Apparatus and shipboard measurement

Continuous underway measurements of atmospheric and surface seawater pCO_2 were made with the CO_2 measuring system (Nippon ANS, Inc.) installed in the R/V *Mirai* of JAMSTEC. The system comprises of a non-dispersive infrared gas analyzer (Li-COR LI-7000, modified by Nippon ANS, Inc.), an air-circulation module and a showerhead-type equilibrator. To measure concentrations (mole fraction) of CO_2 in dry air (xCO_2a), air sampled from the bow of the ship (approx. 30 m above the sea level) was introduced into the NDIR through a dehydrating route with an electric dehumidifier (kept at ~2 °C), a Perma Pure dryer (GL Sciences Inc.), and a chemical desiccant ($Mg(ClO_4)_2$). The flow rate of the air was approx. 500 ml min^{-1}. To measure surface seawater concentrations of CO_2 in dry air (xCO_2s), the air equilibrated with seawater within the equilibrator was introduced into the NDIR through the same flow route as the dehydrated air used in measuring xCO_2a. The flow rate of the equilibrated air was 400 – 900 ml min^{-1}. The seawater was taken by a pump from the intake placed at the approx. 4.5 m below the sea surface. The flow rate of seawater in the equilibrator was 4000 – 5000 ml min^{-1}.

The CO_2 measuring system was set to repeat the measurement cycle such as 4 kinds of CO_2 standard gases (Table 1), xCO_2a (twice), xCO_2s (7 times). This measuring system was run automatically throughout the cruise by a PC control.

Quality control

Concentrations of CO_2 of the standard gases are listed in Table 1, which were calibrated after cruise by the JAMSTEC primary standard gases. The CO_2 concentrations of the primary standard gases were calibrated by the Scripps Institution of Oceanography, La Jolla, CA, USA.

In actual shipboard observations, the signals of NDIR usually reveal a trend. The trends were adjusted linearly using the signals of the standard gases analyzed before and after the sample measurements.

Effects of water temperature increased between the inlet of surface seawater and the equilibrator on xCO_2s were adjusted based on Takahashi *et al.* (1993), although the temperature increases were slight, being usually <0.1 °C.

We checked values of xCO_2a and xCO_2s by examining signals of the NDIR by plotting the xCO_2a and xCO_2s as a function of sequential day, longitude, sea surface temperature and sea surface salinity.

Reference

Takahashi, T., J. Olafsson, J. G. Goddard, D. W. Chipman, and S. C. Southerland (1993) Seasonal variation of CO_2 and nutrients in the high-latitude surface oceans: a comparative study, *Global Biogeochem. Cycles*, 7, 843–878.

Table 1. Concentrations of CO_2 standard gases used during MR16-04.

Cylinder no.	Concentrations (ppmv)
CQC00740	269.07
CQC00739	330.19
CQB09461	359.33
CRC00741	419.30

Meta data summary

Method Description:

Sampling and Equilibrator Design:

Depth of Sea Water Intake: 4.5 m

Location of Sea Water Intake: side at bow

Equilibrator Type: showerhead-type equilibrator

Equilibrator Volume: approx. 1 L

Water Flow Rate: 4000 - 5000 mL min^{-1}

Headspace Gas Flow Rate: 400 - 900 mL min^{-1}

Vented: Yes

Drying Method for CO2 in Water: Electron Cooler, Perma Pure dryer, Chemical Desiccant with $Mg(ClO_4)_2$

Additional Information:

System Design:

Measurement Method:

Manufacturer of Calibration Gas:

CO2 Sensor:

Measurement Method: dispersive infrared gas analyzer

Manufacturer: Nihon ANS, Ltd.

Model: Underway pCO2 measurement system using LI-7000 CO2 Analyzer by LI-COR (modified by Nippon ANS, Inc.)

Environmental Control: none

Frequency: 4.5 min. for CO_2air (2 analysis), and then7 min. for CO_2water (7 analysis)

(except during calibration routines)

Precision of CO2water: 0.1 ppm

Precision of CO2air: 0.05 ppm

Accuracy of CO2water: 1-2 ppm

Accuracy of CO2air: ~0.1 ppm

CO2 Sensor Calibration:

Manufacturer of CO2 calibration gases: Taiyo Nippon Sanso Corporation, Japan

Method References:

CO2 in Marine Air:

Measurement: yes

Location and Height: foremast, 13 m high

Sea Surface Temperature:

Location: bow thruster room

Manufacturer: Sea-Bird Electronics Inc.

Model: SBE38

Accuracy: 0.002 degree

Precision: 0.0002 degree

Calibration: Manufacturer calibration every one year.

Other comments:

Sea Surface Salinity:

Location: sea surface monitoring laboratory

Manufacturer: Sea-Bird Electronics Inc.

Model: SBE45

Accuracy: 0.005

Precision: 0.003

Calibration: Manufacturer calibration every one year.

Other comments:

Equilibrator Temperature:

Location: just upstream of shower head

Manufacturer: THERMOTEX CO. LTD, Japan

Model: Pt100 ohm

Accuracy: 0.08 degree

Precision: 0.03 degree

Calibration: Calibration is performed by a traceable mercury thermometer before the measurement.

Other comments:

Equilibrator Pressure:

Location: equilibration sector of equilibrator

Manufacturer: Druck

Model: RPT410V

Accuracy: 0.5 hPa

Precision:

Calibration: Certified calibration is performed every 2 years.

Other comments:

Atmospheric Pressure:

Location: Weather observation room at captain deck (13m)

Manufacturer: Setra System, USA

Model: Model-370

Accuracy: ±0.02%

Precision: 0.010% FS

Calibration: Comparison with the portable barometer value, PTB220, VAISALA

Other Sensors:

Manufacturer::

Model:

resolution:

Uncertainty:

Calibration:

Other Comments:

Accuracy Info:

Method References: