Every 30 min (exp) Every hour (on buoy)			Every 15 minutes
<b>Air flow rate</b> <b>Water flow rate</b>	0.5-1 L / min			100 mL / min
<b>Thermostating</b>	Sea water cooling			SW cooled; thermistor