

half period of the cruise. However, it acted as a source for or almost equilibrated with atmospheric CO₂ during the latter half period.

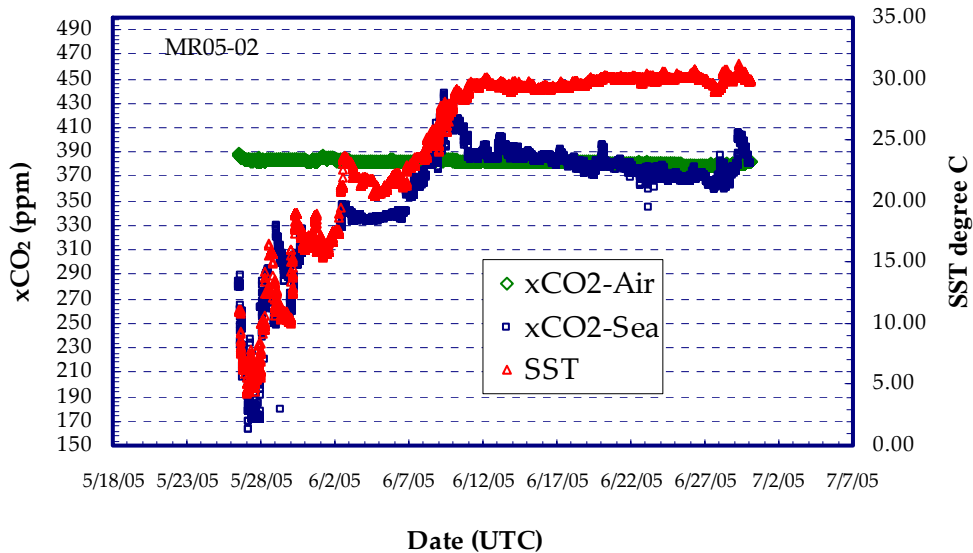


Figure 1. Temporal changes of concentrations of CO₂ (xCO₂) in atmosphere (green) and surface seawater (blue), and SST (red).

3. Hydrography

3.1 CTD/O₂ Measurements (2 July 2005)

Hiroshi Uchida, Masao Fukasawa (JAMSTEC),

Satoshi Ozawa, Naoko Takahashi, Kentaro Oyama and Tomohide Noguchi (MWJ)

3.1.1 Winch arrangements

The CTD package was deployed using 4.5 Ton Traction Winch System (Dynacon, Inc., USA), which was installed on the R/V Mirai in April 2001. The CTD Traction Winch System with the Heave Compensation Systems (Dynacon, Inc., USA) is designed to reduce cable stress resulting from load variation caused by wave or vessel motion. The system is operated passively by providing a nodding boom crane that moves up or down in response to line tension variations. Primary system components include a complete CTD Traction Winch System with up to 10 km of 9.53 mm armored cable (Ocean Cable and Communication Co.), cable rocker and Electro-Hydraulic Power Unit, nodding-boom crane assembly, two hydraulic cylinders and two hydraulic oil/nitrogen accumulators mounted within a single frame assembly. The system also contains related electronic hardware interface and a heave compensation computer control program.

3.1.2 Overview of the equipment

The CTD system, SBE 911plus system (Sea-Bird Electronics, Inc., USA), is a real time data system with the CTD data transmitted from a SBE 9plus underwater unit via a conducting cable to the SBE 11plus deck unit. The SBE 11plus deck unit is a rack-mountable interface which supplies DC power to the underwater unit, decodes the serial data stream, formats the data under microprocessor control, and passes the data to a companion computer. The serial data from the underwater unit is sent to the deck unit in RS-232 NRZ format using a 34,560 Hz carrier-modulated differential-phase-shift-keying (DPSK) telemetry link. The deck unit decodes the serial data and sends them to a personal computer to display, at the same time, to storage in a disk file using SBE SEASOFT software.

The SBE 911plus system acquires data from primary, secondary and auxiliary sensors in the form of binary numbers corresponding to the frequency or voltage outputs from those sensors at 24 samples per second. The calculations required to convert from raw data to engineering units of the parameters are performed by the SBE SEASOFT in real-time. The same calculations can be carried out after the observation using data stored in a disk file.

The SBE 911plus system controls the 36-position SBE 32 Carousel Water Sampler. The Carousel accepts 12-litre water sample bottles. Bottles were fired through the RS-232C modem connector on the back of the SBE 11plus deck unit while acquiring real time data. The 12-litre Niskin-X water sample bottle (General Oceanics, Inc., USA) is equipped externally with two stainless steel springs. The external springs are ideal for applications such as the trace metal analysis because the inside of the sampler is free from contaminants from springs.

SBE's temperature (SBE 3) and conductivity (SBE 4) sensor modules were used with the SBE 9plus underwater unit fixed by a single clamp and "L" bracket to the lower end cap. The conductivity cell entrance is co-planar with the tip of the temperature sensor's protective steel sheath. The pressure sensor is mounted in the main housing of the underwater unit and is ported to outside through the oil-filled plastic capillary tube. A compact, modular unit consisting of a centrifugal pump head and a brushless DC ball bearing motor contained in an aluminum underwater housing pump (SBE 5T) flushes water through sensor tubing at a constant rate independent of the CTD's motion. Motor speed and pumping rate (3,000 rpm) remain nearly constant over the entire input voltage range of 12-18 volts DC. Flow speed of pumped water in standard TC duct is about 2.4 m/s. SBE's dissolved oxygen sensor (SBE 43) was placed between the conductivity sensor module and the pump. Auxiliary sensors, Deep Ocean Standards Thermometer (SBE 35), altimeter and fluorometer, were also used with the SBE 9plus underwater unit. The SBE 35 position in regard to the SBE 3 is shown in Figure 3.1.1.

It is known that the CTD temperature data is influenced by the motion (pitching and rolling) of the CTD package. In order to reduce the motion of the CTD package, a heavy stainless frame (total weight of the CTD package without sea water in the bottles is about 1,000 kg) was used and an aluminum plate (54 x 90 cm) was attached to the frame (Figure 3.1.1).

Summary of the system used in this cruise

Deck unit:

SBE, Inc., SBE 11plus, S/N 0308

Under water unit:

SBE, Inc., SBE 9plus, S/N 79511 (Pressure sensor: S/N 0677)

Temperature sensor:

SBE, Inc., SBE 3, S/N 1464 (primary)

SBE, Inc., SBE 3, S/N 1525 (secondary)

Conductivity sensor:

SBE, Inc., SBE 4, S/N 1203 (primary)

SBE, Inc., SBE 4, S/N 3036 (secondary, from P10N_143 to P10_53)

SBE, Inc., SBE 4, S/N 1088 (secondary, from P10_52 to P10_27)

SBE, Inc., SBE 4, S/N 2854 (secondary, from P10_26 to P10_1)

Oxygen sensor:

SBE, Inc., SBE 43, S/N 0391 (primary, from P10N_143 to P10N_122)

SBE, Inc., SBE 43, S/N 0767 (primary, from P10N_121 to P10_1)

SBE, Inc., SBE 43, S/N 0390 (secondary)

Pump:

SBE, Inc., SBE 5T, S/N 3118 (primary)

SBE, Inc., SBE 5T, S/N 3293 (secondary)

Altimeter:

Benthos Inc., PSA-916T, S/N 1157

Deep Ocean Standards Thermometer:

SBE, Inc., SBE 35, S/N 0045

Fluorometer:

Seapoint sensors, Inc., S/N 2579

(without fluorometer from P10N_134 to 132, P10N_112 to P10_68, and P10_28 to 1)

Carousel Water Sampler:

SBE, Inc., SBE 32, S/N 0278

Water sample bottle:

General Oceanics, Inc., 12-litre Niskin-X (no TEFLON coating)

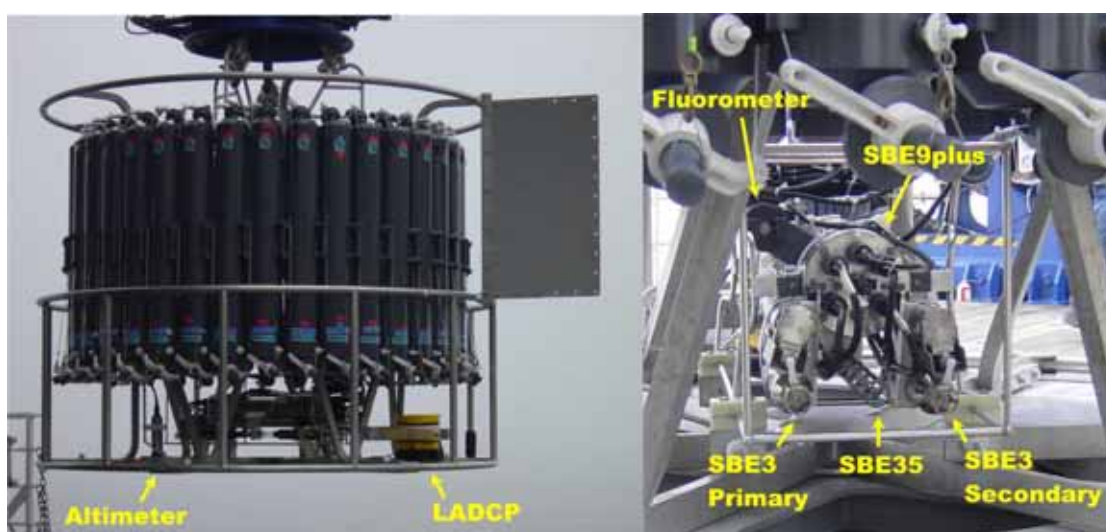


Figure 3.1.1. The CTD package (left) and the SBE 35 position in regard to the SBE 3 temperature sensors (right).

3.1.3 Pre-cruise calibration

(1) Pressure

The Paroscientific series 4000 Digi quartz high pressure transducer (Paroscientific, Inc., USA) uses a quartz crystal resonator whose frequency of oscillation varies with pressure induced stress with 0.01 per million of resolution over the absolute pressure range of 0 to 15,000 psia (0 to 10,332 dbar). Also, a quartz crystal temperature signal is used to compensate for a wide range of temperature changes at the time of an observation. The pressure sensor (MODEL 415K-187) has a nominal accuracy of 0.015 % FS (1.5 dbar), typical stability of 0.0015 % FS/month (0.15 dbar/month) and resolution of 0.001 % FS (0.1 dbar).

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in the SEASOFT:

S/N 0677, 2 July 2002

$$c_1 = -62072.94$$

$$c_2 = -1.176956$$

$$c_3 = 1.954420e-02$$

$$d_1 = 0.027386$$

$$d_2 = 0.0$$

$$t_1 = 30.05031$$

$$t_2 = -4.744833e-04$$

$$t_3 = 3.757590e-06$$

$$t_4 = 3.810700e-09$$

$$t_5 = 0.0$$

Pressure coefficients are first formulated into

$$c = c_1 + c_2 * U + c_3 * U^2$$

$$d = d_1 + d_2 * U$$

$$t_0 = t_1 + t_2 * U + t_3 * U^2 + t_4 * U^3 + t_5 * U^4$$

where U is temperature in degrees Celsius. The pressure temperature, U, is determined according to

$$U (^{\circ}\text{C}) = M * (\text{12 bit pressure temperature compensation word}) - B$$

The following coefficients were used in SEASOFT:

S/N 0677

$$M = 0.0128041$$

$$B = -9.324136$$

(in the underwater unit system configuration sheet dated on 22 February 2002)

Finally, pressure is computed as

$$P (\text{psi}) = c * [1 - (t_0^2 / t^2)] * \{1 - d * [1 - (t_0^2 / t^2)]\}$$

where t is pressure period (μsec). Since the pressure sensor measures the absolute value, it inherently includes atmospheric pressure (about 14.7 psi). SEASOFT subtracts 14.7 psi from computed pressure above automatically.

Pressure sensor calibrations against a dead-weight piston gauge (Bundenberg Gauge Co. Ltd., UK; Model 480DA, S/N 23906) are performed at JAMSTEC (Yokosuka, Kanagawa, JAPAN) by Marine Works Japan Ltd. (MWJ), usually once in a year in order to monitor sensor time drift and linearity. The pressure sensor drift is known to be primarily an offset drift at all pressures rather

than a change of span slope. The pressure sensor hysteresis is typically 0.2 dbar. The following coefficients for the sensor drift correction were also used in SEASOFT through the software module SEACON:

S/N 0677, 13 April 2005

slope = 0.9998953

offset = -0.44425

The drift-corrected pressure is computed as

Drift-corrected pressure (dbar) = slope * (computed pressure in dbar) + offset

Result of the pressure sensor calibration against the dead weight piston gauge is shown in Figure 3.1.2. Time drift of the pressure sensor based on the offset and the slope of the calibrations is also shown in Figure 3.1.3.

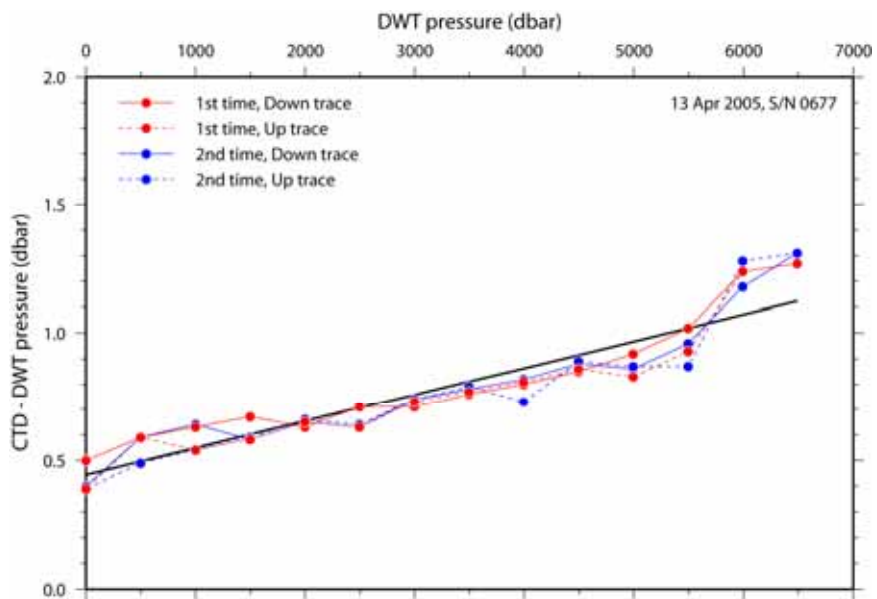


Figure 3.1.2. The residual pressures between the dead weight piston gauge and the CTD pressure (S/N 0677). Black line indicates the residual between the dead weight piston gauge and the calibration line for the CTD pressure.

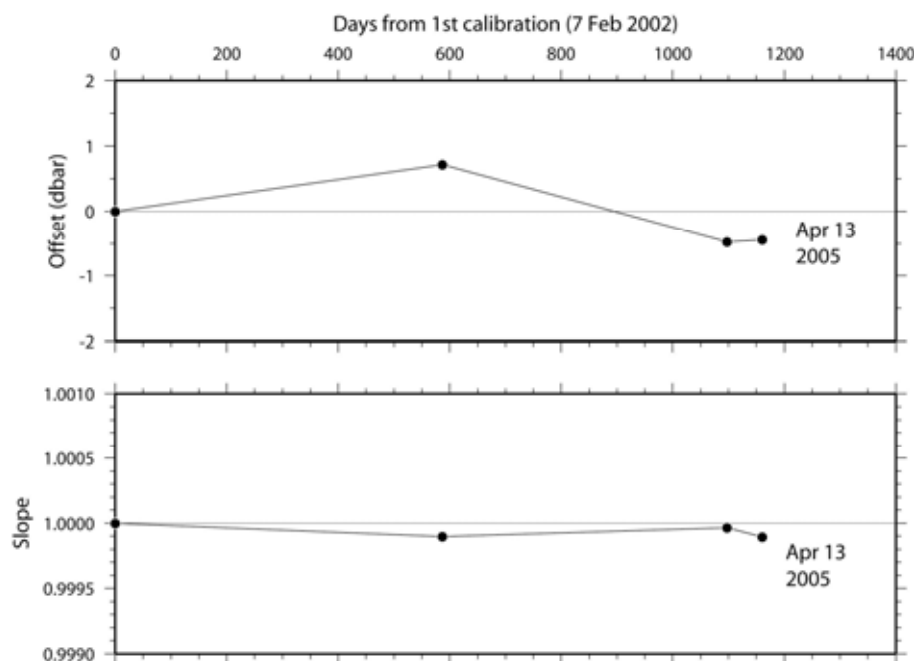


Figure 3.1.3. Pressure sensor (S/N 0677) time drift of offset (upper panel) and slope (lower panel) based on laboratory calibrations.

(2) Temperature (SBE 3)

The temperature sensing element is a glass-coated thermistor bead in a stainless steel tube, providing a pressure-free measurement at depths up to 10,500 (6,800) meters by titanium (aluminum) housing. The sensor output frequency ranges from approximately 5 to 13 kHz corresponding to temperature from -5 to 35 °C. The output frequency is inversely proportional to the square root of the thermistor resistance, which controls the output of a patented Wien Bridge circuit. The thermistor resistance is exponentially related to temperature. The SBE 3 thermometer has a nominal accuracy of 0.001 °C, typical stability of 0.0002 °C/month and resolution of 0.0002 °C at 24 samples per second. The premium temperature sensor, SBE 3plus, is a more rigorously tested and calibrated version of standard temperature sensor (SBE 3). A sensor is designated as an SBE 3plus only after demonstrating drift of less than 0.001 °C during a six-month screening period. In addition, the time response is carefully measured and verified to be 0.065 ± 0.010 seconds.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in SEASOFT:

S/N 1464 (primary), 19 April 2005

$$g = 4.84385804e-03$$

$$h = 6.80766786e-04$$

$$i = 2.69831319e-05$$

$$j = 2.13061451e-06$$

$$f_0 = 1000.000$$

S/N 1525 (secondary), 19 April 2005

$$g = 4.84608198e-03$$

$$h = 6.75358139e-04$$

$$i = 2.65523364e-05$$

$$j = 2.13525896e-06$$

$$f_0 = 1000.000$$

Temperature (ITS-90) is computed according to

Temperature (ITS-90) =

$$1 / \{g + h * [\ln(f_0 / f)] + i * [\ln^2(f_0 / f)] + j * [\ln^3(f_0 / f)]\} - 273.15$$

where f is the instrument frequency (kHz).

Time drift of the SBE 3 temperature sensors based on the laboratory calibrations is shown in Figure 3.1.4.

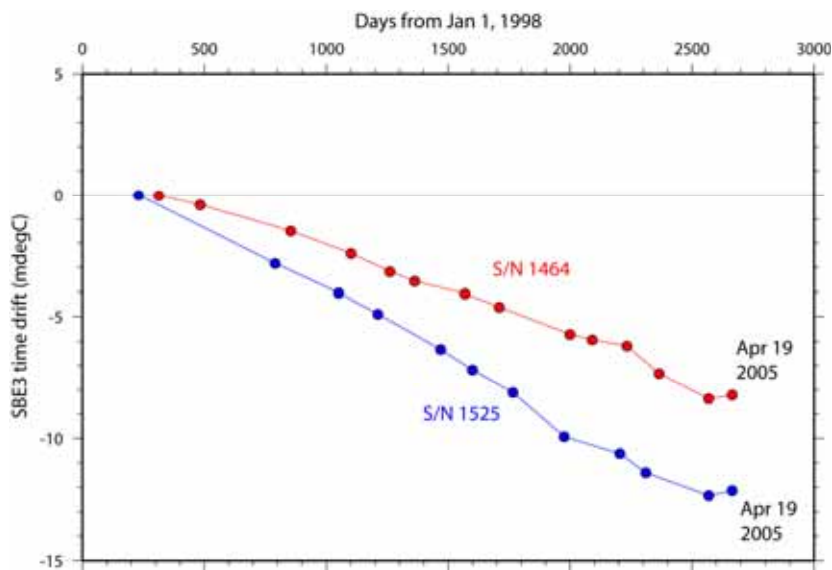


Figure 3.1.4. Time drift of SBE 3 temperature sensors (S/N 1464 and S/N 1525) based on laboratory calibrations performed by SBE, Inc.

(3) Conductivity (SBE 4)

The flow-through conductivity sensing element is a glass tube (cell) with three platinum electrodes to provide in-situ measurements at depths up to 10,500 meters. The impedance between the center and the end electrodes is determined by the cell geometry and the specific conductance of the fluid within the cell. The conductivity cell composes a Wien Bridge circuit with other electric elements of which frequency output is approximately 3 to 12 kHz corresponding to conductivity of the fluid of 0 to 7 S/m. The conductivity cell SBE 4 has a nominal accuracy of 0.0003 S/m, typical stability of 0.0003 S/m/month and resolution of 0.00004 S/m at 24 samples per second.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in SEASOFT:

S/N 1203 (primary), 19 April 2005

$$g = -4.05393563e+00$$

$$h = 4.93901550e-01$$

$$i = 1.74707654e-05$$

$$j = 2.56674141e-05$$

$$CPcor = -9.57e-08 \text{ (nominal)}$$

CTcor = 3.25e-06 (nominal)

S/N 3036 (secondary), 20 January 2005

g = -1.03104164e+01

h = 1.42680631e+00

i = 2.61243729e-04

j = 5.17689837e-05

CPcor = -9.57e-08 (nominal)

CTcor = 3.25e-06 (nominal)

S/N 1088 (secondary), 10 March 2005

g = -4.21020837e+00

h = 5.77013782e-01

i = -1.87512042e-04

j = 4.10775826e-05

CPcor = -9.57e-08 (nominal)

CTcor = 3.25e-06 (nominal)

S/N 2854 (secondary), 22 June 2004

g = -1.02670783e+01

h = 1.41649193e+00

i = -3.19882205e-04

j = 7.82222198e-05

CPcor = -9.57e-08 (nominal)

CTcor = 3.25e-06 (nominal)

Conductivity of a fluid in the cell is expressed as:

$$C \text{ (S/m)} = (g + h * f^2 + i * f^3 + j * f^4) / [10 (1 + CTcor * t + CPcor * p)]$$

where f is the instrument frequency (kHz), t is the water temperature (°C) and p is the water pressure (dbar). The value of conductivity at salinity of 35, temperature of 15 °C (IPTS-68) and pressure of 0 dbar is 4.2914 S/m.

(4) Oxygen (SBE 43)

The SBE 43 oxygen sensor uses a Clark polarographic element to provide in-situ measurements at depths up to 7,000 meters. Calibration stability is improved by an order of magnitude and pressure hysteresis is largely eliminated in the upper ocean (1,000 m) compared with the previous oxygen sensor (SBE 13). Continuous polarization eliminates the wait-time for stabilization after power-up. Signal resolution is increased by on-board temperature compensation. The oxygen sensor is also included in the path of pumped sea water. The oxygen sensor determines the dissolved oxygen concentration by counting the number of oxygen molecules per second (flux) that diffuse through a membrane, where the permeability of the membrane to oxygen is a function of temperature and ambient pressure. Computation of dissolved oxygen in engineering units is done in SEASOFT software. The range for dissolved oxygen is 120 % of surface saturation in all natural waters; nominal accuracy is 2 % of saturation; typical stability is 2 % per 1,000 hours.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were used in SEASOFT:

S/N 0391 (primary), 8 April 2005

Soc = 0.3525

Offset = -0.4761
TCor = 0.0010
PCor = 1.350e-04

S/N 0767 (primary), 11 February 2005

Soc = 0.4320
Offset = -0.4889
TCor = 0.0002
PCor = 1.350e-04

S/N 0390 (secondary), 8 April 2005

Soc = 0.3567
Offset = -0.4965
TCor = 0.0013
PCor = 1.350e-04

Oxygen (ml/l) is computed as

Oxygen (ml/l) = {Soc * (v + Offset)} * exp(TCor * t + PCor * p) * Oxsat(t, s)

Oxsat(t, s) = exp[A₁ + A₂ * (100 / t) + A₃ * ln(t / 100) + A₄ * (t / 100)
+ s * {B₁ + B₂ * (t / 100) + B₃ * (t / 100) * (t / 100)}]

A₁ = -173.4292
A₂ = 249.6339
A₃ = 143.3483
A₄ = -21.8482
B₁ = -0.033096
B₂ = -0.00170

where p is pressure in dbar, t is absolute temperature and s is salinity in psu. Oxsat is oxygen saturation value minus the volume of oxygen gas (STP) absorbed from humidity-saturated air.

(5) Deep Ocean Standards Thermometer

The Deep Ocean Standards Thermometer (SBE 35) is an accurate, ocean-range temperature sensor that can be standardized against Triple Point of Water and Gallium Melt Point cells and is also capable of measuring temperature in the ocean to depths of 6,800 m.

Temperature is determined by applying an AC excitation to reference resistances and an ultrastable aged thermistor with a drift rate of less than 0.001 °C/year. Each of the resulting outputs is digitized by a 20-bit A/D converter. The reference resistor is a hermetically sealed, temperature-controlled VISHAY. The switches are mercury wetted reed relays with a stable contact resistance. AC excitation and ratiometric comparison using a common processing channel removes measurement errors due to parasitic thermocouples, offset voltages, leakage currents, and gain errors. Maximum power dissipated in the thermistor is 0.5 μwatts, and contributes less than 200 μK of overheat error.

The SBE 35 communicates via a standard RS-232 interface at 300 baud, 8 bits, no parity. The SBE 35 can be used with the SBE 32 Carousel Water Sampler and SBE 911plus CTD system. The SBE 35 makes a temperature measurement each time a bottle fire confirmation is received, and stores the value in EEPROM. Calibration coefficients stored in EEPROM allow the SBE 35 to transmit data in engineering units. Commands can be sent to SBE 35 to provide status display, data acquisition setup, data retrieval, and diagnostic test using terminal software.

Following the methodology used for standards-grade platinum resistance thermometers (SPRT), the calibration of the SBE 35 is accomplished in two steps. The first step is to characterize and capture the non-linear resistance vs temperature response of the sensor. The SBE 35 calibrations are performed at SBE, Inc., in a low-gradient temperature bath and against ITS-90 certified SPRTs maintained at Sea-Bird's primary temperature metrology laboratory. The second step is frequent certification of the sensor by measurements in thermodynamic fixed-point cells. Triple point of water (TPW) and gallium melt point (GaMP) cells are appropriate for the SBE 35. The SBE 35 resolves temperature in the fixed-point cells to approximately 25 μ K. Like SPRTs, the slow time drift of the SBE 35 is adjusted by a slope and offset correction to the basic non-linear calibration equation.

Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were stored in EEPROM:

S/N 0045, 27 October 2002 (1st step: linearization)

$$\begin{aligned} a_0 &= 5.84093815e-03 \\ a_1 &= -1.65529280e-03 \\ a_2 &= 2.37944937e-04 \\ a_3 &= -1.32611385e-05 \\ a_4 &= 2.83355203e-07 \end{aligned}$$

Linearized temperature (ITS-90) is computed according to

$$\text{Linearized temperature (ITS-90)} = \frac{1}{\{a_0 + a_1 * [\ln(n)] + a_2 * [\ln^2(n)] + a_3 * [\ln^3(n)] + a_4 * [\ln^4(n)]\}} - 273.15$$

where n is the instrument output. Then the SBE 35 is certified by measurements in thermodynamic fixed-point cells of the TPW (0.0100 $^{\circ}$ C) and GaMP (29.7646 $^{\circ}$ C). Like SPRTs, the slow time drift of the SBE 35 is adjusted by periodic recertification corrections.

S/N 0045, 6 May 2005 (2nd step: fixed point calibration)

$$\begin{aligned} \text{Slope} &= 1.000019 \\ \text{Offset} &= -0.000881 \end{aligned}$$

Temperature (ITS-90) is calibrated according to

$$\text{Temperature (ITS-90)} = \text{Slope} * \text{Linearized temperature} + \text{Offset}$$

The SBE 35 has a time constant of 0.5 seconds. The time required per sample = 1.1 * NCYCLES + 2.7 seconds. The 1.1 seconds is total time per an acquisition cycle. NCYCLES is the number of acquisition cycles per sample. The 2.7 seconds is required for converting the measured values to temperature and storing average in EEPROM. Root mean square (rms) temperature noise for a SBE 35 in a Triple Point of Water cell is typically expressed as 82 / NCYCLES^{1/2} in μ K. In this cruise NCYCLES was set to 4 and the rms noise is estimated to be 0.04 m $^{\circ}$ C.

When using the SBE 911 system with SBE 35, the deck unit receives incorrect signal from the under water unit for confirmation of firing bottle #16. In order to correct the signal, a module (Yoshi Ver. 1, EMS Co. Ltd., JAPAN) was used between the under water unit and the deck unit.

Time drift of the SBE 35 based on the fixed point calibrations is shown in Figure 3.1.5.

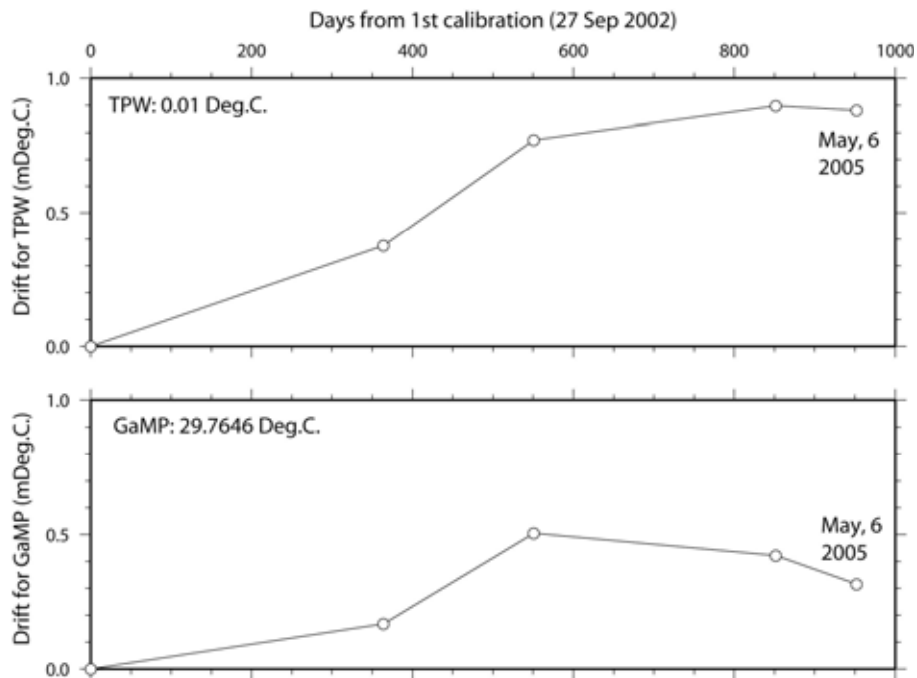


Figure 3.1.5. SBE35 (S/N 0045) time drift based on laboratory fixed point calibrations (triple point of water, TPW and gallium melt point, GaMP) performed by SBE, Inc.

(6) Altimeter

The Benthos PSA-916T Sonar Altimeter (Benthos, Inc., USA) determines the distance of the target from the unit by generating a narrow beam acoustic pulse and measuring the travel time for the pulse to bounce back from the target surface. The PSA-916T is the same as the standard PSA-916 Sonar Altimeter except it is housed in a corrosion-resistant titanium pressure case. It is O-ring-sealed and rated for operation in water depths up to 10,000 meters. In this unit, a 250 microseconds pulse at 200 kHz is transmitted 5 times in a second. The PSA-916T uses the nominal speed of sound of 1,500 m/s. Thus the unit itself, neglecting variations in the speed of sound, can be considered accurate to 5 % or 0.1 meter, whichever is greater. In the PSA-916T the jitter of the detectors is approximately 5 microseconds or +/- 0.4 cm total distance. Since the total travel time is divided by two, the jitter error is +/- 0.2 cm.

The following scale factors were used in SEASOFT:

S/N 1157

$$\text{FSVolt} * 300 / \text{FSRange} = 15$$

$$\text{Offset} = 0.0$$

(7) Fluorometer

The Seapoint Chlorophyll Fluorometer (Seapoint sensors, Inc., USA) is a high-performance, low power instrument to provide in-situ measurements of chlorophyll-a at depths up to 6,000 meters. The instrument uses modulated blue LED lamps and a blue excitation filter to excite chlorophyll-a. The fluorescent light emitted by the chlorophyll-a passes through a red emission filter and is detected by a silicon photodiode. The low level signal is then processed using synchronous demodulation circuitry, which generates an output voltage proportional to chlorophyll-a

concentration.

The following coefficients were used in SEASOFT:

S/N 2579

Gain = 30

Offset = 0.0

Chlorophyll-a concentration is computed as

$$\text{Chlorophyll-a } (\mu\text{g/l}) = (\text{Voltage} * 30 / \text{Gain}) + \text{Offset}$$

3.1.4 Data collection and processing

(1) Data collection

CTD measurements were made using a SBE 9plus CTD equipped with two pumped temperature-conductivity (TC) sensors. The TC pairs were monitored to check drift and shifts by examining the differences between the two pairs. Dissolved oxygen sensor was placed between the conductivity sensor module and the pump. Auxiliary sensors included Deep Ocean Standards Thermometer, altimeter and fluorometer. The SBE 9plus CTD (sampling rate of 24 Hz) was mounted horizontally in a 36-position carousel frame.

CTD system was powered on at least two minutes in advance of the operation and was powered off at least two minutes after the operation in order to acquire pressure data on ship's deck.

The package was lowered into the water from the starboard side and held 10 m beneath the surface for about one minute in order to activate the pump. After the pump was activated the package was lifted to the surface and lowered at a rate of 1.0 m/s to 200 m then the package was stopped in order to operate the heave compensator of the crane. The package was lowered again at a rate of 1.2 m/s to the bottom. The position of the package relative to the bottom was monitored by the altimeter reading. Also the bottom depth was monitored by the SEABEAM multi-narrow beam sounder on board. For the up cast, the package was lifted at a rate of 1.0 m/s except for bottle firing stops. At each bottle firing stops, the bottle was fired 30 seconds after the stop and the package was stayed 5 seconds in order to sample temperature by the Deep Ocean Standards Thermometer. At 200 m from the surface, the package was stopped in order to stop the heave compensator of the crane.

Water samples were collected using a 36-bottle SBE 32 Carousel Water Sampler with 12-litre Niskin-X bottles. Before a cast taken water for CFCs, the 36-bottle frame and Niskin-X bottles were wiped with acetone.

The SBE 11plus deck unit received the data signal from the CTD. Digitized data were forwarded to a personal computer running the SEASAVE data acquisition software. Temperature, conductivity, salinity, oxygen and descent rate profiles were displayed in real-time with the package depth and altimeter reading. Temperature, salinity and oxygen difference between primary and secondary sensor were also displayed in order to monitor the status of the sensors.

Data acquisition software

SBE, Inc., SEASAVE-Win32, version 5.27b

(2) Data collection problems

At station P10N_142, bottle #1 was not fired at the beginning of the up cast. The cast was aborted and the Y-cable was replaced.

At station P10N_137, the primary temperature showed abnormal values at depths between 450 and 430 dbar in the up cast. The connecting cable and connector for the primary temperature sensor was checked and cleaned.

At station P10N_122, the primary oxygen sensor was replaced because the difference between the sensor output and the bottle oxygen was gradually becoming greater (40 $\mu\text{mol/kg}$ near bottom).

At station P10N_113, the primary temperature data was slightly noisy during up cast. And at station P10N_112, the primary temperature signal was lost near bottom. The connecting cable for the temperature sensor was replaced after the cast.

At station P10N_101 and 100, the secondary temperature and conductivity were very noisy from the up cast of P10N_101 because of something in the secondary TC duct. The TC duct was well flushed after the cast.

At station P10_62, the CTD signal was lost at 1,270 dbar in the down cast and the cast was aborted. The second cast was carried out after re-connecting the armored cable and pigtail.

At station P10_53, the secondary conductivity was abnormally biased near bottom. The conductivity sensor was replaced after the cast.

At station P10_27, the secondary conductivity was abnormally biased near bottom. The conductivity sensor was replaced after the cast.

(3) Data processing

SEASOFT consists of modular menu driven routines for acquisition, display, processing, and archiving of oceanographic data acquired with SBE equipment, and is designed to work with a compatible personal computer. Raw data are acquired from instruments and are stored as unmodified data. The conversion module DATCNV uses the instrument configuration and calibration coefficients to create a converted engineering unit data file that is operated on by all SEASOFT post processing modules. Each SEASOFT module that modifies the converted data file adds proper information to the header of the converted file permitting tracking of how the various oceanographic parameters were obtained. The converted data is stored in rows and columns of ascii numbers. The last data column is a flag field used to mark scans as good or bad.

The following are the SEASOFT data processing module sequence and specifications used in the reduction of CTD data in this cruise.

Data processing software

SBE, Inc., SEASOFT-Win32, version 5.27b

DATCNV converted the raw data to scan number, pressure, depth, temperatures, conductivities, oxygen voltage, descent rate, altitude and fluorescence. DATCNV also extracted bottle information where scans were marked with the bottle confirm bit during acquisition. The duration was set to 4.4 seconds, and the offset was set to 0.0 seconds.

ROSSUM created a summary of the bottle data. The bottle position, date, time were output as the first two columns. Scan number, pressure, depth, temperatures, conductivities, oxygen voltage, descent rate, altitude and fluorescence were averaged over 4.4 seconds. Then, salinity, potential temperature, density (σ_θ) and oxygen were computed.

ALIGNCTD converted the time-sequence of conductivity and oxygen sensor outputs into the pressure sequence to ensure that all calculations were made using measurements from the same parcel of water. For a SBE 9plus CTD with the ducted temperature and conductivity sensors and a

3,000-rpm pump, the typical net advance of the conductivity relative to the temperature is 0.073 seconds. So, the SBE 11plus deck unit was set to advance the primary and the secondary conductivity for 1.73 scans ($1.75/24 = 0.073$ seconds). Oxygen data are also systematically delayed with respect to depth mainly because of the long time constant of the oxygen sensor and of an additional delay from the transit time of water in the pumped plumbing line. This delay was compensated by 6 seconds advancing oxygen sensor output (oxygen voltage) relative to the temperature.

WILDEDIT marked extreme outliers in the data files. The first pass of WILDEDIT obtained an accurate estimate of the true standard deviation of the data. The data were read in blocks of 1000 scans. Data greater than 10 standard deviations were flagged. The second pass computed a standard deviation over the same 1000 scans excluding the flagged values. Values greater than 20 standard deviations were marked bad. This process was applied to all variables.

CELLTM used a recursive filter to remove conductivity cell thermal mass effects from the measured conductivity. Typical values used were thermal anomaly amplitude $\alpha = 0.03$ and the time constant $1/\beta = 7.0$.

FILTER performed a low pass filter on pressure with a time constant of 0.15 seconds. In order to produce zero phase lag (no time shift) the filter runs forward first then backwards.

WFILTER performed a median filter to remove spikes in the Fluorometer data. A median value was determined from a window of 49 scans.

SECTION selected a time span of data based on scan number in order to reduce a file size. The minimum number was set to be the start time when the CTD package was beneath the sea-surface after activation of the pump. The maximum number was set to be the end time when the package came up from the surface. Data to check the CTD pressure drift were prepared before SECTION.

LOOPEDIT marked scans where the CTD was moving less than the minimum velocity of 0.0 m/s (traveling backwards due to ship roll).

DERIVE was used to compute oxygen.

BINAVG averaged the data into 1-dbar pressure bins. The center value of the first bin was set equal to the bin size. The bin minimum and maximum values are the center value plus and minus half the bin size. Scans with pressures greater than the minimum and less than or equal to the maximum were averaged. Scans were interpolated so that a data record exists every dbar.

DERIVE was re-used to compute salinity, potential temperature, and density (σ_θ).

SPLIT was used to split data into the down cast and the up cast.

As for a 1-dbar-pressure bin averaged the data less than 10 scans, data of the bin was eliminated. As for remaining spikes in the Fluorometer data near surface, those data quality flags were set to 4. Remaining spikes in the salinity data were manually eliminated for raw data. When the data was eliminated over 1 dbar, the data gap was linearly interpolated with a quality flag of 6. Remaining spikes in the oxygen data are going to be eliminated after the cruise.

3.1.5 Post-cruise calibration

(1) Pressure

The CTD pressure sensor drift in the period of the cruise is estimated from the pressure readings on the ship deck. For best results the Paroscientific sensor has to be powered for at least 10 minutes before the operation and carefully temperature equilibrated. However, CTD system was powered only several minutes before the operation at most of stations. In order to get the calibration data for the pre- and post-cast pressure sensor drift, the CTD deck pressure is averaged over first and last two minutes, respectively. Then the atmospheric pressure deviation from a standard atmospheric pressure (14.7 psi) is subtracted from the CTD deck pressure. The atmospheric pressure was measured at the captain deck (20 m high from the base line) and sub-sampled one-minute interval for a meteorological data. Time series of the CTD deck pressure is shown in Figure 3.1.6.

The CTD pressure sensor drift is estimated from the deck pressure obtained above. Mean of the pre- and the post-casts data over the whole period for gave an estimation of the pressure sensor offset from the pre-cruise calibration. Mean residual pressure between the dead weight piston gauge and the calibrated CTD data at 0 dbar of the pre-cruise calibration is subtracted from the mean deck pressure. Offset of the pressure data is estimated to be -0.40 dbar (Table 3.1.1). So the post-cruise calibration is not deemed necessary for the pressure sensors.

Table 3.1.1. Offset of the pressure data. Mean and standard deviation are calculated from time series of the average of the pre- and the post-cast deck pressures.

S/N	Mean deck Pressure (dbar)	Standard deviation (dbar)	Residual pressure (dbar)	Estimated offset (dbar)
0677	-0.42	0.05	-0.02	-0.40

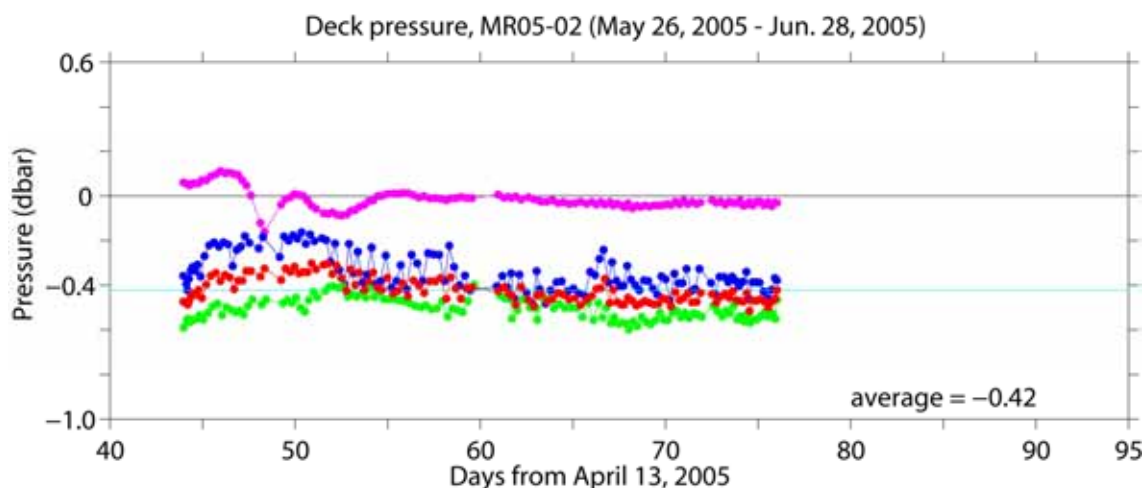


Figure 3.1.6. Time series of the CTD deck pressure. Pink dot indicates atmospheric pressure anomaly. Blue and green dots indicate pre- and post-cast deck pressures, respectively. Red dot indicates an average of the pre- and the post-cast deck pressures.

(2) Temperature (preliminary)

The CTD temperature sensor (SBE 3) is made with a glass encased thermistor bead inside a needle. The needle protects the thermistor from seawater. If the thermistor bead is slightly large of specification it receives mechanical stress when the needle is compressed at high pressure (Budeus and Schneider, 1998). The pressure sensitivity for a SBE 3 sensor is usually less than +2 m°C / 6000 dbar. It is somewhat difficult to measure this effect in the laboratory and it is one of the primary reasons to use the SBE 35 at sea for critical work. Also SBE 3 measurements may be affected by viscous heating (about +0.5 m°C) that occurs in a TC duct and does not occur for un-pumped SBE 35 measurements (Larson and Pederson, 1996). Furthermore the SBE 35 calibrations have some uncertainty (about 0.2 m°C) and SBE 3 calibrations have some uncertainty (about 1 m°C). So the practical corrections for CTD temperature data can be made by using a SBE 35, correcting the SBE 3 to agree with the SBE 35 (a linear pressure correction, a viscous heating correction and an offset for drift and/or calibration uncertainty).

Post-cruise sensor calibration for the SBE 35 are going to be performed immediately after the cruise. In this report the CTD temperature data is preliminarily calibrated using the SBE 35 data.

The discrepancy between the CTD temperature and the standard thermometer (SBE 35) is considered to be a function of pressure and time. Since the pressure sensitivity is thought to be constant in time at least during observation period, the CTD temperature is calibrated as

$$\text{Calibrated temperature} = T - (c_0 * P + c_1 * t + c_2)$$

where T is CTD temperature in °C, P is pressure in dbar, t is time in days from pre-cruise calibration date of CTD temperature and c_0 , c_1 , and c_2 are calibration coefficients. The best fit sets of coefficients are determined by minimizing the sum of absolute deviation from the SBE 35 data. The MATLAB[®] function FMINSEARCH is used to determine the sets. The FMINSEARCH uses the simplex search method (Lagarias et al., 1998). This is a direct search method that does not use numerical or analytic gradients.

The calibration is performed for the primary and secondary temperature data. The CTD data created by the software module ROSSUM are used. The deviation of CTD temperature from the SBE 35 at depth shallower than 2,000 dbar is large for determining the coefficients with sufficient accuracy since the vertical temperature gradient is strong in the regions. So the coefficients are determined using the data in the depth deeper than 1,950 dbar.

The number of data used for the calibration and the mean absolute deviation from the SBE 35 are listed in Table 3.1.2 and the calibration coefficients are listed in Table 3.1.3. The results of the post-cruise calibration for the CTD temperature are summarized in Table 3.1.4 and shown in Figure 3.1.7 and 3.1.8.

Table 3.1.2. Number of data used for the calibration (pressure >= 1,950 dbar) and mean absolute deviation (ADEV) between the CTD temperature and the SBE 35. The SBE 35 data should be verified by the post-cruise laboratory calibration.

S/N	Number of data	ADEV (m°C)	Note
1464	1586	0.10	
1525	1583	0.10	

Table 3.1.3. Calibration coefficients for the CTD temperature sensor.

S/N	c_0 (°C/dbar)	c_1 (°C/day)	c_2 (°C)
1464	-1.0013e-7	2.4017e-6	0.56e-3
1525	-7.9037e-9	2.8765e-6	0.29e-3

Table 3.1.4. Difference between the CTD temperature and the SBE 35 after the post-cruise calibration. Mean and standard deviation (Sdev) are calculated below and above 1,950 dbar. Number of data used is also shown.

S/N	Pressure \geq 1,950 dbar			Pressure $<$ 1,950 dbar		
	Num	Mean (m°C)	Sdev (m°C)	Num	Mean (m°C)	Sdev (m°C)
1464	1586	0.00	0.14	2171	-0.35	8.3
1525	1583	0.00	0.13	2153	-0.52	6.3

(3) Salinity and dissolved oxygen

The CTD salinity and dissolved oxygen are going to be calibrated using in-situ salinity and dissolved oxygen data obtained from sampled water after the sampled data is quality controlled and the CTD temperature is calibrated. Difference between uncorrected CTD salinity and bottle salinity is shown in Figure 3.1.9. Difference between uncorrected CTD oxygen and bottle oxygen is also shown in Figure 3.1.10.

3.1.6 Preliminary results

Date, time and locations of the CTD casts are listed in station summary file (49MR0502_1_sum.txt). Vertical section of potential temperature and salinity are shown in Figure 3.1.11 and Figure 3.1.12. Uncorrected CTD data is preliminarily used.

References

- Budeus, G. and W. Schneider (1998): In-situ temperature calibration: A remark on instruments and methods, *Intl. WOCE Newsletter*, 30, 16-18.
- Lagarias, J.C., J.A. Reeds, M.H. Wright and P. E. Wright (1998): Convergence properties of the Nelder-Mead simplex method in low dimensions, *SIAM Journal of Optimization*, 9, 112-147.
- Larson, N. and A. Pederson (1996): Temperature measurements in flowing water: Viscous heating of sensor tips, 1st IGHEM Meeting, Montreal, Canada.
(http://www.seabird.com/technical_references/paperindex.htm)

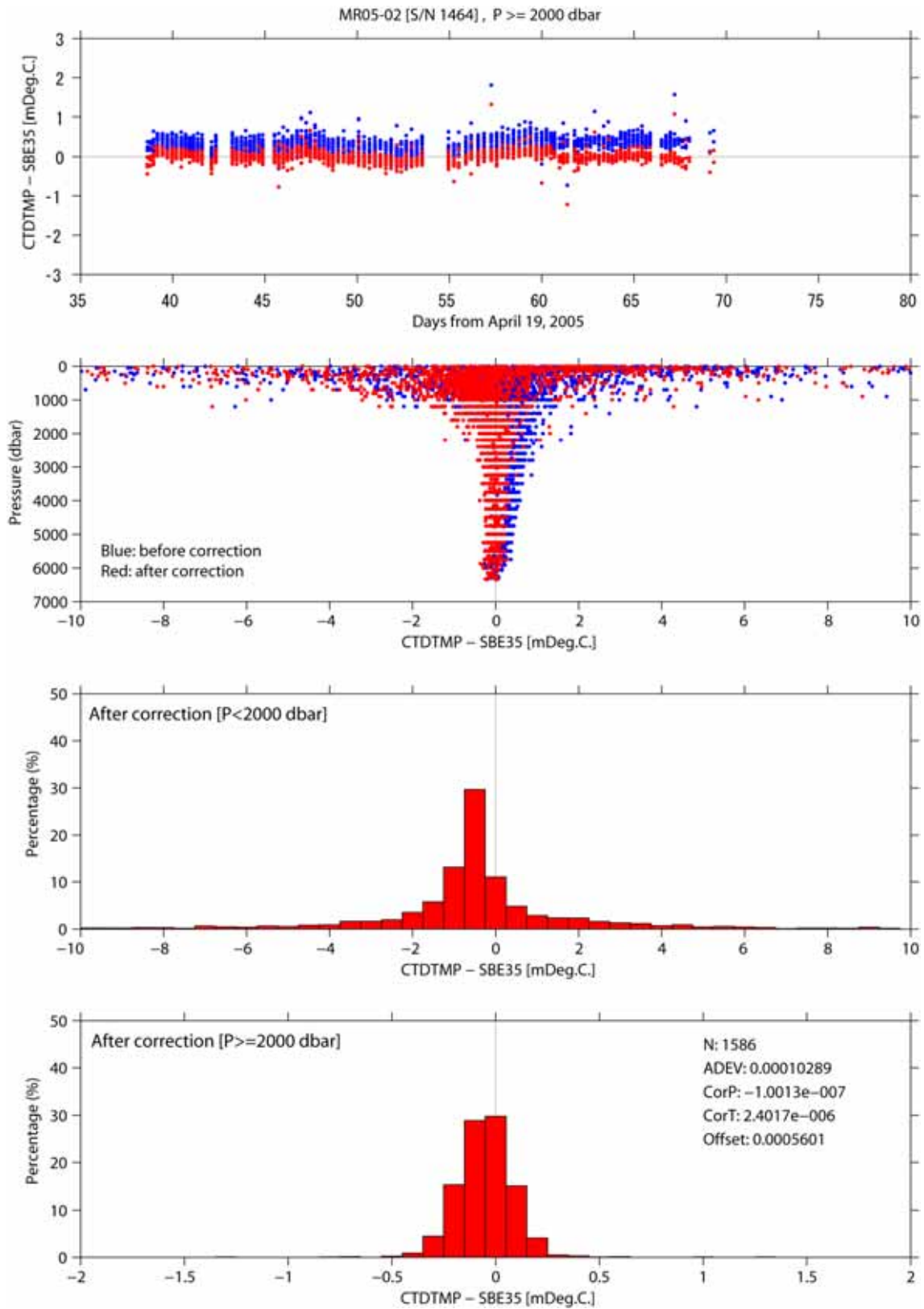


Figure 3.1.7. Difference between the CTD temperature (primary) and the Deep Ocean Standards thermometer (SBE 35). Blue and red dots indicate before and after the post-cruise calibration using the SBE 35 data, respectively. Lower two panels show histogram of the difference after the calibration. The SBE 35 data should be verified by the post-cruise laboratory calibration.

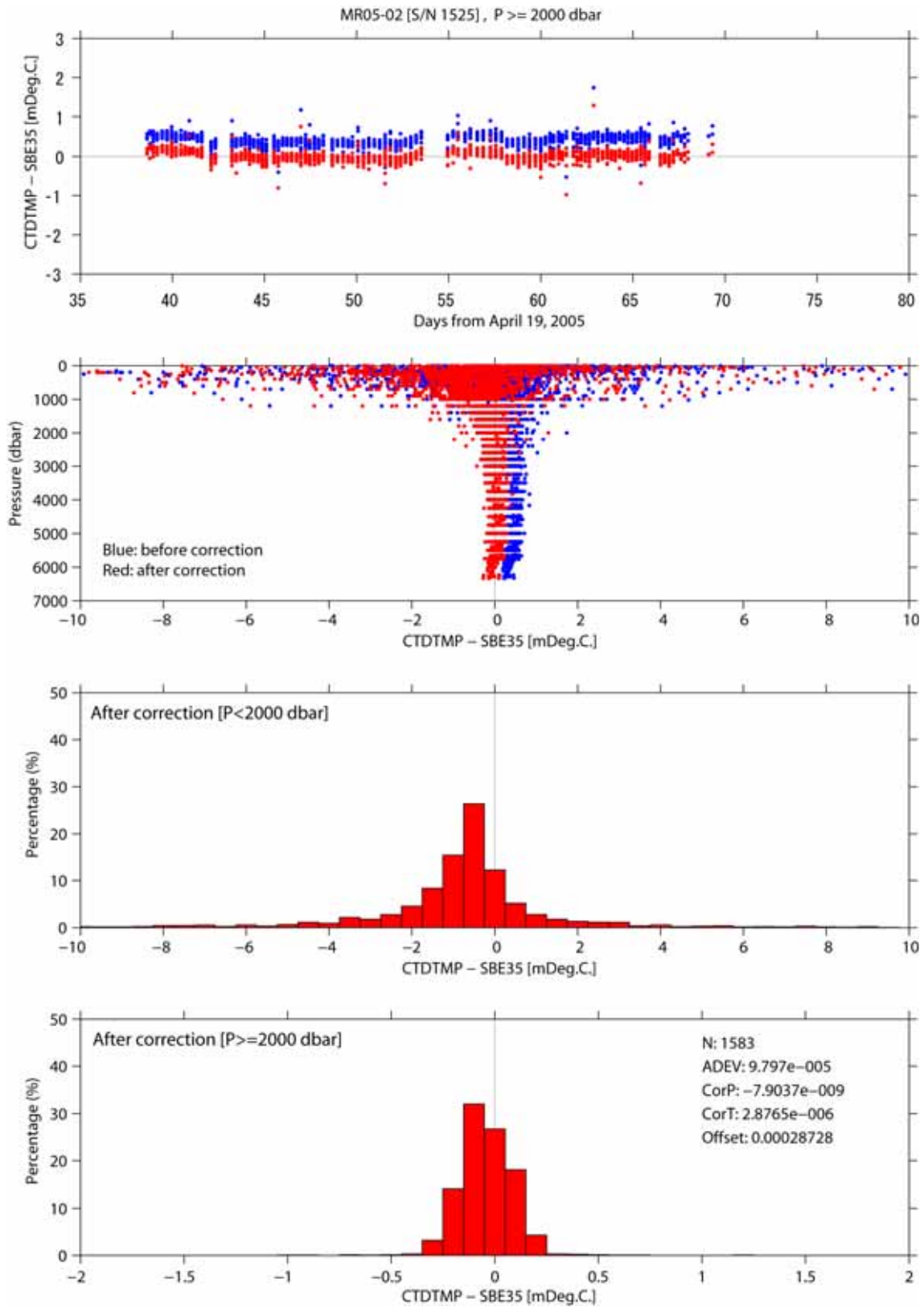


Figure 3.1.8. Same as Figure 3.1.7, but for the secondary CTD temperature.

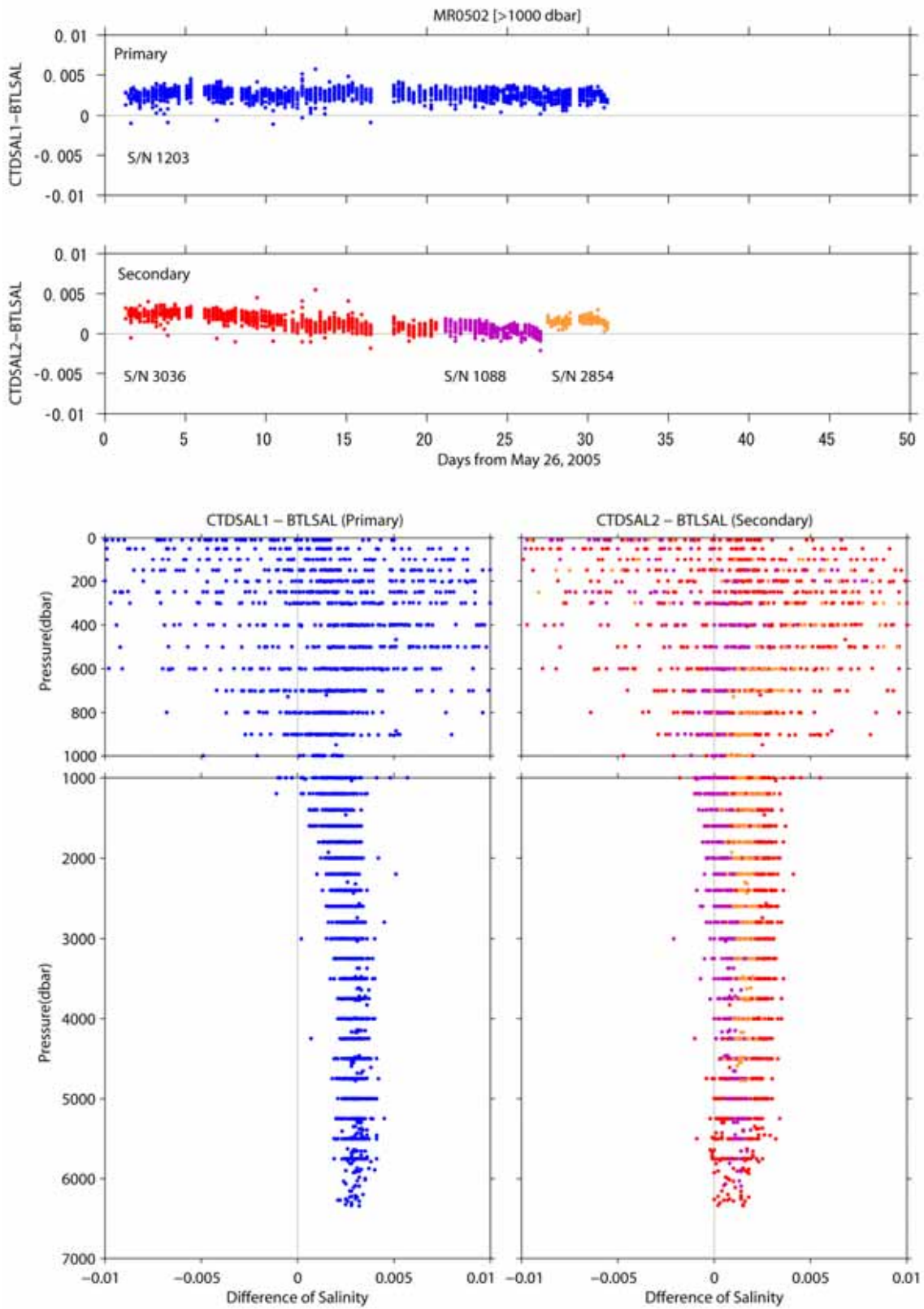


Figure 3.1.9. Difference between the CTD salinity and the bottle salinity. Time series for deeper than 1,000 dbar (upper two panel) and vertical distribution (lower two panel) are shown for primary and secondary sensors.

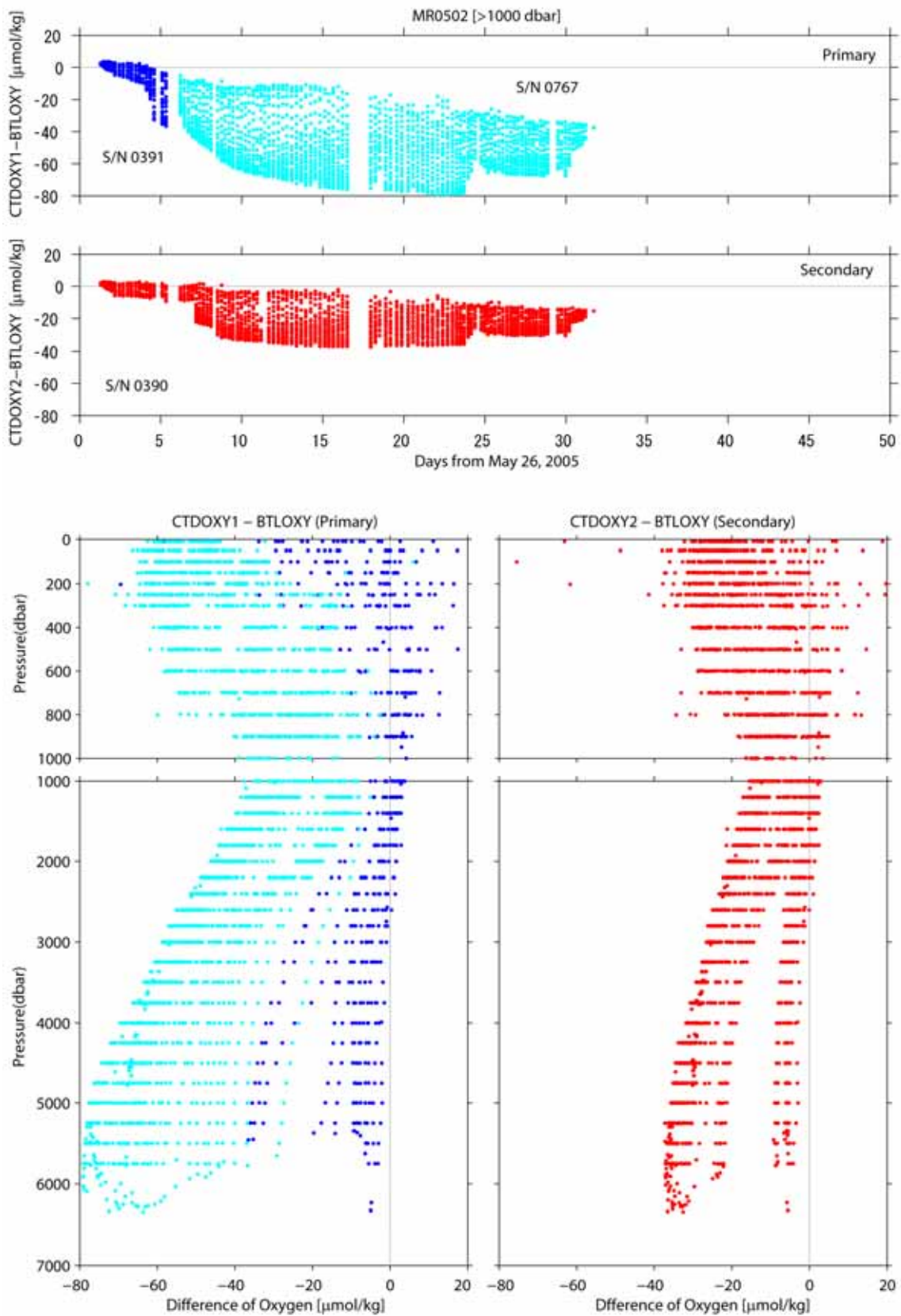


Figure 3.1.10. Difference between the CTD oxygen and the bottle oxygen. Time series for deeper than 1,000 dbar (upper two panel) and vertical distribution (lower two panel) are shown for primary and secondary sensors.

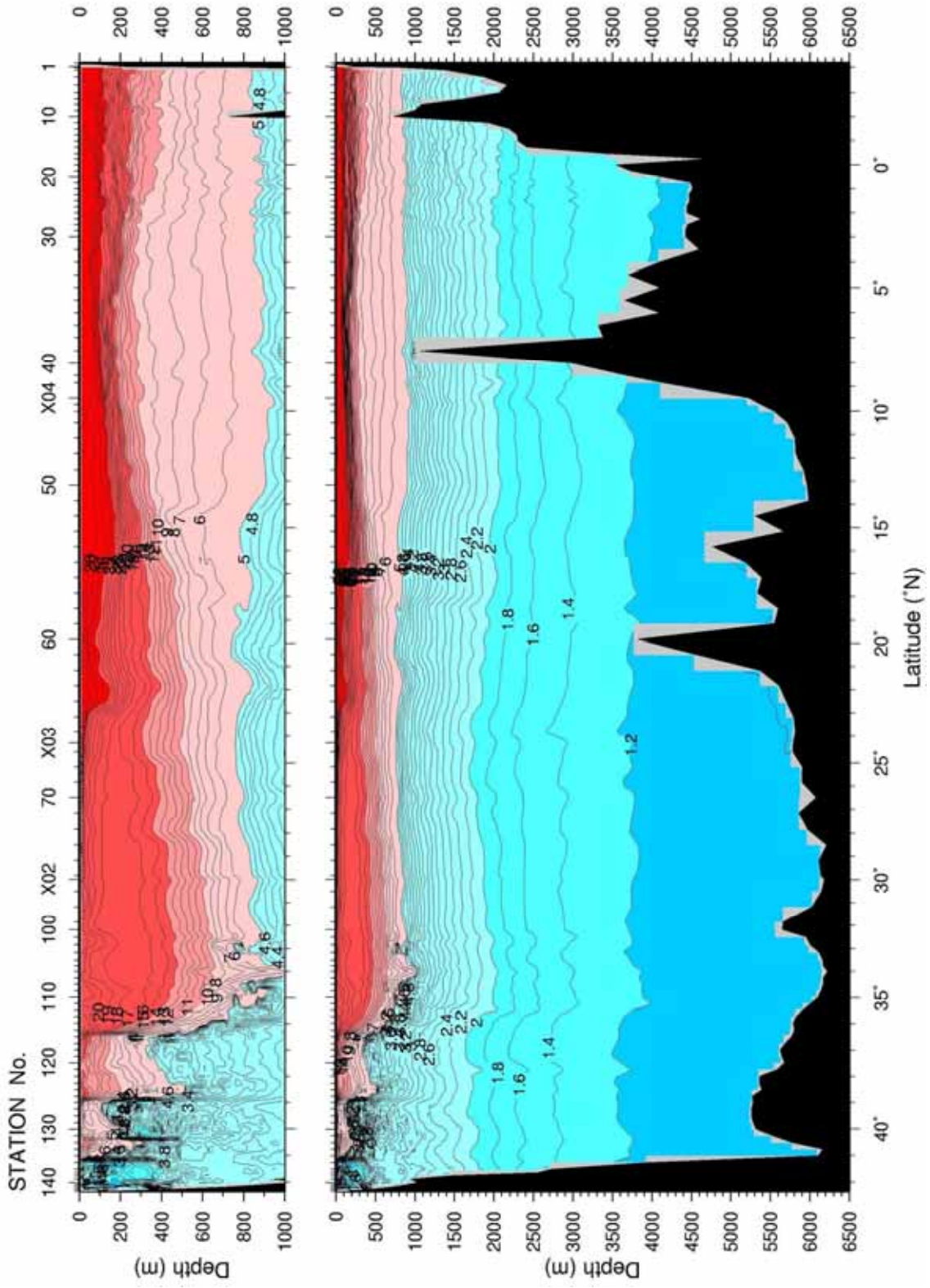


Figure 3.1.11. Vertical section of potential temperature. Uncorrected CTD data is used.

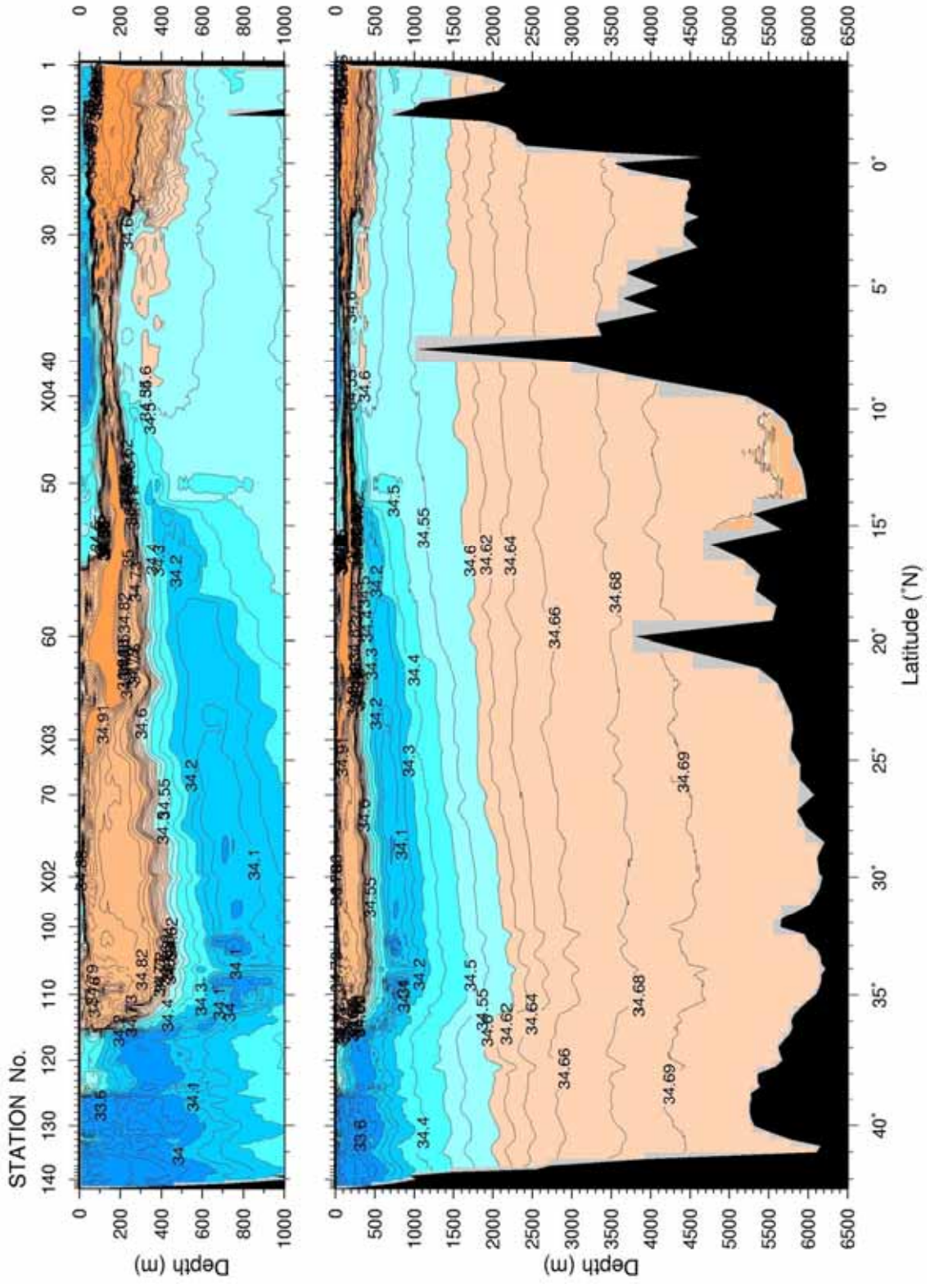


Figure 3.1.12. Vertical section of CTD salinity. Uncorrected CTD data is used.

3.2 Bottle Salinity

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Kenichi Katayama (MWJ)

Tatsuya Tanaka (MWJ)

Takeshi Kawano (JAMSTEC)

3.2.1 Objectives

1. To measure bottle salinity obtained by CTD casts, bucket sampling, and EPCS
2. To calibrate CTD salinity

3.2.2 Instrument and Method

3.2.2.1 Salinity Sample Collection

Seawater samples were collected with 12 liter Niskin-X bottles, bucket, and the EPCS. The salinity sample bottle of the 250ml brown glass bottle with screw cap was used to collect the sample water. Each bottle was rinsed three times with sample water, and was filled with sample water to the bottle shoulder. Its cap was also thoroughly rinsed. The bottle was stored more than 12 hours in 'AUTOSAL ROOM' before the salinity measurement.

The kind and number of samples are shown as follows ;

Table 3.2.3.1 number of samples

Samples	Number of Samples
Samples for CTD	4,570
Samples for EPCS	60
Total	4,630

3.2.2.2 Instruments and Method

The salinity analysis was carried out on R/V MIRAI during the cruise of MR05-02 using the salinometer (Model 8400B "AUTOSAL" ; Guildline Instruments Ltd.: S/N 62556) with additional peristaltic-type intake pump (Ocean Scientific International, Ltd.). We also used two pairs of precision digital thermometers (Model 9540 ; Guildline Instruments Ltd.). One thermometer monitored an ambient temperature and the other monitored a bath temperature.

The specifications of AUTOSAL salinometer and thermometer are shown as follows ;

Salinometer (Model 8400B "AUTOSAL" ; Guildline Instruments Ltd.)

Measurement Range : 0.005 to 42 (PSU)

Accuracy : Better than ± 0.002 (PSU) over 24 hours
without restandardization

Maximum Resolution : Better than ± 0.0002 (PSU) at 35 (PSU)

Thermometer (Model 9540 ; Guildline Instruments Ltd.)

Measurement Range : -180 to +240 deg C

Resolution : 0.001

Limits of error \pm deg C : 0.01 (24 hours @ 23 deg C \pm 1 deg C)
Repeatability : \pm 2 least significant digits

The measurement system was almost same as Aoyama *et al.* (2003). The salinometer was operated in the air-conditioned ship's laboratory 'AUTOSAL ROOM' at a bath temperature of 24 deg C, very stable and varied within 24 deg C \pm 0.002 deg C on rare occasion.

The measurement for each sample was done with a double conductivity ratio that is defined as median of 31 times reading of the salinometer. Data collection was started in 5 seconds after filling sample into the cell and it took about 10 seconds to collect 31 readings by a personal computer. Data were taken for the sixth and the seventh filling of the cell. In case the difference between the double conductivity ratio of these two fillings is smaller than 0.00002, the average value of these double conductivity ratio was used to calculate the bottle salinity with the algorithm for practical salinity scale, 1978 (UNESCO, 1981). If the difference was greater than or equal to 0.0003, we measured eighth filling of the cell. In case the double conductivity ratio of eighth filling did not satisfy the criteria above, we measured ninth and tenth filling of the cell and the median of the double conductivity ratios of five fillings are used to calculate the bottle salinity.

The measurement was conducted about 16hours per day (typically from 7:00 to 23:00) and the cell was cleaned with ethanol or soap or both after the measurement of the day.

3.2.3 Preliminary Result

3.2.3.1 Stand Seawater

Standardization control of the salinometer with serial number of 62556 was set to 491. During the measurement, the STANDBY of 62556 was 5509 \pm 0001 and ZERO was 0.00001. We used IAPSO Standard Seawater batch P145 which conductivity ratio was 0.99981 (double conductivity ratio is 1.99962) as the standard for salinity. We measured 179 bottles of P145. There were 5 bad bottles which conductivities are extremely high or low. Data of these 5 bottles are not taken into consideration hereafter.

Fig.3.2.3.1 shows the history of double conductivity ratio of the Standard Seawater batch P145. During this cruise, we did flushing cell twice using ultrasonic washing machine for cleaning the cell. The average of double conductivity ratio from Stn.143 to Stn.071 was 1.99962 and the standard deviation was 0.00001, which is equivalent to 0.0002 in salinity. The average from Stn.070 to Stn.023 was 1.99963 and the standard deviation was 0.00001. We reduce 0.00001 to the measured double conductivity ratio during this period. The average of double conductivity ratio from Stn.022 to Stn.001 was 1.99962 and the standard deviation was 0.00001, which is equivalent to 0.0002 in salinity.

The specifications of SSW used in this cruise are shown as follows ;

Standard seawater (SSW)	
batch	: P145
conductivity ratio	: 0.99981
salinity	: 34.993
preparation date	: 15-Jul.-2004

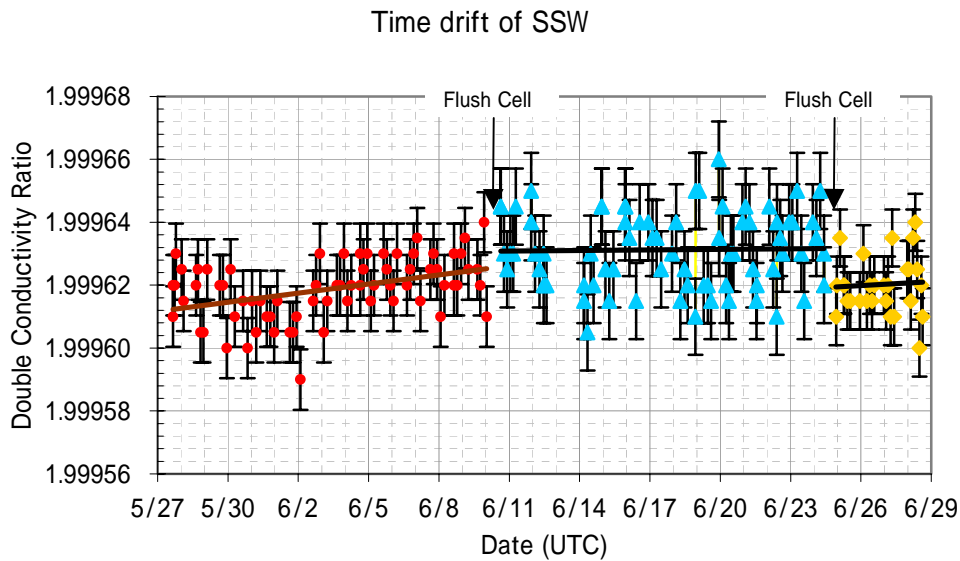


Fig. 3.2.3.1 The history of double conductivity ratio of the Standard Seawater batch P145

3.2.3.2 Sub-Standard Seawater

We also used sub-standard seawater, which was deep-sea water filtered by pore size of 0.45 micrometer, stored in a 20 liter container made of polyethylene, and stirred for at least 24 hours before measuring. It was measured every six samples in order to check the possible sudden drift of the salinometer. During the whole measurements, there was no detectable sudden drift of the salinometer.

The specifications of SUB used in this cruise are shown as follows ;

Sub standard seawater (SUB)

sampling cruise ID : MR04-ENG
 sampling depth : 5,000dbar
 filtration date : 29-May-2004

sampling cruise ID : MR04-05
 sampling depth : 2,000dbar
 filtration date : 10-Sep.-2004

3.2.3.3 Replicate and Duplicate Samples

We took 666 pairs of replicate and 55 pairs of duplicate samples. Fig.3.2.3.2 (a) and (b) shows the histogram of the absolute difference between replicate samples and duplicate samples, respectively. There were 6 bad measurements and 18 questionable measurements of replicate samples and 6 questionable measurements of duplicate samples. Excluding these measurements, the standard deviation of the absolute difference of 642 pairs of replicate samples was 0.0002 in salinity and that of 48 pairs of duplicate samples was 0.0002 in salinity.

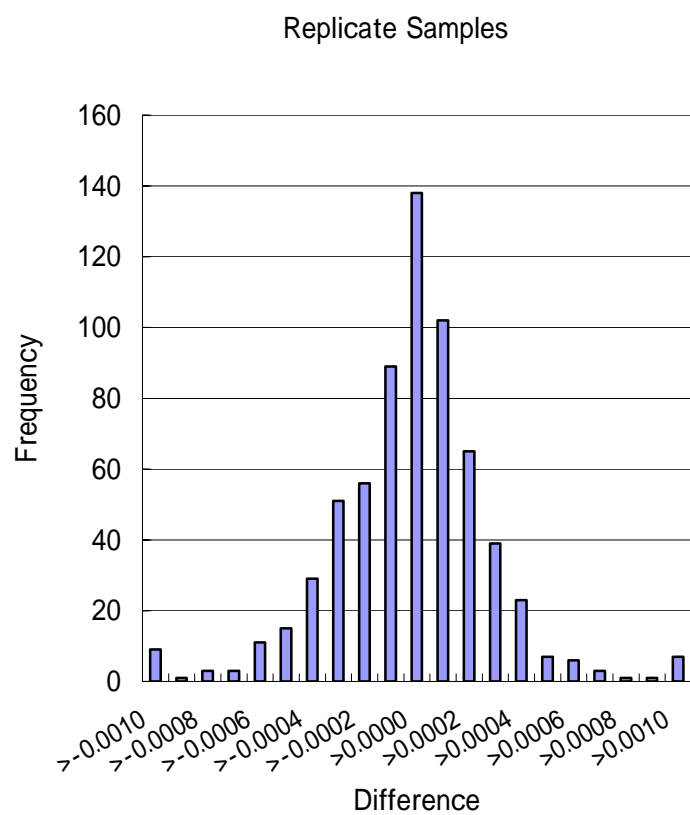


Fig. 3.2.3.2 (a) The histogram of the difference between replicate samples

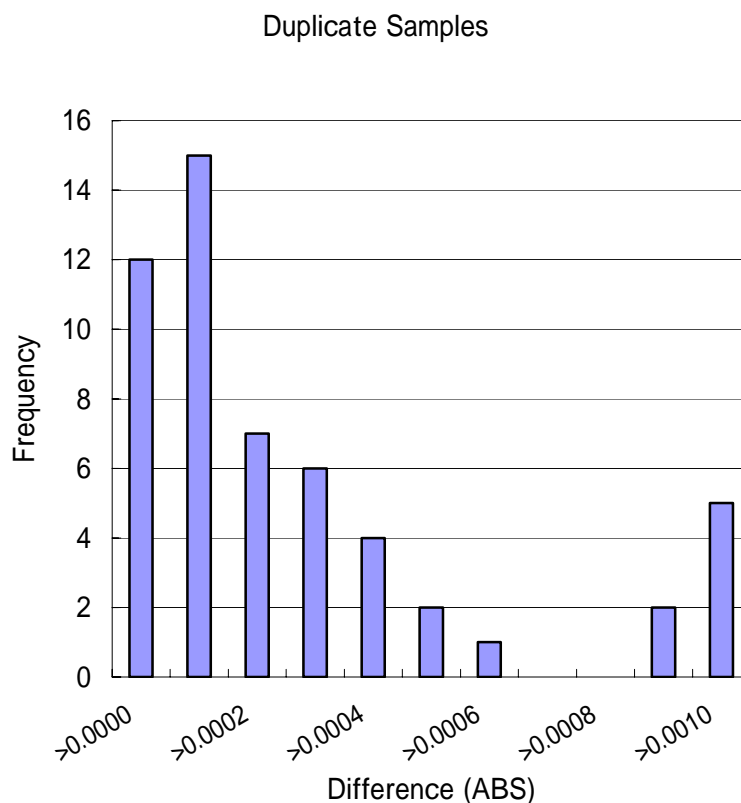


Fig. 3.2.3.2 (b) The histogram of the absolute difference between duplicate samples

3.2.3.4 Figures

We measured 4,630 samples during this cruise. As a preliminary result, we will show a several figures without any interpretation. Fig.3.2.4.3 shows a vertical section of bottle salinity, vertical profile of bottle salinity and Sigma4-Salinity diagram produced by Ocean Data View.

3.2.4 Further data quality check

All data will be checked once again in detail with other parameters such as dissolved oxygen and nutrients.

3.2.5 Reference

- Aoyama, M., T. Joyce, T. Kawano and Y. Takatsuki: Standard seawater comparison up to P129. *Deep-Sea Research*, I, Vol. 49, 1103 ~ 1114, 2002
- UNESCO: Tenth report of the Joint Panel on Oceanographic Tables and Standards. *UNESCO Technical Papers in Marine Science*, 36, 25 pp., 1981

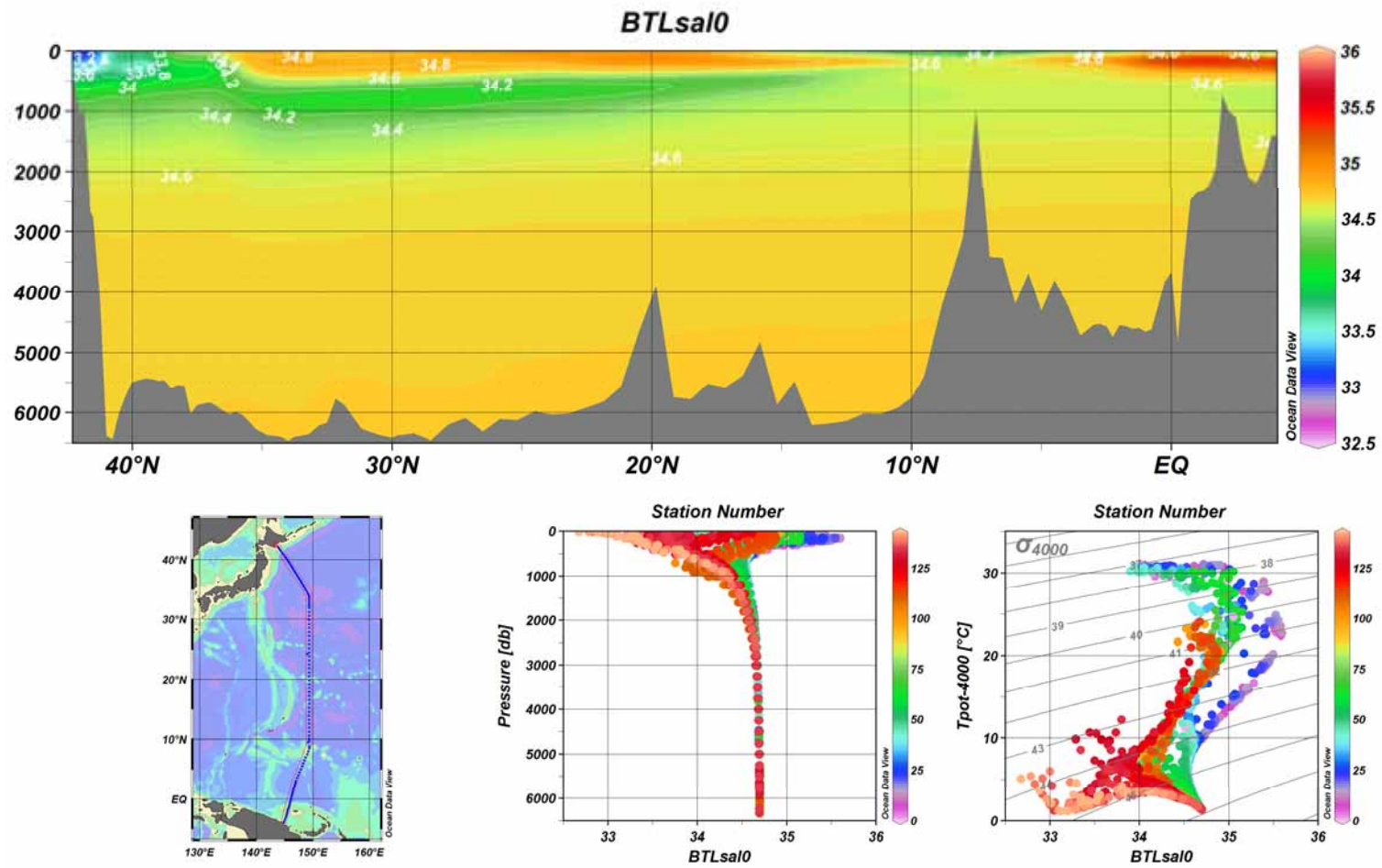


Fig. 3.2.4.3 Vertical section, vertical profile of bottle salinity and Sigma4-Salinity diagram

3.3 Bottle Oxygen (2-July-2005)

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2) Marine Works Japan Co. Ltd

3.3.1 Objectives

Dissolved oxygen is a significant tracer for the ocean circulation study. Recent studies in the North Pacific indicated that dissolved oxygen concentration in intermediate layers decreased in basin wide scale during the past decades. The causes of the decrease, however, are still unclear. During MR05-02, we measured dissolved oxygen concentration from surface to bottom layers at all the hydrocast stations. The stations from 29°N to 4°S reoccupied WHP P10 stations in 1993. Our purpose is to evaluate decadal change of dissolved oxygen in the western Pacific.

3.3.2 Reagents

Pickling Reagent I: Manganous chloride solution (3M)

Pickling Reagent II: Sodium hydroxide (8M) / sodium iodide solution (4M)

Sulfuric acid solution (5M)

Sodium thiosulfate (0.025M)

Potassium iodate (0.001667M)

CSK standard of potassium iodate: Lot ASE8280, Wako Pure Chemical Industries Ltd., 0.0100N

3.3.3 Instruments

Burette for sodium thiosulfate;

APB-510 manufactured by Kyoto Electronic Co. Ltd. / 10 cm³ of titration vessel

Burette for potassium iodate;

APB-410 manufactured by Kyoto Electronic Co. Ltd. / 20 cm³ of titration vessel

Detector; Automatic photometric titrator manufactured, Kimoto Electronic Co. Ltd.

3.3.4 Seawater sampling

Following procedure is based on a determination method in the WHP Operations Manual (Dickson, 1996). Seawater samples were collected from Niskin sampler bottles attached to the CTD-system. Seawater for bottle oxygen measurement was transferred from the Niskin sampler bottle to a volume calibrated glass flask (ca. 100 cm³). Three times volume of the flask of seawater was overflowed. Sample temperature was measured by a thermometer during the overflowing. Then two reagent solutions (Reagent I, II) of 0.5 cm³ each were added immediately into the sample flask and the stopper was inserted carefully into the flask. The sample flask was then shaken vigorously to mix the contents and to disperse the precipitate finely throughout. After the precipitate has settled at least halfway down the flask, the flask was shaken again vigorously to disperse the precipitate. The sample flasks containing pickled samples were stored in a laboratory until they were titrated.

3.3.5 Sample measurement

At least two hours after the re-shaking, the pickled samples were measured on board. A magnetic stirrer bar and 1 cm³ sulfuric acid solution were added into the sample flask and stirring began. Samples were titrated by sodium thiosulfate solution whose molarity was determined by potassium iodate solution (section 3.3.6). Temperature of sodium thiosulfate during titration was recorded by a thermometer. During this cruise we measured dissolved oxygen concentration using two sets of the titration apparatus, DOT-1 and DOT-2. Dissolved oxygen concentration ($\mu\text{mol kg}^{-1}$) was calculated by the sample temperature during the sampling, CTD salinity, flask volume, and titrated volume of the sodium thiosulfate solution.

3.3.6 Standardization

Concentration of sodium thiosulfate titrant (ca. 0.025M) was determined by potassium iodate solution. Pure potassium iodate was dried in an oven at 130°C. 1.7835 g potassium iodate weighed out accurately was dissolved in deionized water and diluted to final volume of 5 dm³ in a calibrated volumetric flask (0.001667M). 10 cm³ of the standard potassium iodate solution was added to a flask using a volume-calibrated dispenser. Then 90 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I were added into the flask in order. Amount of titrated volume of sodium thiosulfate gave the molarity of the sodium thiosulfate titrant. Table 3.3-1 shows result of the standardization during this cruise. Error (C.V.) of the each standardization was less than 0.08 % (n = 5).

3.3.7 Determination of the blank

The oxygen in the pickling reagents I (0.5 cm³) and II (0.5 cm³) was assumed to be 3.8×10^{-8} mol (Dickson, 1996). The blank from the presence of redox species apart from oxygen in the reagents (the pickling reagents I, II, and the sulfuric acid solution) was determined as follows. 1 and 2 cm³ of the standard potassium iodate solution were added to two flasks respectively. Then 100 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I were added into the two flasks in order. The blank was determined by difference between the two times of the first (1 cm³ of KIO₃) titrated volume of the sodium thiosulfate and the second (2 cm³ of KIO₃) one. The results of the blank determination are also shown in Table 3.3-1. The averaged blank of DOT-1 and DOT-2 were -0.007 and -0.010 cm³, respectively.

Table 3.3-1 Results of the standardization and the blank determinations during MR05-02.

Date (UTC)	KIO ₃		DOT-1 (cm ³)			DOT-2 (cm ³)			Samples (Stations)
	#	bottle	Na ₂ S ₂ O ₃	E.P.	blank	Na ₂ S ₂ O ₃	E.P.	blank	
2005/5/26	1	20050420-01	20050523-1	3.959	-0.006	20050523-2	3.961	-0.011	135-143
2005/5/28		20050420-02	20050523-1	3.960	-0.005	20050523-2	3.961	-0.008	131-134
2005/5/29		20050420-03	20050523-3	3.957	-0.008	20050523-4	3.961	-0.011	127-130
2005/5/30		20050420-04	20050523-3	3.960	-0.006	20050523-4	3.964	-0.008	123-126
2005/5/31		20050420-05	20050529-1	3.959	-0.006	20050529-2	3.961	-0.009	119-122
2005/6/2		20050420-06	20050529-1	3.959	-0.006	20050529-2	3.959	-0.009	115-118
2005/6/3		20050420-07	20050529-3	3.959	-0.007	20050529-4	3.960	-0.008	111-114
2005/6/4		20050420-08	20050529-3	3.958	-0.006	20050529-4	3.961	-0.009	107-110
2005/6/5		20050420-13	20050603-1	3.954	-0.007	20050603-2	3.957	-0.011	103-106
2005/6/6	20050420-14	20050603-1	3.956	-0.006	20050603-2	3.956	-0.011	99-102	
2005/6/7	20050420-15	20050603-3	3.956	-0.007	20050603-4	3.958	-0.011	96,X02,97,98	
2005/6/8	20050420-16	20050603-3	3.955	-0.008	20050603-4	3.959	-0.009	69-73,95	
2005/6/10	2	20050420-17	20050609-1	3.953	-0.009	20050609-2	3.955	-0.010	66,X03,67,68
2005/6/10		20050420-17	20050609-1	3.961	-0.008	20050609-2	3.960	-0.011	67
2005/6/11		20050420-18	20050609-1	3.953	-0.005	20050609-2	3.955	-0.010	62-65
2005/6/13		20050420-19	20050609-3	3.952	-0.008	20050609-4	3.954	-0.009	58-61
2005/6/14		20050420-20	20050609-3	3.954	-0.008	20050609-4	3.956	-0.010	54-57
2005/6/16		20050420-25	20050613-1	3.951	-0.007	20050613-2	3.953	-0.009	50-53
2005/6/17		20050420-26	20050613-1	3.953	-0.006	20050613-2	3.954	-0.009	46-49
2005/6/18	20050420-27	20050613-3	3.953	-0.008	20050613-4	3.954	-0.010	42,X04,44,45	
2005/6/19	3	20050420-28	20050613-3	3.953	-0.008	20050613-4	3.954	-0.008	36-41
2005/6/20		20050420-29	20050618-1	3.960	-0.008	20050618-2	3.962	-0.010	31-35
2005/6/21		20050420-30	20050618-1	3.960	-0.007	20050618-2	3.962	-0.010	27-30
2005/6/22		20050420-32	20050618-3	3.960	-0.009	20050618-4	3.962	-0.010	23-26
2005/6/23		20050420-31	20050618-3	3.959	-0.009	20050618-4	3.960	-0.010	18-22
2005/6/25		20050420-40	20050622-1	3.958	-0.007	20050622-2	3.960	-0.010	12-17
2005/6/26	4	20050420-39	20050622-1	3.957	-0.005	20050622-2	3.959	-0.010	5-11
2005/6/27		20050420-38	20050622-3	3.957	-0.009	20050622-4	3.961	-0.008	1-4

Batch number of the KIO₃ standard solution.

3.3.8 Reagent blank

The blank determined in the section 3.3.7, pure water blank ($V_{\text{blk, dw}}$) can be represented by equation 1,

$$V_{\text{blk, dw}} = V_{\text{blk, ep}} + V_{\text{blk, reg}} \quad (1)$$

where

$V_{\text{blk, ep}}$ = blank due to differences between the measured end-point and the equivalence point;

$V_{\text{blk, reg}}$ = blank due to oxidants or reductants in the reagent.

Here, the reagent blank ($V_{\text{blk, reg}}$) was determined by following procedure. 1 cm³ of the standard potassium iodate solution and 100 cm³ of deionized water were added to two flasks. 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I each were added into the first flask in order. Then into the second flask, two times volume of the reagents (2 cm³ of sulfuric acid solution, and 1.0 cm³ of pickling reagent solution II and I each) was added. The reagent blank was determined by difference between the first (2 cm³ of the total reagent volume added) titrated volume of the sodium thiosulfate and the second (4 cm³ of the total reagent volume added) one. We also carried out experiments for three and four times volume of the reagents. The results are shown in Figure 3.3-1.

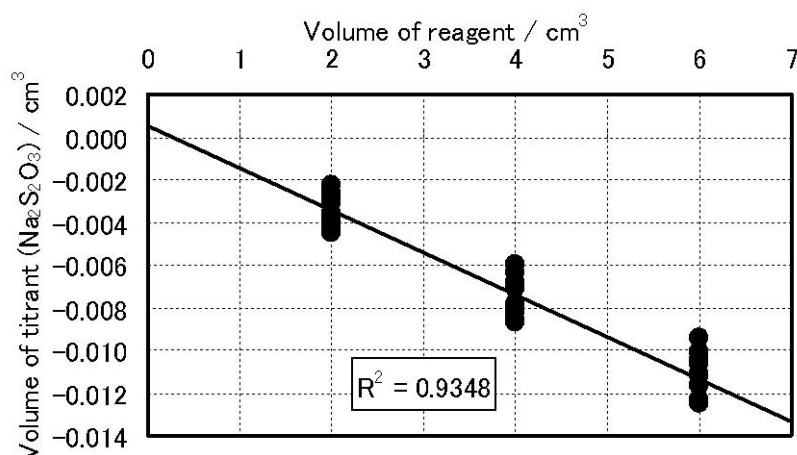


Figure 3.3-1 Blank (cm³) due to redox species apart from oxygen in the reagents

The relation between the reagent blank ($V_{\text{blk, reg}}$) and the volume of the reagents (V_{reagent}) is expressed by equation 2,

$$V_{\text{blk, reg}} = -0.0020 V_{\text{reagent}} + 0.0005 \quad (2).$$

There was no difference between the results of DOT-1 and DOT-2. $V_{\text{blk, reg}}$ was estimated to be about -0.004 cm³, suggesting that about 0.02 μmol of reductants was contained in every 2 cm³ of the reagents added. In other words, the difference of the pure water blank ($V_{\text{blk, dw}}$) between DOT-1 and DOT-2, determined in the section 3.3.7, was due to the difference of the end-point blank ($V_{\text{blk, ep}}$) between the two titration apparatus (-0.003 and -0.006 cm³ for DOT-1 and DOT-2, respectively).

3.3.9 Sample blank

Blank due to redox species other than oxygen in the sample ($V_{\text{blk, spl}}$) can be a potential source of measurement error. Total blank during the seawater measurement, seawater blank ($V_{\text{blk, sw}}$) can be represented by equation 3,

$$V_{\text{blk, sw}} = V_{\text{blk, spl}} + V_{\text{blk, ep}} + V_{\text{blk, reg}} \quad (3).$$

If the end-point blank ($V_{\text{blk, ep}}$) is identical in pure water and in seawater, the difference between the

seawater blank and the pure water one gives the sample blank ($V_{\text{blk, spl}}$),

$$V_{\text{blk, sw}} - V_{\text{blk, dw}} = V_{\text{blk, spl}} \quad (4).$$

$V_{\text{blk, spl}}$ was determined by following procedure. Seawater sample was collected in the volume calibrated glass flask (ca. 100 cm³) without the pickling. Then 1 cm³ of the standard potassium iodate solution, 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I each were added into the flask in order. Additionally a flask contained 1 cm³ of the standard potassium iodate solution, 100 cm³ of deionized water, 1 cm³ of sulfuric acid solution, and 0.5 cm³ of pickling reagent solution II and I were prepared. The difference the titrant volumes between the seawater flask and the deionized water one gave the sample blank ($V_{\text{blk, spl}}$).

Table 3.3-2 Results of the sample blank determinations during MR05-02.

Station: P10N-097 30.5°N / 149.3°E			Station: P10-019 0.3°N / 146.2°E		
Sample No. (Niskin No.)	CTD Pres. dbar	Sample blank $\mu\text{mol kg}^{-1}$	Sample No. (Niskin No.)	CTD Pres. dbar	Sample blank $\mu\text{mol kg}^{-1}$
35	51	0.5	35	51	0.4
33	151	0.6	33	150	0.7
31	249	0.6	31	251	0.7
29	402	0.7	29	401	0.9
27	602	0.6	27	601	0.7
25	800	0.6	25	801	0.7
23	1001	0.6	23	1001	0.7
21	1400	0.7	21	1400	0.7
17	2200	0.7	19	1802	0.7
15	2599	0.7	17	2200	0.7
13	3000	0.7	15	2600	0.7
11	3499	0.6	13	2999	0.7
9	4002	0.7	11	3499	0.7
7	4502	0.7	1	3770	0.9
5	4999	0.7			
3	5500	0.7			
1	6251	0.7			

During this cruise we measured vertical profiles of the sample blanks at two stations (Table 3.3-2) using DOT-1 system. The sample blank ranged from 0.4 to 0.9 $\mu\text{mol kg}^{-1}$ and its vertical and horizontal variations are small. There are a few reports of the sample blank estimation of oxygen analysis in the open ocean. Our results agree with reported values ranged from 0.4 to 0.8 $\mu\text{mol kg}^{-1}$ (Culberson *et al.*, 1991). If we ignore that the sample blank introduces systematic errors into the oxygen calculations, but these errors are expected to be the same for all investigators and not to affect the comparison of results from different investigators (Culberson, 1994).

3.3.10 Replicate sample measurement

Replicate samples were taken at every CTD cast. Total amount of the replicate sample pairs in good measurement (flag=2) was 452. The standard deviation of the replicate measurement was 0.11 $\mu\text{mol}/\text{kg}$ and there was no significant difference between DOT-1 and DOT-2 measurements. The standard deviation was calculated by a procedure (SOP23) in DOE (1994). Figure 3.3-2 is plots of oxygen difference in the replicate measurement as a function of station sequential number and indicates the improvement of measurement skill during the cruise. There found large differences during the primary stage of the cruise. If we exclude the data at the initial ten stations from the calculation of standard deviation, it decreases to 0.09 $\mu\text{mol}/\text{kg}$.

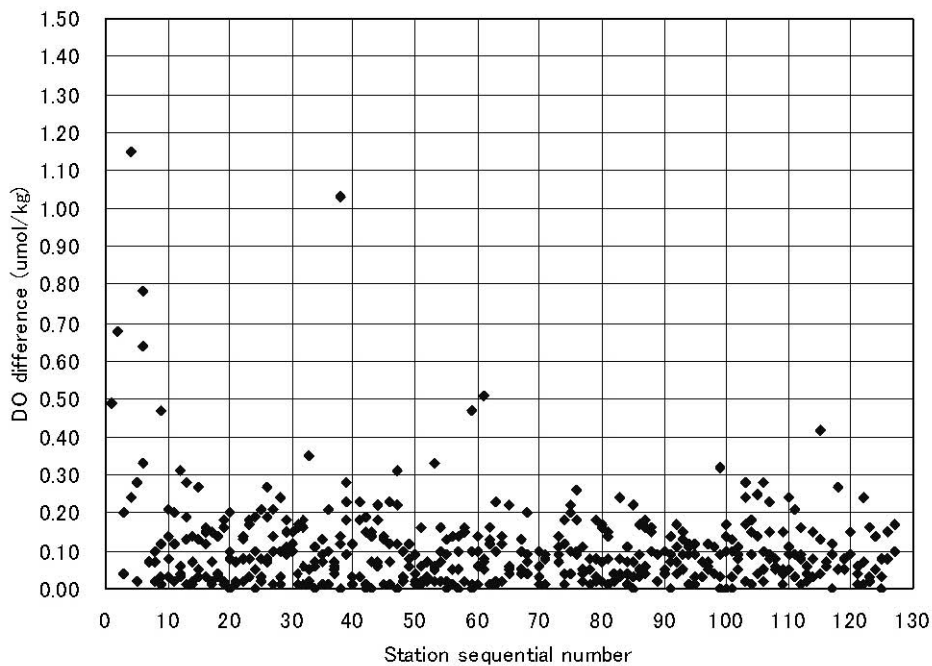


Figure 3.3-2 Difference in the replicate measurements against station sequential number.

As shown in Figure 3.3-3, the layers of replicate sampling are localized at the surface layer, 1200, 3000 and 5000 dbar depths. Since scattering of the plots somewhat depend on depths, we classified replicate data in the following categories: surface (<20 dbar), intermediate (500-1500dbar) and deep (>1500dbar) layers. Standard deviation for each category is 0.16, 0.11, and 0.07 $\mu\text{mol}/\text{kg}$, respectively.

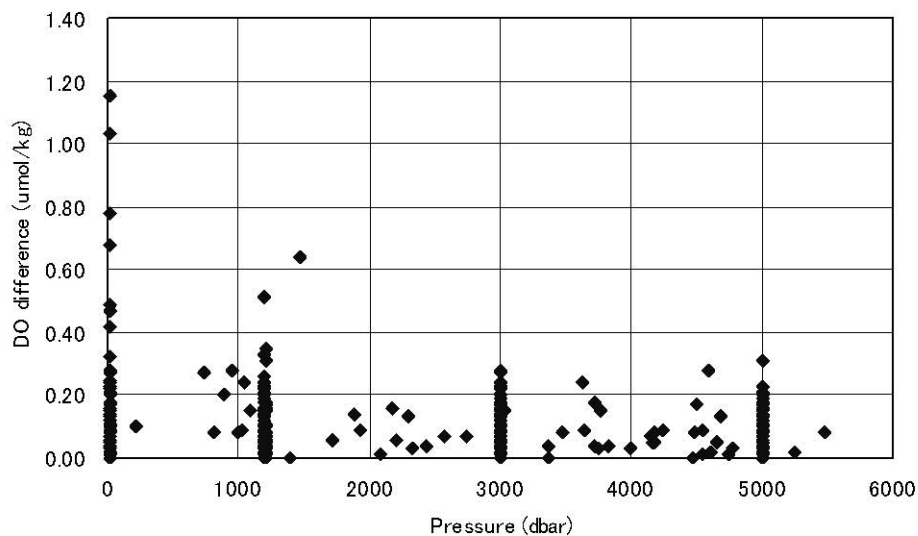


Figure 3.3-3 Difference in the replicate measurements against sampling depth (pressure).

3.3.11 Duplicate sample measurement

We also collected seawater samples from two Niskin samplers that were fired at same depth (duplicate sampling). Duplicate samples were taken at 49 stations in the deep layer below 2000 dbar, and 48 duplicate sample pairs were obtained successfully. From Figure 3.3-4, variation in

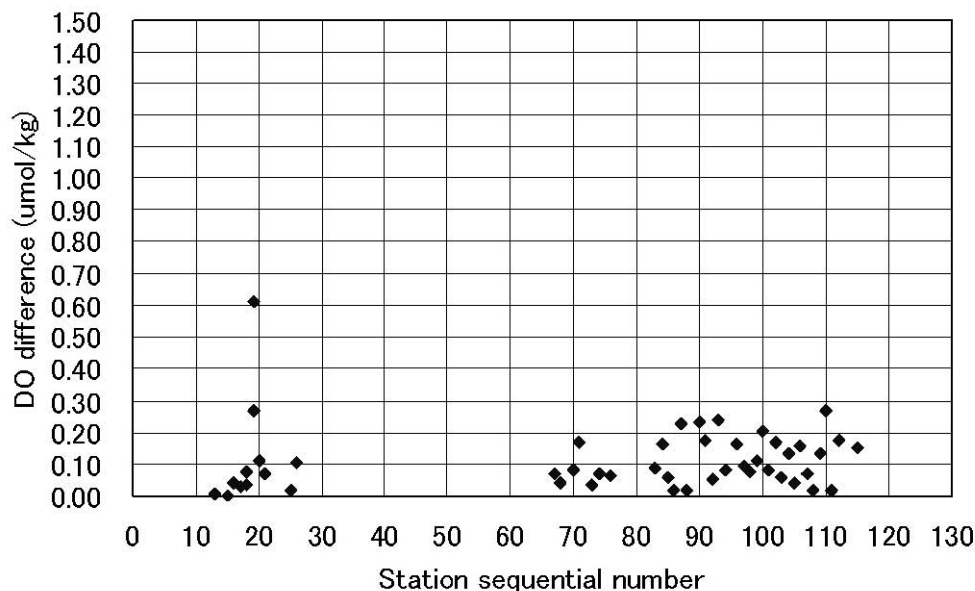


Figure 3.3-4 Difference in the duplicate measurements against station sequential number.

measurement resolution is not clear during the period of this cruise. The standard deviation of the total duplicate measurement was about 0.11 $\mu\text{mol/kg}$. This value is roughly close to the standard deviation of the replicate measurement for the intermediate and deep layers (>500dbar). Thus, we conclude that our measurement resolution of bottle oxygen is about 0.1 $\mu\text{mol/kg}$ or less for

MR05-02 cruise.

3.3.12 CSK standard measurements

The CSK standard solution is a commercial potassium iodate solution (0.0100 N) for analysis of oxygen in seawater. During this cruise, we measured concentration of the CSK standard solution (Lot ASE8280) against our KIO₃ standard in order to confirm accuracy of our oxygen measurement on board (Table 3.3-3). Averaged values of DOT-1 and DOT-2 were 0.009999 ± 0.000002 N and 0.009999 ± 0.000002 N respectively, which indicates that there was no systematic difference between DOT-1 and DOT-2 measurements. The averaged value of the CSK standard solution was so close to the certified value (0.0100 N) that we did not correct sample measurements with the CSK standard measurements. Additionally, we also measured another batch of the CSK standard solution, Lot TCK8677 that was also measured during our last cruise in 2003 (MR03-K04). We found that the measurements of the two batches of the CSK standard agreed well, suggesting there was no systematic difference between our oxygen measurements in 2003 and in 2005.

Table 3.3-3 Results of the CSK standard measurements.

Date (UTC)	KIO ₃ batch#	DOT-1		DOT-2	
		Conc. (N)	error (N)	Conc. (N)	error (N)
2005/6/2	ASE8280-1	0.009997	0.000003	0.010002	0.000003
2005/6/11	ASE8280-2	0.010002	0.000003	0.009997	0.000003
2005/6/21	ASE8280-3	0.009999	0.000003	0.009997	0.000003
2005/6/27	ASE8280-4	0.009999	0.000005	0.009999	0.000003
Average		0.009999	0.000002	0.009999	0.000002
2005/6/11	TCK8677	0.009999	0.000003	0.009997	0.000003

3.3.13 Quality control flag assignment

Quality flag values were assigned to oxygen measurements using the code defined in Table 0.2 of WHP Office Report WHPO 91-1 Rev.2 section 4.5.2 (Joyce *et al.*, 1994). Measurement flags of 2, 3, 4, and 5 have been assigned (Table 3.3-4). For the choice between 2 (good), 3 (questionable) or 4 (bad), we basically followed a flagging procedure as listed below:

- a. On a station-by-station basis, bottle oxygen and difference between bottle oxygen and CTD oxygen at the time of rosette sampling were plotted against CTD pressure. Any points not lying on a generally smooth trend were noted.
- b. Dissolved oxygen was then plotted against potential temperature for several stations. If a datum deviated from a group of plots, it was flagged 3 or 4.
- c. If the bottle flag was 4 (Did not trip correctly), a datum was noted and flagged 4, respectively.

In case of the bottle flag 3 (Leaking), a datum was flagged based on steps a and b.

Before the publishing of these data, as a post-cruise quality control for bottle oxygen, we will carry out one more pass of flagging with the data at all stations. The following steps will be added.

- d. Vertical sections against depth and potential density will be drawn. If a datum is anomalous on the section plots, datum flag will be degraded from 2 to 3, or from 3 to 4.
- e. In the relationships between oxygen and other properties, data flagged 3 and 4 will be examined

once more and upgraded if necessary.

Table 3.3-4 Summary of assigned quality control flags.

Flag	Definition	
2	Good	3746
3	Questionable	8
4	Bad	14
5	Not report (missing)	14
Total		3782

References

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- DOE (1994) Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. A.G. Dickson and C. Goyet (eds), ORNL/CDIAC-74.
- Joyce, T., and C. Corry, eds., C. Corry, A. Dessier, A. Dickson, T. Joyce, M. Kenny, R. Key, D. Legler, R. Millard, R. Onken, P. Saunders, M. Stalcup, contrib. (1994) Requirements for WOCE Hydrographic Programme Data Reporting, WHPO Pub. 90-1 Rev. 2, May 1994 Woods Hole, Mass., USA.

3.4 Nutrients

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3.4.1 Objectives

The objectives of nutrients analyses during the R/V Mirai MR0502 cruise along 149E line in the Western North Pacific are as follows;

Describe the present status of nutrients in the present in good traceability.

The target nutrients are nitrate, nitrite, phosphate and silicate (Although silicic acid is correct, we use silicate because a term of silicate is widely used in oceanographic community.)

Study the temporal and spatial variation of nutrients based on the previous high quality

experiments data of WOCE, GOESECS, IGY and so on.

Study of temporal and spatial variation of nitrate: phosphate ratio, so called Redfield ratio.

Obtain more accurate estimation of total amount of nitrate, phosphate and silicate in the interested area.

Provide more accurate nutrients data for physical oceanographers to use as tracers of water mass movement.

3.4.2 Equipment and techniques

3.4.2.1 Analytical detail using TRAACS 800 systems (BRAN+LUEBBE)

The phosphate analysis is a modification of the procedure of Murphy and Riley (1962).

Molybdic acid is added to the seawater sample to form phosphomolybdic acid which is in turn reduced to phosphomolybdous acid using L-ascorbic acid as the reductant.

Nitrate + nitrite and nitrite are analyzed according to the modification method of Grasshoff (1970).

The sample nitrate is reduced to nitrite in a cadmium tube inside of which is coated with metallic copper. The sample stream with its equivalent nitrite is treated with an acidic, sulfanilamide reagent and the nitrite forms nitrous acid which reacts with the sulfanilamide to produce a diazonium ion. N1-Naphthylethylene-diamine added to the sample stream then couples with the diazonium ion to produce a red, azo dye. With reduction of the nitrate to nitrite, both nitrate and nitrite react and are measured; without reduction, only nitrite reacts. Thus, for the nitrite analysis, no reduction is performed and the alkaline buffer is not necessary. Nitrate is computed by difference.

The silicate method is analogous to that described for phosphate. The method used is essentially that of Grasshoff et al. (1983), wherein silicomolybdic acid is first formed from the silicic acid in the sample and added molybdic acid; then the silicomolybdic acid is reduced to silicomolybdous acid, or "molybdenum blue," using ascorbic acid as the reductant.

The flow diagrams and reagents for each parameter are shown in Figures 3.4.1-3.4.4.

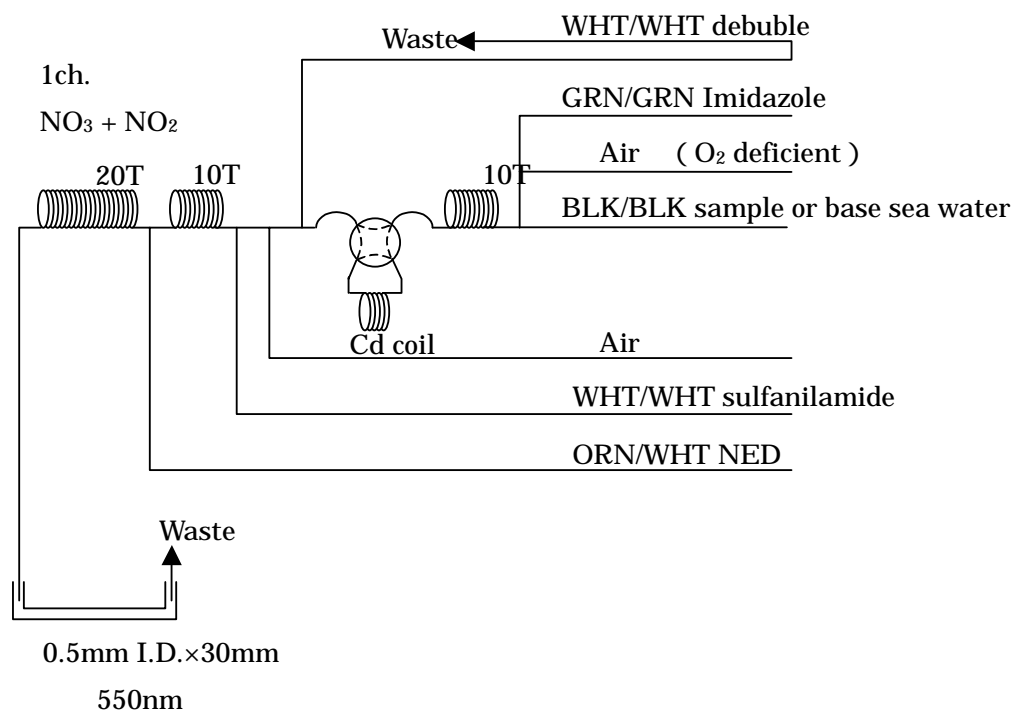


Figure 3.4.1: 1ch. (NO₃+NO₂) Flow diagram.

Nitrate Reagents

Imidazole (buffer), 0.06M (0.4% w/v)

Dissolve 4g imidazole, C₃H₄N₂, in ca. 900ml DIW; add 2ml concentrated HCl; make up to 1000ml with DIW. After mixing, 1ml Triton(R)X-100 (50% solution in ethanol) is added.

Sulfanilamide, 0.06M (1% w/v) in 1.2M HCl

Dissolve 10g sulfanilamide, 4-NH₂C₆H₄SO₃H, in 1000ml of 1.2M (10%) HCl. After mixing, 1ml Triton(R)X-100 (50% solution in ethanol) is added.

N-1-Naphthylethylene-diamine dihydrochloride, 0.004 M (0.1% w/v)

Dissolve 1 g NEDA, C₁₀H₇NHCH₂CH₂NH₂ · 2HCl, in 1000ml of DIW; containing 10ml concentrated HCl. Stored in a dark bottle.

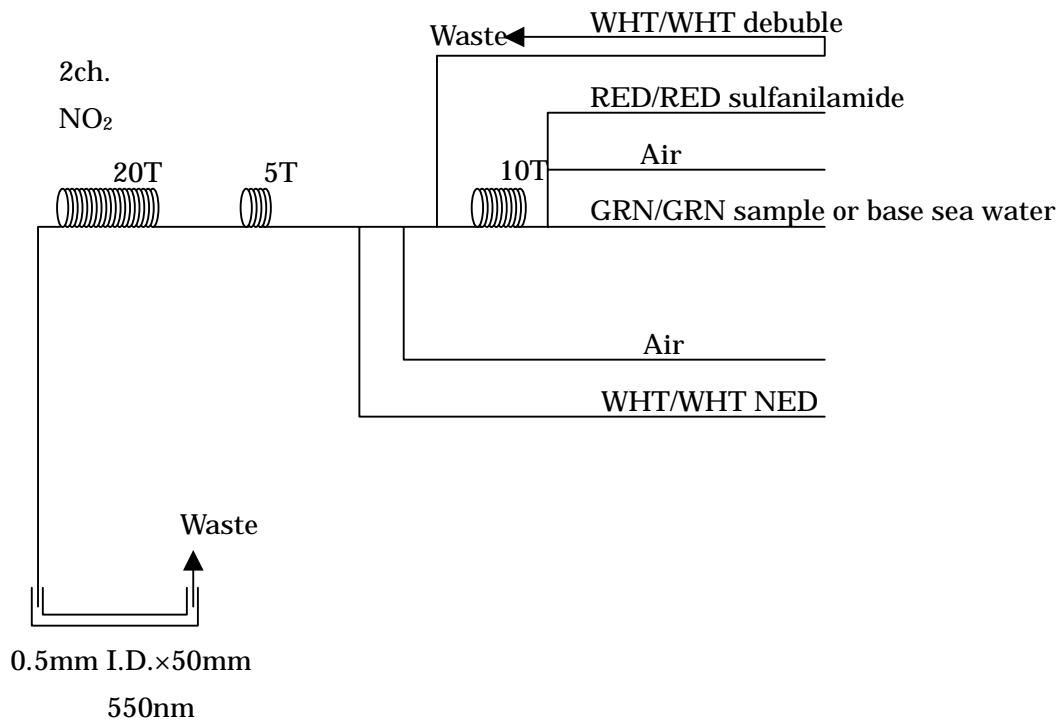


Figure 3.4.2: 2ch. (NO₂) Flow diagram.

Nitrite Reagents

Sulfanilamide, 0.06M (1% w/v) in 1.2M HCl

Dissolve 10g sulfanilamide, 4-NH₂C₆H₄SO₃H, in 1000ml of 1.2M (10%) HCl. After mixing, 1ml Triton(R)X-100 (50% solution in ethanol) is added.

N-1-Naphthylethylene-diamine dihydrochloride, 0.004 M (0.1% w/v)

Dissolve 1 g NEDA, C₁₀H₇NHCH₂CH₂NH₂ · 2HCl, in 1000ml of DIW; containing 10ml concentrated HCl. Stored in a dark bottle.

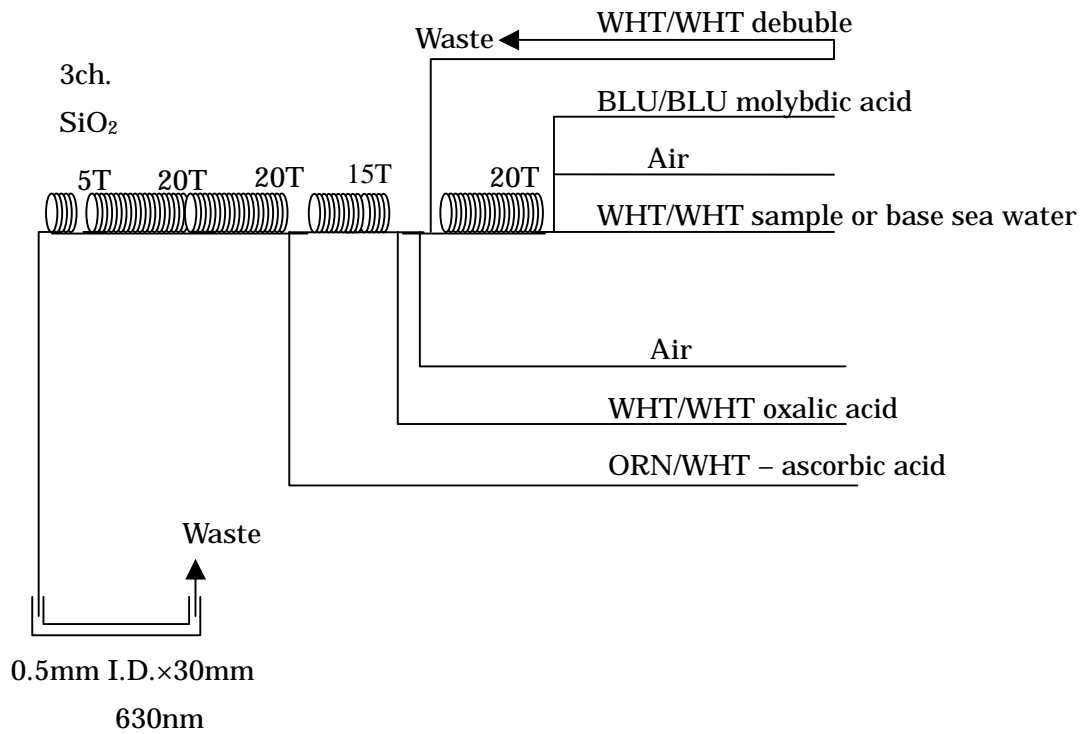


Figure 3.4.3: 3ch. (SiO₂) Flow diagram.

Silicic Acid Reagents

Molybdic acid, 0.06M (2% w/v)

Dissolve 15g Disodium Molybdate(VI) Dihydrate, Na₂MoO₄ · 2H₂O, in 1000ml DIW containing 6ml H₂SO₄. After mixing, 20ml sodium dodecyl sulphate (15% solution in water) is added.

Oxalic acid, 0.6M (5% w/v)

Dissolve 50g Oxalic Acid Anhydrous, HOOC: COOH, in 1000ml of DIW.

Ascorbic acid, 0.01M (3% w/v)

Dissolve 2.5g L (+)-Ascorbic Acid, C₆H₈O₆, in 100ml of DIW. Stored in a dark bottle and freshly prepared before every measurement.

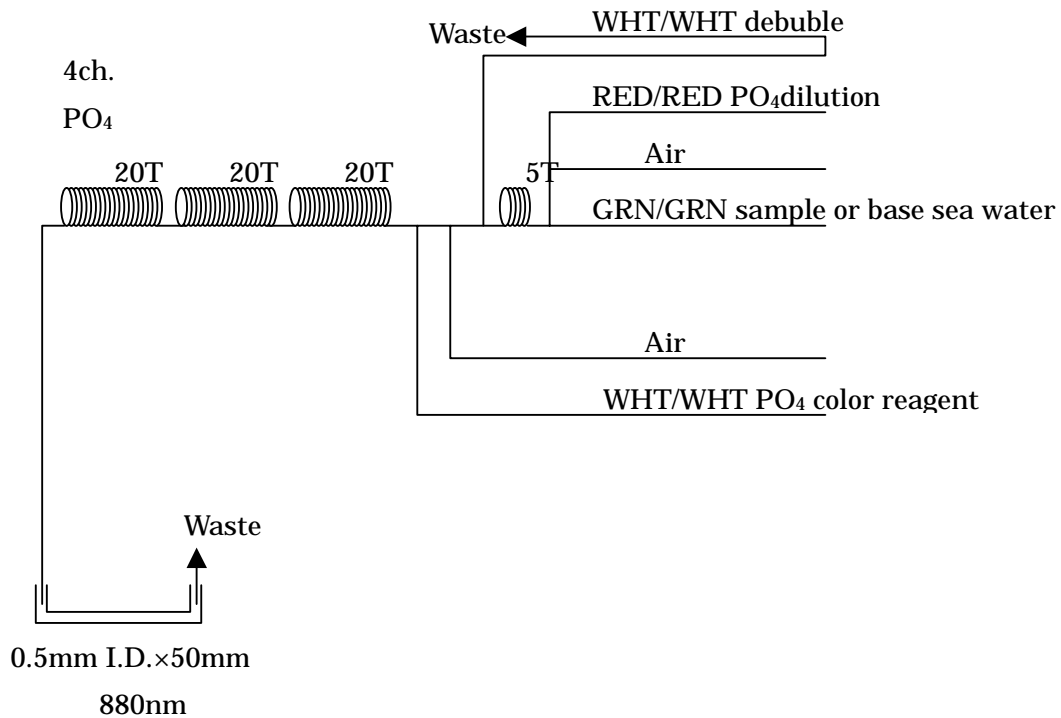


Figure 3.4.4: 4ch. (PO₄) Flow diagram.

Phosphate Reagents

Stock molybdate solution, 0.03M (0.8% w/v)

Dissolve 8g Disodium Molybdate(VI) Dihydrate, Na₂MoO₄ · 2H₂O, and 0.17g Antimony Potassium Tartrate, C₈H₄K₂O₁₂Sb₂ · 3H₂O, in 1000ml of DIW containing 50ml concentrated H₂SO₄.

Mixed Reagent

Dissolve 0.8g L (+)-Ascorbic Acid, C₆H₈O₆, in 100ml of stock molybdate solution. After mixing, 2ml sodium dodecyl sulphate (15% solution in water) is added. Stored in a dark bottle and freshly prepared before every measurement.

PO₄ dilution

Dissolve Sodium Hydrate, NaCl, 10g in ca. 900ml, add 50ml Acetone and 4ml concentrated H₂SO₄, make up to 1000ml. After mixing, 5ml sodium dodecyl sulphate (15% solution in water) is added.

3.4.2.2 Sampling procedures

Sampling of nutrients followed that oxygen, trace gases and salinity. Samples were drawn into two of virgin 10 ml polyacrylates vials without sample drawing tubes. These were rinsed three times before filling and vials were capped immediately after the drawing. The vials are put into water bath at 26 deg. C in 10 minutes before use to stabilize the temperature of samples.

No transfer was made and the vials were set an auto sampler tray directly. Samples were analyzed after collection basically within 17 hours.

3.4.2.3 Data processing.

Raw data from TRAACS800 were treated as follows;

Check baseline shift.

Check the shape of each peak and positions of peak values taken, and then change the positions of peak values taken if necessary.

Carriover correction and baseline drift correction were applied to peak heights of each samples followed by sensitivity correction.

Baseline correction and sensitivity correction were done basically using liner regression.

Load pressure and salinity from CTD data to calculate density of seawater.

Calibration curves to get nutrients concentration were assumed second order equations.

3.4.3 Nutrients standards

3.4.3.1 In-house standards

3.4.3.1.1 Volumetric Laboratory Ware.

All volumetric glass- and plastic (PMP)-ware used were gravimetrically calibrated. Plastic volumetric flasks were gravimetrically calibrated at the temperature of use within 2-3 K.

Volumetric flasks.

Volumetric flasks of Class quality (Class A) are used because their nominal tolerances are 0.05% or less over the size ranges likely to be used in this work. Class A flasks are made of borosilicate glass, and the standard solutions were transferred to plastic bottles as quickly as possible after they are made up to volume and well mixed in order to prevent excessive dissolution of silicic acid from the glass. High quality plastic (polymethylpentene, PMP, or polypropylene) volumetric flasks were gravimetrically calibrated and used only within 3-4 K of the calibration temperature.

The computation of volume contained by glass flasks at various temperatures other than the calibration temperatures were done by using the coefficient of linear expansion of borosilicate crown glass.

Because of their larger temperature coefficients of cubical expansion and lack of tables constructed for these materials, the plastic volumetric flasks were gravimetrically calibrated over the temperature range of intended use and used at the temperature of calibration within 3-4 K. The weights obtained in the calibration weightings were corrected for the density of water and air buoyancy.

Pipettes and pipettors.

All pipettes have nominal calibration tolerances of 0.1% or better. These were gravimetrically calibrated in order to verify and improve upon this nominal tolerance.

3.4.3.1.2 REAGENTS, GENERAL CONSIDERATIONS

General Specifications.

All reagents were of very high purity such as "Analytical Grade," "Analyzed Reagent Grade" and others. And assay of nitrite was determined according JISK8019 and assays of nitrite salts were 98.9%. We use that value to adjust the weights taken.

For the silicate standards solution, we use commercial available silicon standard solution for atomic absorption spectrometry of 1000mg L^{-1} . Since this solution is alkaline solution of 0.5 M KOH, an aliquot of 40ml solution were diluted to 500ml as B standard together with an aliquot of 20ml of 1M HCl. Then the pH of B standard for silicate prepared to be 6.9.

Ultra pure water.

Ultra pure water (MilliQ water) freshly drawn was used for preparation of reagents, higher concentration standards and for measurement of reagent and system blanks.

Low-Nutrient Seawater (LNSW).

Surface water having low nutrient concentration was taken and filtered using $0.45\ \mu\text{m}$ pore size membrane filter. This water is stored in 20 liter cubitainer with paper box. The concentrations of nutrient of this water were measured carefully in March 2005.

3.4.3.1.3 Concentrations of nutrients for A, B and C standards

Concentrations of nutrients for A, B and C standards are set as shown in Table 3.4.1. The C standard is prepared according recipes as shown in Table 3.4.2. All volumetric laboratory tools were calibrated prior the cruise as stated in chapter (i). Then the actual concentration of nutrients in each fresh standard was calculated based on the ambient, solution temperature and determined factors of volumetric lab. wares.

Table 3.4.1: Nominal concentrations of nutrients for A, B and C standards

	A	B	C-1	C-2	C-3	C-4	C-5
$\text{NO}_3(\mu\text{M})$	45000	900	0	9	27	45	54
$\text{NO}_2(\mu\text{M})$	4000	20	0	0.2	0.6	1.0	1.2
$\text{SiO}_2(\mu\text{M})$	36000	2880	0	29	86	143	172
$\text{PO}_4(\mu\text{M})$	3000	60	0	0.6	1.8	3.0	3.6

Table 3.4.2: Working calibration standard recipes

C-STD	B-1 STD	B-2 STD	MAT
C-1	0 ml	0 ml	60 ml
C-2	5 ml	5 ml	50 ml
C-3	15 ml	15 ml	30 ml
C-4	25 ml	25 ml	10 ml
C-5	30 ml	30 ml	0 ml

B-1 STD: Mixture of nitrate, silicate and phosphate

B-2 STD: Nitrite

3.4.3.1.4 Renewal of in-house standard solutions.

In-house standard solutions as stated in (iii) were renewed as shown in Table 3.4.3.

Table 3.4.3: Timing of renewal of in-house standards.

NO₃, NO₂, SiO₂, PO₄	Renewal
A-1 Std. (NO ₃)	maximum 1 month
A-2 Std. (NO ₂)	maximum 1 month
A-3 Std. (SiO ₂)	commercial prepared solution
A-4 Std. (PO ₄)	maximum 1 month
B-1 Std. (mixture of NO ₃ , SiO ₂ , PO ₄)	3 days
B-2 Std. (NO ₂)	6 days
<hr/>	
C Std	Renewal
C-1 ~ C-5 Std (mixture of B1 and B2 Std.)	24 hours
<hr/>	
Reduction estimation	Renewal
D-1 Std.	when A-1 renewed
43µM NO ₃	when C-std renewed
47µM NO ₂	when C-std renewed

3.4.3.2 RMNS

To get the more accurate and high quality nutrients data to achieve the objectives stated above, huge numbers of the bottles of the reference material of nutrients in seawater (hereafter RMNS) are prepared (Aoyama et al., submitted). In the previous world wide expeditions, such as WOCE cruises, the higher reproducibility and precision of nutrients measurements were required (Joyce and Corry, 1994). Since no standards were available for the measurement of nutrients in seawater at that time, the requirements were described in term of reproducibility. The required reproducibility was 1%, 1-2%, 1-3% for nitrate, phosphate and silicate, respectively. Although nutrient data from the WOCE one-time survey was of unprecedented quality and coverage due to much care in sampling and measurements, the differences of nutrients concentration at crossover points are still found among the expeditions (Aoyama and Joyce, 1996, Mordy et al., 2000, Gouretski and Jancke, 2001). For instance, the mean offset of nitrate concentration at deep waters was 0.5 µmol kg⁻¹ for 345 crossovers at world oceans, though the maximum was 1.7 µmol kg⁻¹ (Gouretski and Jancke, 2001). At the 31 crossover points in the Pacific WHP one-time lines, the WOCE standard of reproducibility

for nitrate of 1% was fulfilled at about half of the crossover points and the maximum difference was 7% at deeper layers below 1.6 deg. C in potential temperature (Aoyama and Joyce, 1996).

3.4.3.3 RMNS preparation

RMNS preparation and homogeneity for previous lots.

The study on reference material for nutrients in seawater (RMNS) on the seawater base has been carried out to establish traceability on nutrient analyses in seawater since 1994 in Japan. Autoclaving to produce RMNS has been studied (Aminot and Kerouel, 1991, 1995) and autoclaving was used to stabilize the samples for the 5th intercomparison exercise in 1992/1993 (Aminot and Kirkwood, 1995). Aminot and Kerouel (1995) concluded that nitrate and nitrite were extremely stable throughout their 27 months storage experiment with overall standard deviations lower than 0.3% (range 5-50 $\mu\text{mol l}^{-1}$) and 0.8% (range 0.5-5 $\mu\text{mol l}^{-1}$), respectively. For phosphate, slight increase by 0.02-0.07 $\mu\text{mol l}^{-1}$ per year was observed due to the leaching from the container glass. The main source of nutrient variation in seawater is believed to be microorganism activity, hence, production of RMNS depends on biological inactivation of samples. In this point of view, previous study showed that autoclaving to inactivate the biological activity is acceptable for RMNS preparation.

In the R/V Mirai BEAGLE2003 cruise, which was around the world cruise along ca. 30 deg. S and conducted in 2003 and 2004, RMNS was analyzed at about 500 stations throughout cruises. The results of BEAGLE2003 cruise will be available soon. (Databook of BEAGLE2003, in press)

The seawater for RMNS production was sampled in the North Pacific Ocean at the depths of surface where the nutrients are almost depleted and 1500-2000 meters depth where the nutrients concentrations are the maximum. The seawater was gravity-filtered through a membrane filter with a pore size of 0.45 μm (Millipore HA). The latest procedure of autoclaving for RMNS preparation is that the seawater in a stainless steel container of 40 liters was autoclaved at 120 deg. C, 2 hours, 2 times during two days. The filling procedure of autoclaved seawater was basically same throughout our study. Following cooling at room temperature in two days, polypropylene bottle of 100 ml capacity were filled by the autoclaved seawater of 90 ml through a membrane filter with a pore size of 0.2 μm (Millipore HA) at a clean bench in a clean room. The polypropylene caps were immediately tightly screwed on and a label containing lot number and serial number of the bottle was attached on all of the bottles. Then the bottles were vacuum-sealed to avoid potential contamination from the environment.

RMNSs for this cruise

RMNS lots BC,AV,AX,AY and BA, which covers full range of nutrients concentrations in the western North Pacific are prepared as packages. These packages were renewed daily and analyzed every 2-6 runs on the same day. 150 bottles of RMNS lot AZ are prepared to use every analysis at every hydrographic station. These RMNS assignment were completely done based on random number. The RMNS bottles were stored at a room, REGENT STORE, where the temperature was maintained around 26-28 deg. C.

3.4.3.4 The homogeneity of RMNSs

The homogeneity of lot BC and analytical precisions are shown in Table 3.4.4. These are for the assessment of the magnitude of homogeneity of the RMNS bottles those are used during the cruise.

As shown in Table 3.4.4, the homogeneity of RMNS lot BC for nitrate and silicate are the same magnitude of analytical precision derived from fresh raw seawater. The homogeneity for phosphate, however, exceeded the analytical precision at some extent.

Table 3.4.4: Homogeneity of lot BC and previous lots derived from simultaneous 30 samples measurements and analytical precision onboard R/V Mirai in May 2005.

	Nitrate CV%	Phosphate CV%	Silicate CV%
BC	0.22	0.32	0.19
(AH)	(0.39%)	(0.83%)	(0.13)
(K)	(0.3%)	(1.0%)	(0.2%)
Precision	0.22%	0.22%	0.12%

Note: N=30 x 2

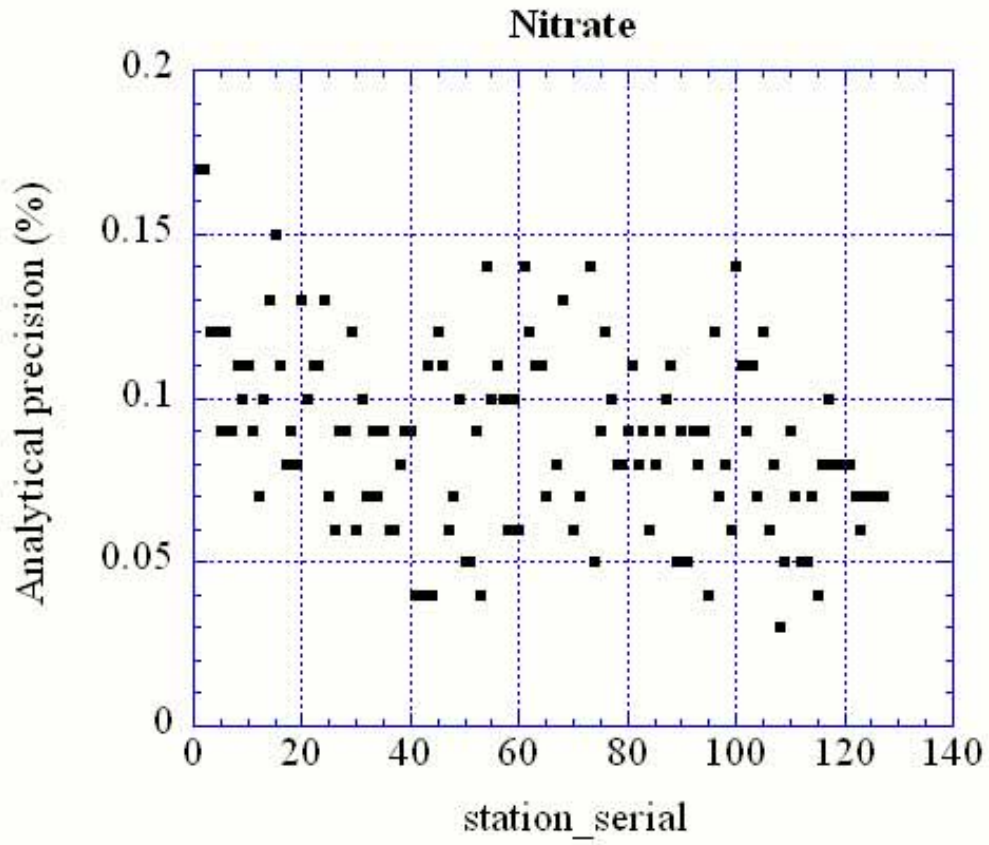
3.4.4 Quality control

3.4.4.1 Precision of nutrients analyses during the cruise

Precision of nutrients analyses during the cruise was evaluated based on the 12 measurements, which are measured every 12 samples, during a run at the concentration of C-5. We also evaluated the reproducibility based on the replicate analyses of five samples in each run. Summary of precisions are shown in Table 3.4.5. As shown in Table 3.4.5 and Figures 3.4.5-3.4.7, the precisions for each parameter are generally good considering the analytical precisions estimated from the simultaneous analyses of 60 samples in May 2005. Analytical precisions previously evaluated were 0.22% for phosphate, 0.22% for nitrate and 0.12% for silicate, respectively. During this cruise, analytical precisions were 0.12% for phosphate, 0.09% for nitrate and 0.08% for silicate in terms of median of precision, respectively. Then we can conclude that the analytical precisions for phosphate, nitrate and silicate were maintained or better throughout this cruise comparing the pre-cruise evaluations. The time series of precision are shown in Figures 3.4.5-3.4.7.

Table 3.4.5: Summary of precision based on the replicate analyses of 12 samples in each run through out cruise.

	Nitrate CV%	Phosphate CV%	Silicate CV%
Median	0.09	0.11	0.07
Mean	0.09	0.12	0.08
Maximum	0.17	0.29	0.19
Minimum	0.03	0.05	0.03
N	126	126	126



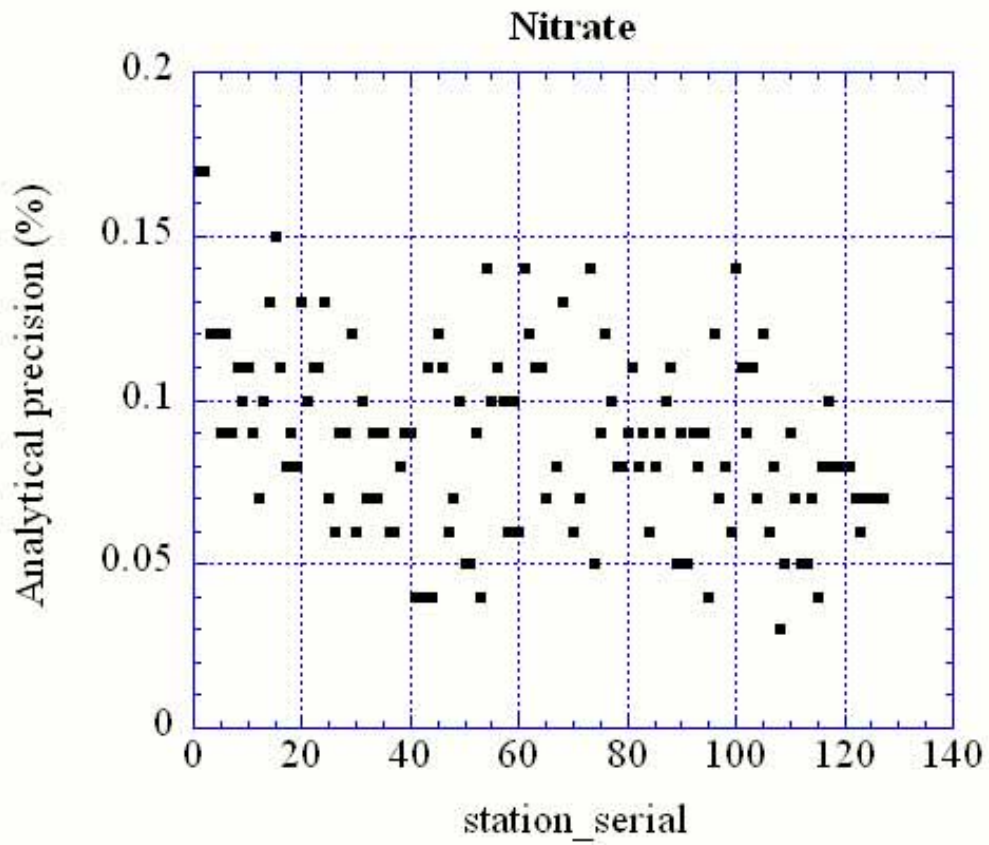


Figure: 3.4.5 Time series of precision of nitrate

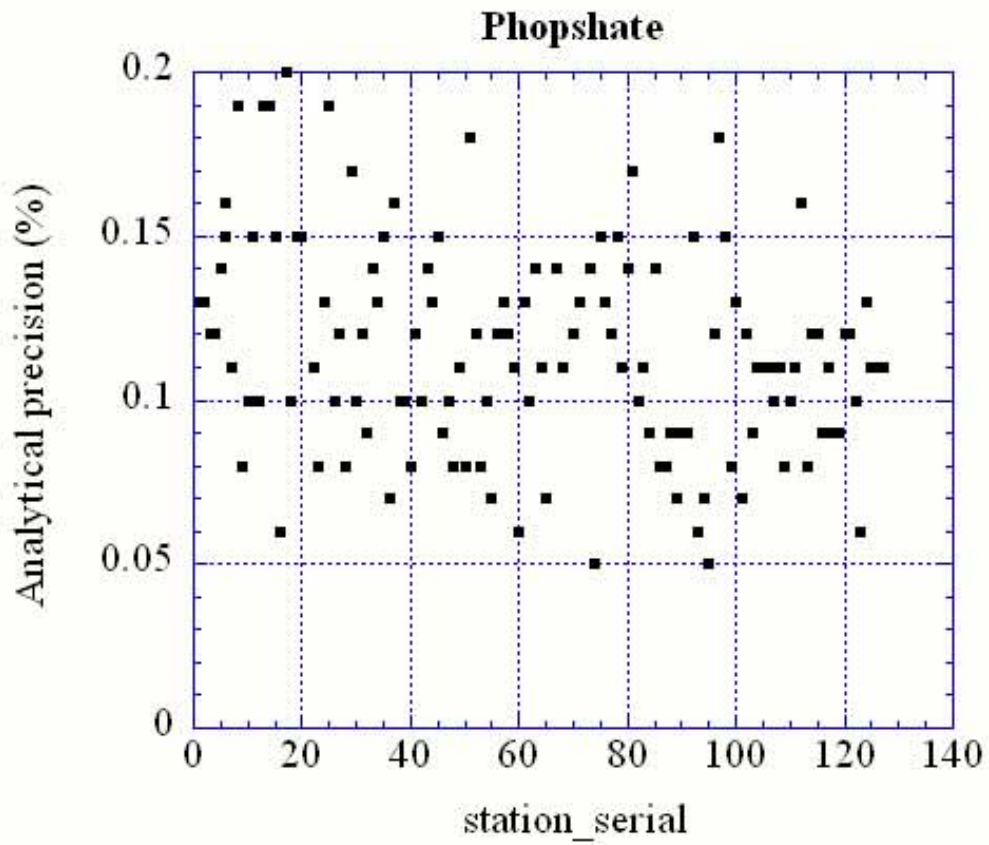


Figure: 3.4.6 Time series of precision of phosphate

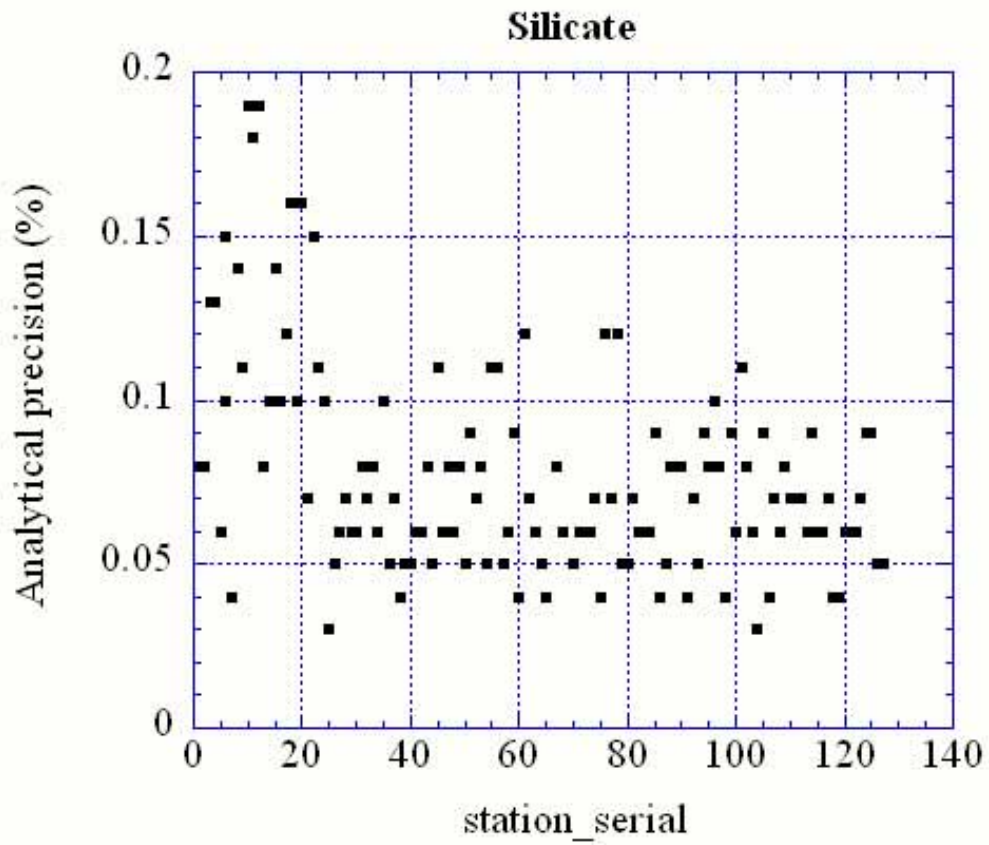


Figure: 3.4.7 Time series of precision of silicate

3.4.4.2 Carry over

We can also summarize the magnitudes of carry over throughout the cruise. These are as shown in Table 3.4.6.

Table 3.4.6: Summary of carry over through out cruise.

	Nitrate	Phosphate	Silicate
	%	%	%
Median	0.30	0.24	0.21
Mean	0.30	0.25	0.21
Maximum	0.50	0.71	0.38
Minimum	0.10	0.00	0.03
N	126	126	126

3.4.4.3 Evaluation of trueness of nutrients concentrations using RMNSs

We have been using RMNS for all runs, then, we can evaluate the trueness of nutrients concentration throughout cruise. Results of RMNS measurements are shown in Figures 3.4.8-3.4.10.

The uncertainties of nitrate, phosphate and silicate measurements for this cruise were evaluated as functions of concentrations of those. Uncertainties of nitrate measurement are expressed by eq. (1).

$$\text{Uncertainties (\%)} = 0.13 + 1.66 / C_{\text{nitrate}} \quad \dots \quad (1)$$

Where C_{nitrate} is nitrate concentration in micro mol kg^{-1} .

Uncertainties of phosphate measurement are expressed eq. (2).

$$\text{Uncertainties (\%)} = -0.11 + 1.032 / C_{\text{phos}} \quad \dots \quad (2)$$

Where C_{phos} is phosphate concentration in micro mol kg^{-1} .

Uncertainties of silicate measurement are expressed eq. (3).

$$\text{Uncertainties (\%)} = 0.095 + 4.92 / C_{\text{silicate}} \quad \dots \quad (3)$$

Where C_{silicate} is silicate concentration in micro mol kg^{-1} .

Then, three columns to show the uncertainties of nutrients measurement were created in the sea file of this cruise.

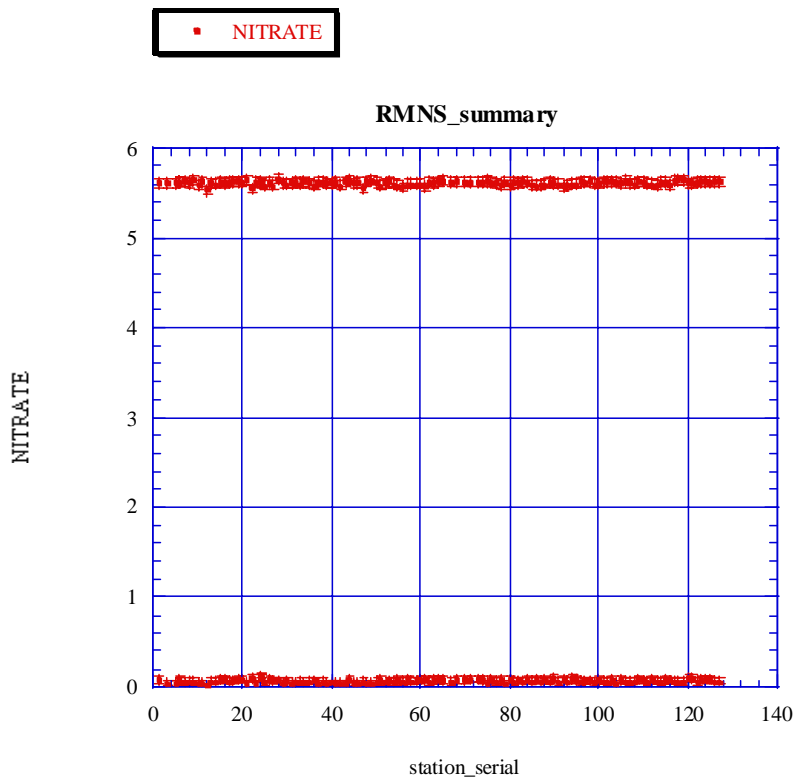
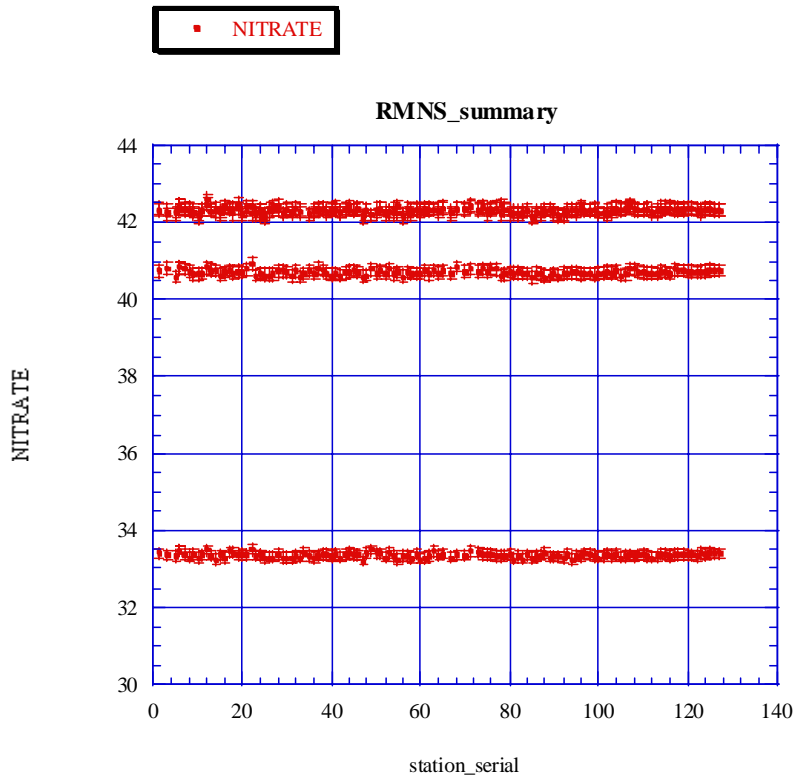


Figure: 3.4.8: Time series of nitrate concentration for RMNSs

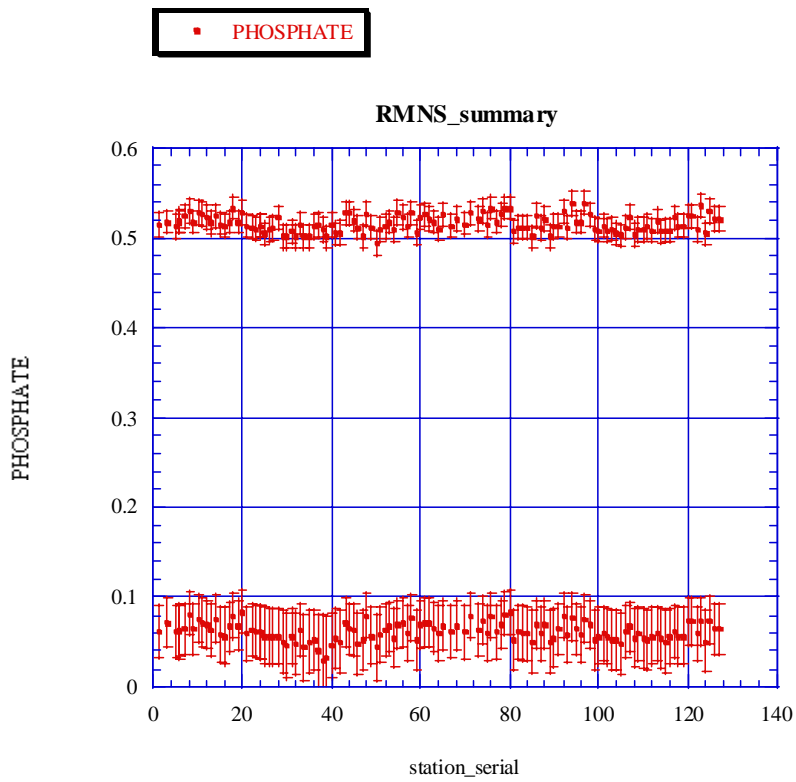
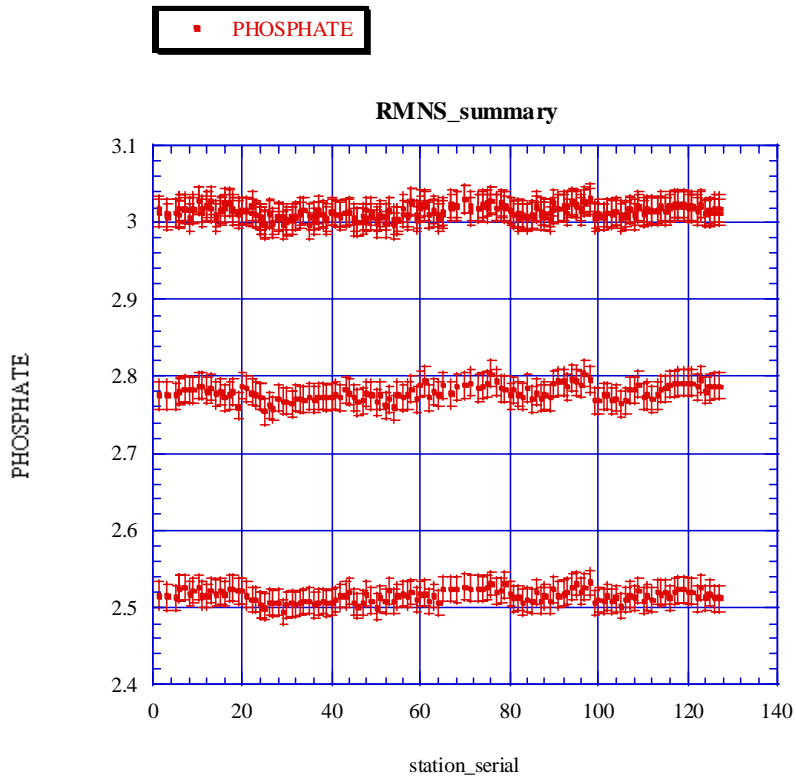


Figure: 3.4.9: Same as Figure 3.4.8, but for phosphate

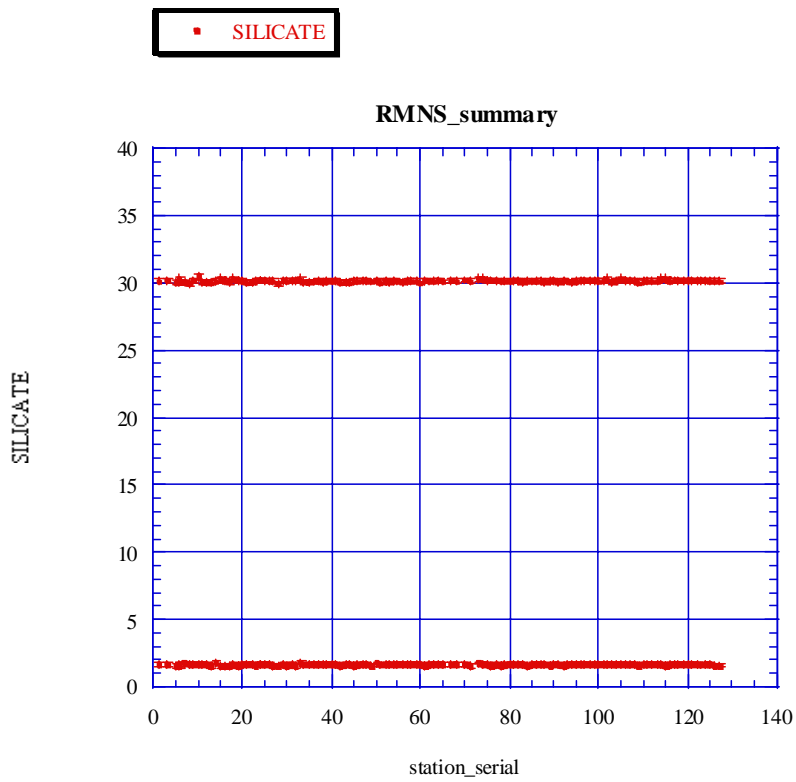
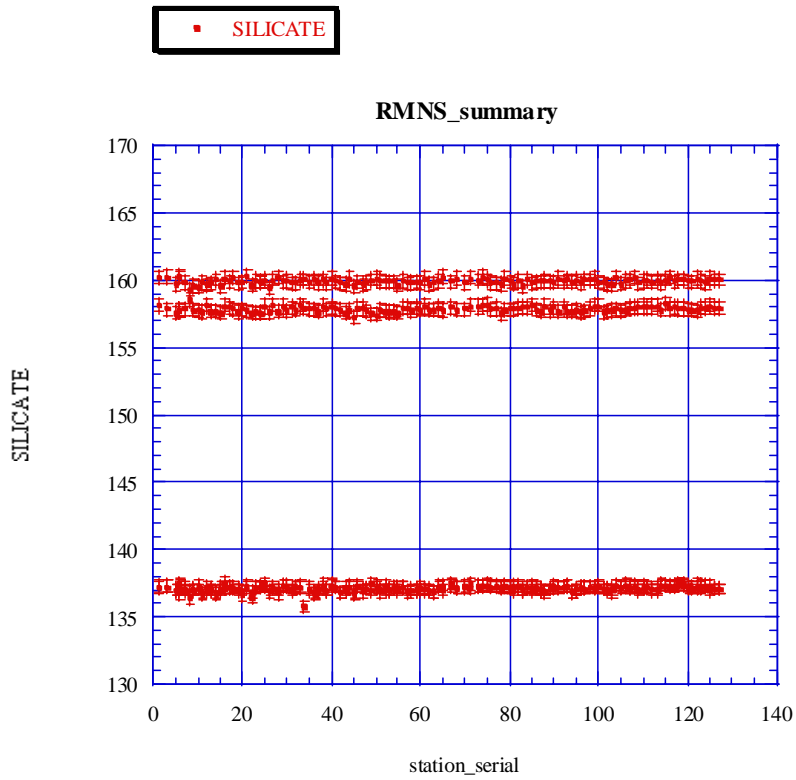


Figure: 3.4.10: Same as Figure 3.4.8, but for silicic acid

3.4.5 Cruise-to-cruise traceability

Cruise-to-cruise traceability was examined based on the results of the previous results of RMNSs obtained among several cruises and laboratory analyses. As shown in table 3.4.7, the nutrients concentration of RMNSs were in good agreement among experiments.

Table 3.4.7: Cruise to cruise tracerbility

Cruise/Lab	RM Lots				
	AX	AV	BC	AZ	AH
	Nitrate				
BEAGLE2003					35.3
RY0501	21.8			41.9	35.5
MR0501	21.5	33.4			35.5
Pre-MR0502			40.8		
KANSO2005	21.4	33.2	40.5	41.9	35.9
MR0502	21.5	33.4	40.7	42.3	
	Phosphate				
BEAGLE2003					2.10
RY0501	1.52			2.99	2.08
MR0501	1.62	2.52			2.13
Pre-MR0502			2.78		
KANSO2005	1.59	2.48	2.72	3.01	2.03
MR0502	1.61	2.52	2.78	3.01	
	Silicate				
BEAGLE2003					133.8
RY0501	59.9			135.6	133.8
MR0501	59.4	157.7			135.5
Pre-MR0502			160.7		
KANSO2005	59.5	156.6	159.5	136.3	135.4
MR0502	59.5	157.9	159.9	137.1	

3.4.6 Problems/improvements occurred and solutions.

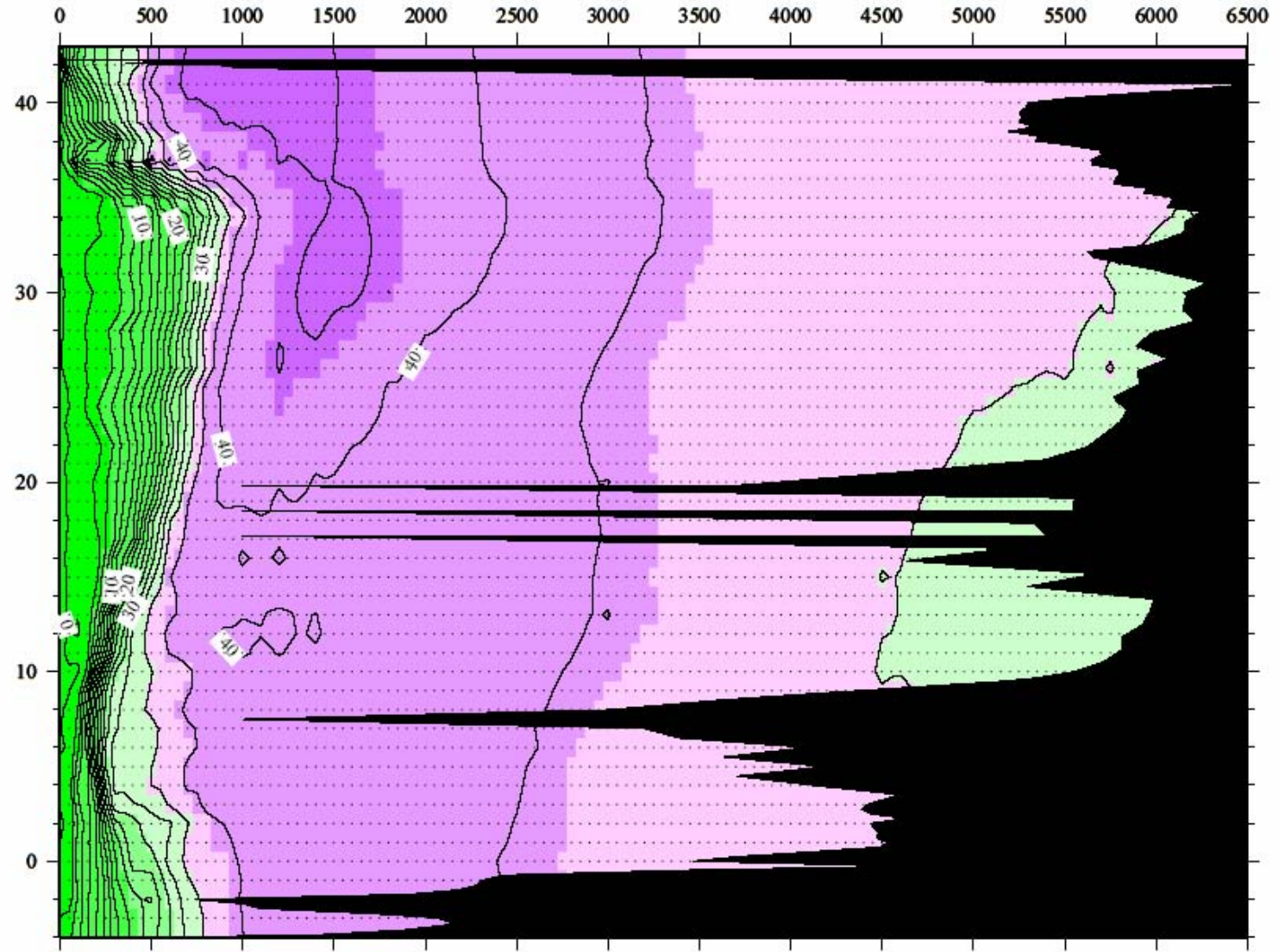
As shown in Figure 3.4.7, the precisions of silicate concentration reached to 0.15-0.19% at several stations before station 118, of which serial number of the station is 26. The cause of relatively higher precisions was attributed to be larger ambient temperature variability up to 1 deg. C around 30 minutes interval. We re-arranged a setting of room temperature control to be more stable and got less room temperature variability around 0.5 deg. C. Then we can see much better precision of silicate analyses after re-arrangement as shown in Figure 3.4.7.

Reference

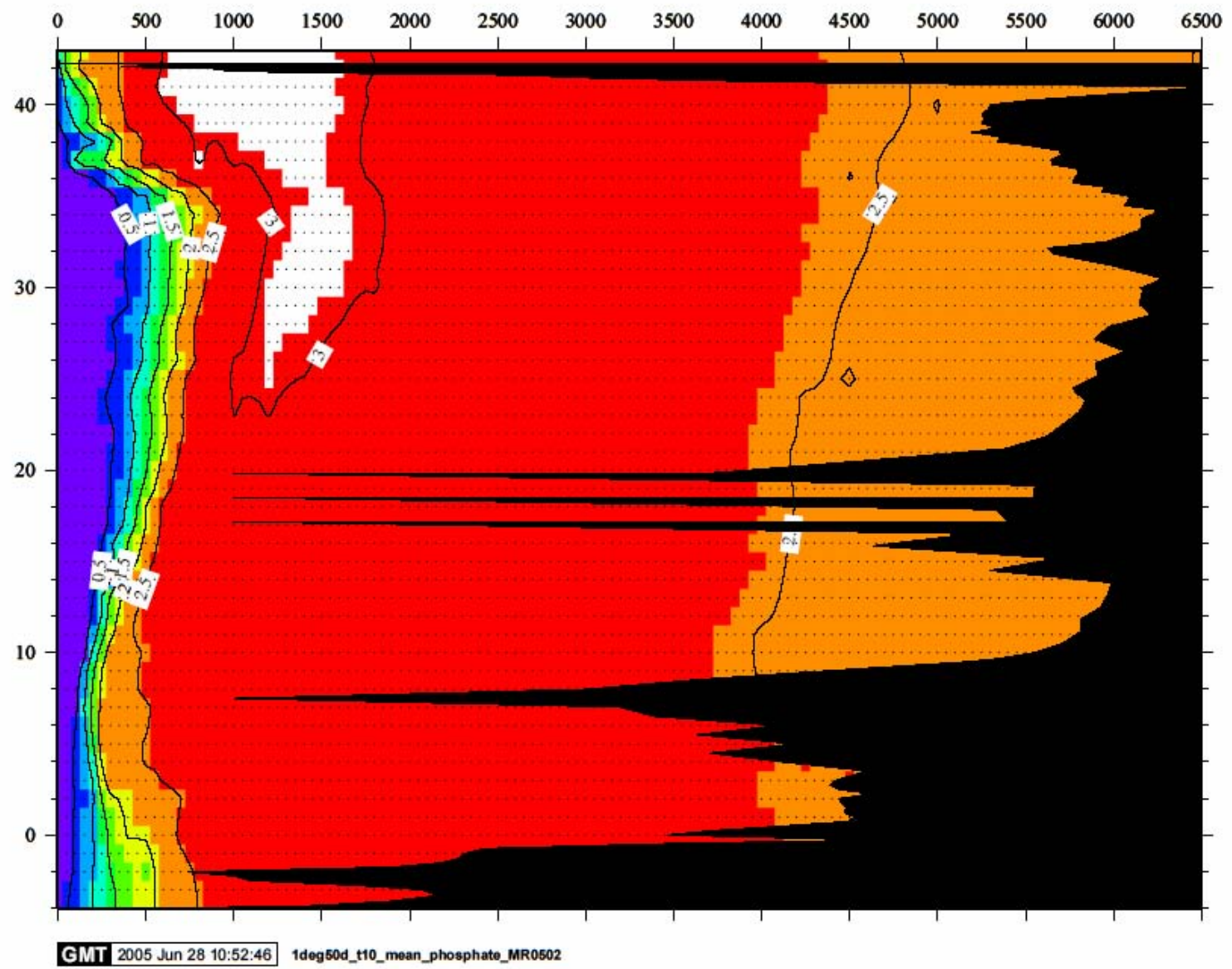
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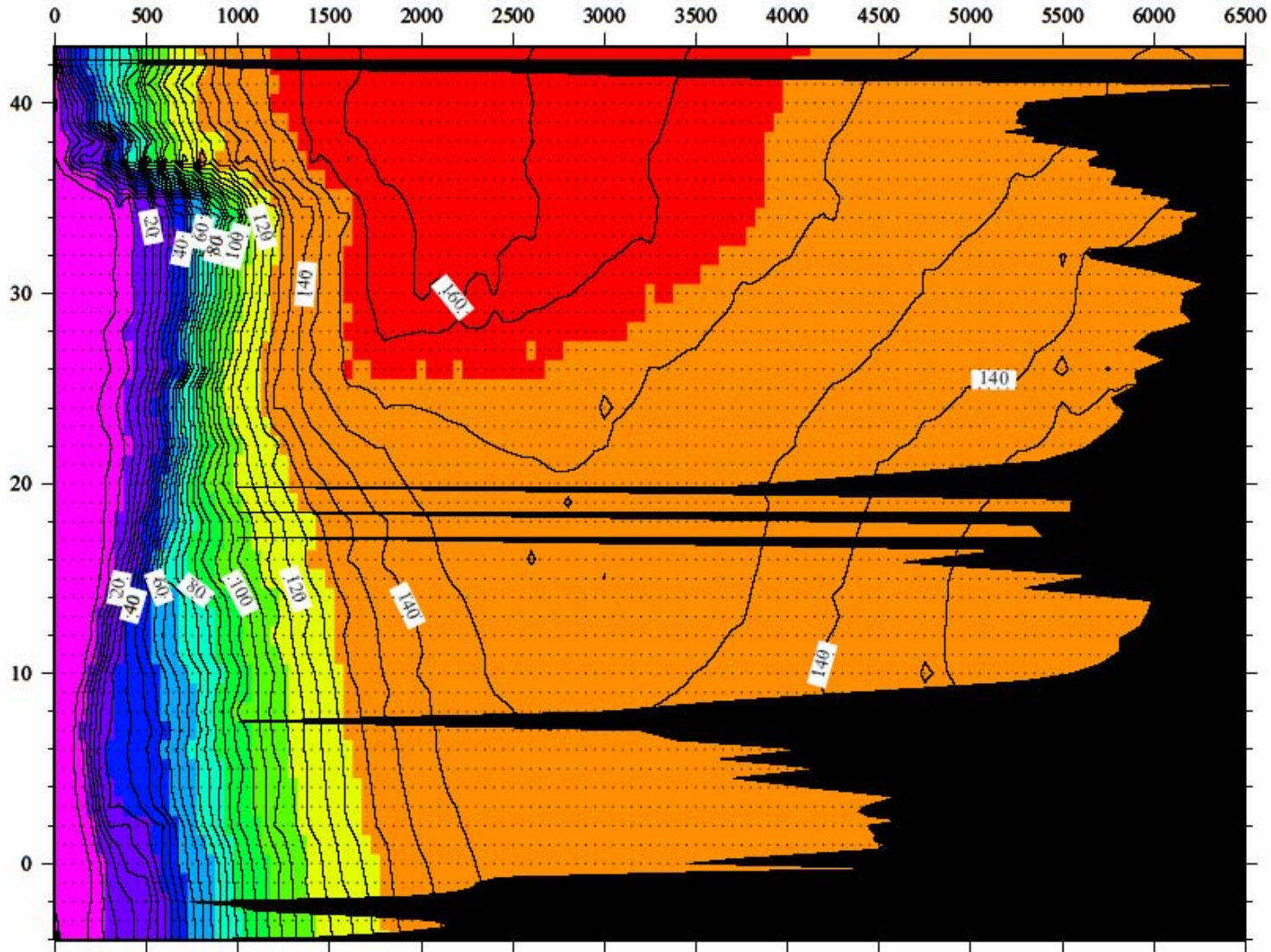
Appendix 1

1. Section of Nitrate (Tentative value)
2. Section of Phosphate (Tentative value)
3. Section of Silicate (Tentative value)



GMT 2005 Jun 28 10:52:47 1deg50d_t10_mean_nitrate_MR0502





3.5 Chlorofluorocarbons

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2) Marine Works Japan Co. Ltd

3.5.1 Objectives

Chlorofluorocarbons (hereafter CFCs) are chemically and biologically stable gases that have been artificially synthesized at 1930's or later. The atmospheric CFCs can slightly dissolve in sea surface water and then circulate in the ocean. Three chemical species of CFCs, namely CFC-11 (CCl₃F), CFC-12 (CCl₂F₂) and CFC-113 (C₂Cl₃F₃), can be used as transient tracers for decadal scale circulation of the ocean. We determined these CFCs concentrations in seawater on board.

3.5.2 Apparatus

Dissolved CFCs are detected by an electron capture detector – gas chromatograph attached with a purging & trapping system.

Table 3-5-1 Instruments

Gas Chromatograph:	GC-14B (Shimadzu Ltd.)
Detector:	ECD-14 (Shimadzu Ltd)
Analytical Column:	
Pre column:	Silica Plot capillary columns [i.d.: 0.53 mm, length: 4 m, film thickness: 6 μm]
Main column:	Connected two capillary columns (Pola Bond-Q [i.d.: 0.53 mm, length: 7 m, film thickness: 10 μm] followed by Silica Plot [i. d.: 0.53 mm, length: 22 m, tick: 6 μm])

3.5.3 Procedures

3.5.3.1 Sampling

Seawater sub-samples for CFCs measurement were collected from 12 liter Niskin bottles to 300ml glass bottle. The bottle was filled by nitrogen gas before sampling. Two times of the bottle volumes of seawater sample were overflowed. The bottles filled by seawater sample were kept in water bathes roughly controlled on sample temperature. The CFCs concentrations were determined as soon as possible after sampling (within 24 hr in maximum). These procedures were needed in order to minimize contamination from atmospheric CFCs.

Air samples for CFCs measurement were collected to 100ml glass cylinder attached magnesium perchlorate dryer tube at the navigation deck on R/V "MIRAI".

3.5.3.2 Analysis

The CFCs analytical system is modified from the original design of Bullister and Weiss (1988). Constant volume of sample water (50ml) is taken into the purging & trapping system. Dissolved CFCs are de-gassed by N₂ gas purge and concentrated in a trap column cooling to -45 degree

centigrade. The CFCs are desorbed by heating the trap column to 140 degree centigrade within 1.5 minutes, and lead into an electron capture detector - gas chromatograph (ECD-GC). The analytical conditions are listed following table in detail.

Table 3-5-2 Analytical conditions of dissolved CFCs in seawater.

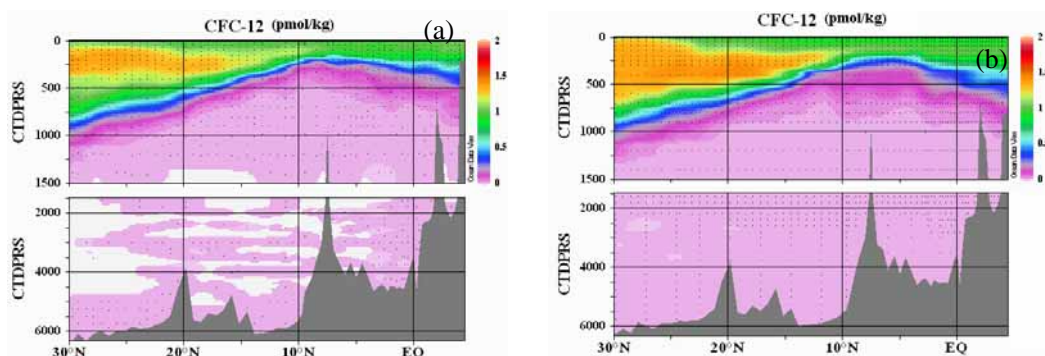
Temperature	
Analytical Column:	95 deg-C
Detector (ECD):	240 deg-C
Trap column:	-45 deg-C (at adsorbing) & 140 deg-C (at desorbing)
Mass flow rate of nitrogen gas (99.9999%)	
Carrier gas:	20 ml/min
Detector Make UP:	16 ml/min
Back flush gas:	20 ml/min
Sample purge gas:	200 ml/min
Standard gas (Japan Fine Products co. ltd.)	
Base gas:	Nitrogen
CFC-11:	300 ppt (v/v)
CFC-12:	160 ppt (v/v)
CFC-113:	30 ppt (v/v)

3.5.3.3 Performance

The analytical precisions are estimated from replicate sample analyses. The precisions were calculated to be ± 0.012 pmol/kg ($n = 220$), ± 0.007 pmol/kg ($n = 219$) and ± 0.007 pmol/kg ($n = 218$) for CFC-11, -12 and -113, respectively. The standard gases used in this cruise will be calibrated to SIO scale standard gases after the cruise, and then the data will be corrected.

3.5.4 Results

Penetration depths of CFCs were around 1500 m at northern region (higher than 30 degree North) and shallower than 1000 m at low latitude. CFC-113 maximum was found around 500 – 1000 m between 35 degree-N and 20 degree-N. We detected significant increase in CFCs around 250 – 1000 m in this decade (Fig 3-5-1)



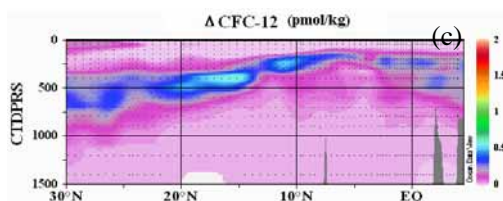


Fig. 3-5-1 Comparison between CFC-12 distributions of WOCE P10 data (a) and this cruise (b). Shallower part (<1500 m) is expanded. Distribution of difference in CFC-12 concentration between two observations is plotted (c).

3.5.5 Data archive

All data will be submitted to JAMSTEC Data Management office (DMO) and under its control.

3.5.6 Reference

Bullister, J.L and Weiss R.F. 1988. Determination of CCl₃F and CCl₂F₂ in seawater and air. Deep Sea Research, 35, 839-853.

3.6. Carbon items

Akihiko Murata (JAMSTEC)

Fuyuki Shibata (MWJ)

Mikio Kitada (MWJ)

Taeko Ohama (MWJ)

Yoshiko Ishikawa (MWJ)

3.6.1 Objectives

Concentrations of CO₂ in the atmosphere are now increasing at a rate of 1.5 ppmv y⁻¹ owing to human activities such as burning of fossil fuels, deforestation, and cement production. It is an urgent task to estimate as accurately as possible the absorption capacity of the oceans against the increased atmospheric CO₂, and to clarify the mechanism of the CO₂ absorption, because the magnitude of the anticipated global warming depends on the levels of CO₂ in the atmosphere, and because the ocean currently absorbs 1/3 of the 6 Gt of carbon emitted into the atmosphere each year by human activities.

In this cruise, we were aimed at quantifying how much anthropogenic CO₂ is absorbed in the North Pacific Ocean, especially in North Pacific Intermediate Water. For the purpose, we measured CO₂-system parameters such as dissolved inorganic carbon (C_T), total alkalinity (A_T) and pH.

3.6.2 Apparatus

(1) C_T

Measurements of C_T was made with two total CO₂ measuring systems (systems A and B; Nippon ANS, Inc.), which are slightly different from each other. The systems comprise of a sea water dispensing system, a CO₂ extraction system and a coulometer (Model 5012, UIC Inc.).

The seawater dispensing system has an auto-sampler (6 ports), which takes seawater in a 300 ml borosilicate glass bottle and dispenses the seawater to a pipette of nominal 20 ml volume by

PC control. The pipette was kept at 20 °C by a water jacket, in which water from a water bath set at 20 °C is circulated.

CO₂ dissolved in a seawater sample is extracted in a stripping chamber of the CO₂ extraction system by adding phosphoric acid (10 % v/v). The stripping chamber is made approx. 25 cm long and has a fine frit at the bottom. To degass CO₂ as quickly as possible, a heating wire kept at 40 °C is rolled from the bottom to a 1/3 height of the stripping chamber. The acid is added to the stripping chamber from the bottom of the chamber by pressurizing an acid bottle for a given time to push out the right amount of acid. The pressurizing is made with nitrogen gas (99.9999 %). After the acid is transferred to the stripping chamber, a seawater sample kept in a pipette is introduced to the stripping chamber by the same method as in adding an acid. The seawater reacted with phosphoric acid is stripped of CO₂ by bubbling the nitrogen gas through a fine frit at the bottom of the stripping chamber. The CO₂ stripped in the chamber is carried by the nitrogen gas (flow rates of 130 ml min⁻¹ and 140 ml min⁻¹ for systems A and B, respectively) to the coulometer through a dehydrating module. For system A, the module consists of two electric dehumidifiers (kept at 1 – 2 °C) and a chemical desiccant (Mg(ClO₄)₂). For system B, it consists of three electric dehumidifiers with a chemical desiccant.

The measurement sequence such as system blank (phosphoric acid blank), 2 % CO₂ gas in a nitrogen base, seawater samples (6) was programmed to repeat. The measurement of 2 % CO₂ gas was made to monitor response of coulometer solutions (from UIC, Inc.).

(2) A_T

Measurement of A_T was made using a titration system (Nippon ANS, Inc.). The system comprise of a water dispensing unit, an auto-burette (Metrohm), a pH meter (Thermo Electron), and a pair of electrodes (Reference electrode: REF201 (Radiometer), Glass pH Electrode: pHG201-7 (Radiometer)), or combination electrodes (ROSS 8102BN: Thermo Electron Corporation), which is automatically controlled by a PC.

A seawater of approx. 40 ml is transferred from a sample bottle (borosilicate glass bottle; 130 ml) into a water-jacketed (25 °C), and is introduced into a water-jacketed (25 °C) titration cell. The seawaters are titrated by an acid titrant, which was 0.05 M HCl in 0.65 M NaCl in this cruise.

Calibration of the acid titrant was made by measuring A_T of 5 solutions of Na₂CO₃ in 0.7 M NaCl solutions. The computed A_Ts were approx. 0, 100, 1000, 2000 and 2500 μmol kg⁻¹. The measured values of A_T (calculated by assuming 0.05 M) should be a linear function of the A_T contributed by the Na₂CO₃. The line was fitted by the method of least squares. Theoretically, the slope should be unity. If the measured slope is not equal to one, the acid normality should be adjusted by dividing initial normality by the slope, and the whole set of calculations is repeated until the slope = 1

Calculation of A_T was made based on a modified Gran approach.

(3) pH

Measurement of pH was made by a pH measuring system (Nippon ANS, Inc.), which adopts a method for the spectrophotometric determination. The system comprises of a water dispensing unit and a spectrophotometer (Carry 50 Scan, Varian). For an indicator, *m*-cresol purple (2 mM) was used.

Seawater is transferred from borosilicate glass bottle (300 ml) to a sample cell in the

spectrophotometer. The length and volume of the cell are 8 cm and 13 ml, respectively, and the sample cell is kept at 25.00 ± 0.05 °C in a thermostated compartment. First, absorbances of seawater only are measured at three wavelengths (730, 578 and 434 nm). Then the indicator is injected and circulated for about 3 or 3.5 minutes, to mix the indicator and seawater sufficiently. After the pump is stopped, the absorbances of seawater + indicator are measured at the same wavelengths. The pH was calculated based on the following equation (Clayton and Byrne, 1993):

$$pH = pK_2 + \log\left(\frac{A_1 / A_2 - 0.00691}{2.2220 - 0.1331(A_1 / A_2)}\right),$$

where A_1 and A_2 indicate absorbances at 578 and 434 nm, respectively, and pK_2 is calculated as a function of water temperature and salinity.

Reference

Clayton T.D. & R.H. Byrne (1993) Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale calibration of m-cresol purple and at-sea results. *Deep-Sea Research* 40, 2115-2129.

3.6.3 Performances

(1) C_T

The two systems had worked well during the leg without a major malfunction. Replicate analysis was made for 3 – 4 pair samples at each water column. The repeatability for systems A and B were estimated to be 0.8 (n = 117 pairs) and 1.7 (n = 94 pairs) $\mu\text{mol kg}^{-1}$, respectively. The combined result was 1.2 $\mu\text{mol kg}^{-1}$ (n = 211 pairs).

(2) A_T

The systems conducted a high speed titration (5 - 6 min.) compared to systems used in previous studies. A few replicate samples were taken on every station. The repeatability was estimated to be 1.8 $\mu\text{mol kg}^{-1}$ (n = 212 pairs).

(3) pH

The system had worked well with no troubles. The average of absolute differences between replicate samples was 0.0008 pH unit (n = 207 pairs).

3.6.4 Results

Cross sections of C_T , A_T and pH along the observation line are illustrated in Fig. 1.

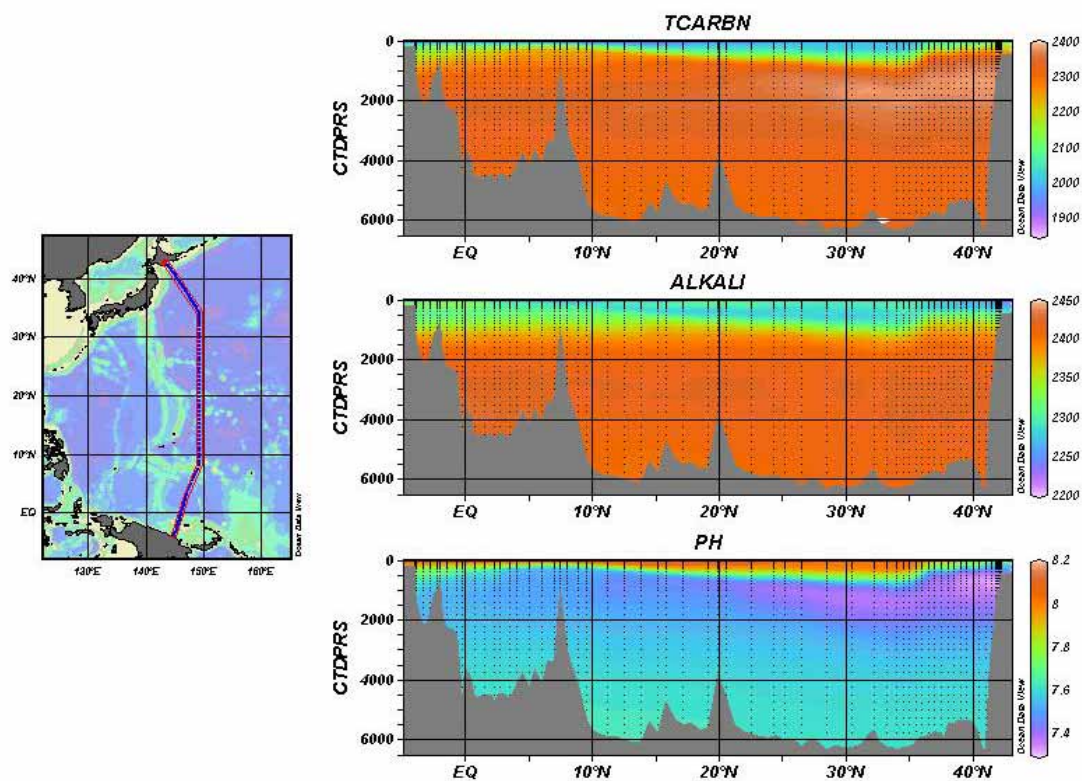


Fig. 1 Distributions of C_T , A_T and pH along the observation line

3.7 Samples taken for other chemical measurement

3.7.1 Carbon-14, carbon-13 (2-July-2005)

Yuichiro KUMAMOTO

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3.7.1.1 Objective

In order to investigate water circulation and carbon cycle in the western Pacific, seawater for carbon-14 (C-14; radiocarbon) and carbon-13 (C-13; stable carbon isotope) of total dissolved inorganic carbon (TDIC) was collected by the hydrocasts from surface to bottom.

3.7.1.2 Sample collection

The sampling stations and number of samples are summarized in Table 3.7.1-1. All samples for carbon isotope ratios were collected at 19 stations using 12 liter Niskin bottles. The seawater

sample was siphoned into a 250 cm³ glass bottle with enough seawater to fill the glass bottle 3 times. Immediately after sampling, 10 cm³ of seawater was removed from the bottle and poisoned by 0.1 cm³ µl of saturated HgCl₂ solution. Then the bottle was sealed by a glass stopper with Apiezon grease M and stored in a cool and dark space on board.

3.7.1.3 Sample preparation and measurements

In our laboratory, dissolved inorganic carbon in the seawater samples will be stripped cryogenically and split into three aliquots: radiocarbon measurement (about 200 µmol), C-13 measurement (about 100 µmol), and archive (about 200 µmol). The extracted CO₂ gas for radiocarbon will be then converted to graphite catalytically on iron powder with pure hydrogen gas. The C-13 of the extracted CO₂ gas will be measured using Finnigan MAT252 mass spectrometer. The carbon-14 in the graphite sample will be measured by Accelerator Mass Spectrometry (AMS).

Table 3.7.1-1. The sampling stations and number of samples for carbon isotope ratios.

Station	No. samples	No. replicate samples	Max. sampling pressure /db
P10N-136	19	1	2001.7
P10N-130	36	2	5404.4
P10N-120	19	1	2000.0
P10N-110	36	2	6211.2
P10N-100	19	1	2000.4
P10-073	36	2	6333.4
P10-068	19	1	2001.7
P10-064	36	2	5811.2
P10-060	19	1	1999.4
P10-056	35	2	5484.1
P10-051	19	1	2000.2
P10-047	36	2	5909.5
P10-040	19	1	2000.5
P10-034	31	2	4242.0
P10-029	19	1	2002.5
P10-024	31	2	4548.4
P10-017	33	2	4775.7
P10-010	12	1	727.8
P10-005	20	1	2173.1
Total	494	28	

3.7.2 Radionuclides (*draft as of 30 June, 2005*)

Michio Aoyama (*Meteorological Research Institute / Japan Meteorological Agency, Principal Investigator*)

3.7.2.1 Objectives

- 1) Study more about present distribution of ¹³⁷Cs in the subtropical gyre originated mainly from atmospheric nuclear weapons tests conducted in the 1960s.
- 2) Provide detail artificial radionuclides database for general circulation model validation

3.7.2.2 Target radionuclides

Main target radionuclides are ¹³⁷Cs, and Pu..

3.7.2.3 Sampling procedures

Sampling of seawater samples of radionuclides in water column were done followed that all parameters. The additional bottles were available by chance, then, the samples volumes for water column varied from 6 liter to 20 liter. Samples were drawn into 10 or 20 liter cubitainers from the Niskin bottles. Concentrated Nitric Acid was added to the samples to keep pH1.6.

Surface water samples were drawn through intake pump below several meters from the surface. Seawater of 85 liter were collected for ¹³⁷Cs and Pu.

3.7.2.4 Samples accomplished during the cruise

A total of 7 samples were collected for surface sample.

At the 7 stations, a total of 50 samples were collected for water column.

3.7.2.5 Problem occurred and solutions.

No problem occurred.

3.7.2.6 Sampling summary

Station#	Lat.	Long.	Sampling layer	Number of layers
64	22 30.00 N	149 20.00 E	Sur, 100-600,800,1000	9 layers
62	21 10.00 N	149 20.00 E	Sur, 100-600,800,1000	9 layers
60	19 50.00 N	149 20.00 E	Sur, 100-600,800,1000	9 layers
58	18 30.00 N	149 20.00 E	Sur, 100-600,800,1000	9 layers
56	17 10.00 N	149 20.00 E	Sur, 100-600,800	8 layers
54	15 50.00 N	149 20.00 E	Sur, 100-600	7 layers
52	14 30.00 N	149 20.00 E	Sur, 100-600	7 layers

3.7.3 C-13, N-15

Tomomi Takamura and Hisayuki Y. Inoue (not on board)

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(1) Objective

While the ocean is known as one of the major sinks for atmospheric CO₂, the magnitude of the oceanic CO₂ uptake is unclear. It is necessary to clarify how and to what extent the carbonate system in the ocean affects the atmospheric CO₂ concentration via the changes in air-sea CO₂ flux. The air-sea CO₂ flux is conventionally estimated by the products of the gas transfer velocity, solubility of CO₂, and the difference in partial pressure of CO₂ in surface seawater (pCO_{2sw}) and that in overlying air (pCO_{2air}). The pCO_{2sw} is changed by the following factors: biological activities, the ocean dynamics (lateral transport, vertical mixing) and thermodynamic effects derived from changes in surface sea temperature and salinity. In the western North Pacific Subtropical Gyre (NPSG), the pCO_{2sw} variations were mostly caused by the change in DIC as well as the effect of thermodynamics. But the contribution of biological activities and the ocean dynamics to the DIC change is still unclear.

In this cruise, we collect water samples for measurements of $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) and $\delta^{15}\text{N}$ of suspended particulate nitrogen. The objective of these collections of samples is to describe the oceanic CO₂ system in the western North Pacific and clarify the effect of biological activities to CO₂ system in this region.

(2) Sampling and Methods

(a) $\delta^{13}\text{C}$ of DIC:

Seawater samples for analysis of $\delta^{13}\text{C}$ of DIC were taken from Niskin bottles on CTD/carousel sampler at the total of 23 hydrographic stations (~2000m). Seawater samples were collected in 100 ml glass bottles with butyl gum cap and sealed by aluminum cap. The samples were poisoned with 100 μl of saturated mercuric chloride solution and preserve at room temperature.

(b) $\delta^{15}\text{N}$ of suspended particulate nitrogen

For measurements of $\delta^{15}\text{N}$ of suspended particulate nitrogen, surface seawater sample was taken by using a bucket from broadside. In order to isolate the suspended particulate matter, about 20 liters of water were filtered through pre-combusted (450°C, 4 hours) GF/F filters (Whatman; 47 mm diameter). Filters are stored in a refrigerator (<-20°C) until isotopic analysis will be made.

(3) Results

Measurements of $\delta^{13}\text{C}$ of DIC and $\delta^{15}\text{N}$ of suspended particulate nitrogen will be made at the laboratory in Hokkaido University in the near future.

3.7.4 Distribution of diazotrophs, its rate of nitrogen fixation, and nutrients

(This observation was not done in the EEZ and TW of Papua New Guinea)

Satoshi Kitajima and Ken Furuya

Department of Aquatic Bioscience, Graduate School of Agricultural and Life Sciences

University of Tokyo

(1) Objective

Cyanobacteria are taxonomically, physiologically and ecologically diverse, and dominant phytoplankters in the subtropical and tropical ocean. Spatial distribution of planktonic cyanobacteria has been well studied in the western subtropical and tropical Pacific Ocean, and their importance in nitrogen fixation is repeatedly emphasized. Particularly, some new diazotrophs, such as unicellular cyanobacteria or proteobacteria have been found in the subtropical and tropical ocean. Our results obtained during MR04-07 suggested importance of these unicellular diazotrophs. Nitrogen fixation is controlled by environmental factors such as availability of nutrients. In this cruise, we examined the correlation between nitrogen fixation rates, nutrients, and phytoplankton assemblages.

(2) Sampling and Methods

For measurement of nitrogen fixation rate, 1800 mL of seawater were collected by a bucket at the surface layer of stations between 37 to 3° N. The seawater was poured into three or five - 1200 mL PET bottle, then placed in an on-deck incubator under natural sunlight with running near surface water pumped up from 5 m depth. Samples were spiked with 10% acetylene and return to the incubator. Subsampling was done at 0 (initial) and 24 hours after the acetylene addition to measure ethylene production using a gas chromatograph (GC-17A, Shimadzu). The ethylene production was converted to an amount of fixed nitrogen with a ratio of C₂H₂: N₂ = 1:4. After the sampling, seawater left in the vial was fixed for later microscopic observation. Nitrogen fixation by *Trichodesmium*, and *R. intracellularis* collected with horizontal hauls of a plankton net were also measured at selected stations.

Along with the nitrogen fixation rate measurements, following determination and sample preparation were made; flow cytometric count of *Synechococcus*, and *Prochlorococcus*, chlorophyll *a*, algal pigments by HPLC, microscopic observation of *Trichodesmium*, *R. intracellularis* associated with diatoms, unicellular cyanobacteria. Chlorophyll *a* and nitrogen fixation rate has already measured on board.

(3) Future Works

Samples and specimens prepared during the cruise will be analyzed and examined. Following determinations will be on land: flow cytometric analysis fixed with 1% glutaraldehyde, pigments analysis prepared by a gentle filtration (< 18 mmHg) of particles on GF/F filters, nutrients analysis. These samples were immediately frozen and transferred to land laboratory. Samples taken with plankton net and fixed seawater samples will be also brought back to land laboratory to make further study.

3.8 LADCP(Lowered Acoustic Doppler Current Profiler)

Shinya Kouketsu (JAMSTEC)

Yasushi Yoshikawa (JAMSTEC)

3.8.1 Instrument and method

Direct flow measurement from sea surface to the bottom was carried out using a lowered acoustic Doppler current profiler (LADCP). The instrument used was the RDI Workhorse Monitor 307.2kHz unit (RD Instruments, USA). The instrument was attached on the CTD/RMS frame, orientating downward. The CPU firmware version was 16.05. The firmware was updated at station P10-002 to version 16.27.

One ping raw data were recorded. Settings for the collecting data are listed in Table 3.8.1. A total of 128 operations were made with the CTD observations. The performance of the LADCP instrument was good in northern stations (in the subarctic region of North Pacific). Profiles were obtained over 100m distance from LADCP in shallow depth and almost 60m in deeper depth. On the other hand in southern stations (in the subtropical region of North Pacific) the performance was bad. In the deeper depth, good quality data were obtained only 3 or 4 bins, which means the LADCP could observe only about 25m. It would due to a weak echo intensity, which agreed with ship's ADCP. Data transfer errors were often occurred during upload process from the LADCP to PC.

Table 3.8.1

Station	143-50, 48,47	49	46	45	44,X04	42-
Bin length	8m	8m	12m	12m	12m	16m
Bin number	24	20	16	20	16	10
Standard deviation	2cm/s	2cm/s	1.6cm/s	1.6cm/s	1.6cm/s	1.4cm/s
Ping interval	1.2sec	1sec	1.2sec	1.2sec	1.2sec	1sec
Percent Good	Collect	Collect	Collect	Collect	Not collect	Not collect

3.8.2 Preliminary results

Vertical profiles of velocity field are obtained by integrating vertical velocity shears from the surface to the bottom. The detailed method is described in Fischer and Visbeck (1993). In the integration of upcasts, the first bin data from the LADCP are not used because the data were greatly influenced by the turbulent velocity by the CTD frame. The GPS navigation data are used

in the calculation of the reference velocities and the bottom-track data are used for the correction of the reference velocities. Shipboard ADCP data are not included in the calculation. At this stage the CTD data are used for the sound speed and depth calculation. Figure 3.8.1 and 3.8.2 show the results of the cross-section velocity in the subarctic North Pacific (eastward is positive) and the eastward velocity in equatorial zone, where the difference between the upcast and downcast velocity profiles are not so large. The major currents in the Western Pacific such as the Kuroshio Extension (P10N-116-114), the Equatorial Under Current (around P10-18), and New Guinea Coastal Under Current (P10-002) appeared in the figures. These currents also appeared in the ship-board ADCP current fields. But, in the subtropical region, the difference between the upcast and downcast velocity profiles is so much large. It is probably due to the short range of the LADCP signal, which makes the shears suspicious. In the estimation of the velocity from LADCP data, it is the biggest problem that there is less information of the CTD frame motion, which is only determined from bottom track data and GPS data.

After this cruise, we will re-estimate the velocity profiles by the inversion method described in Visbeck (2002). The reliability of the LADCP velocities will be considered comparing with the velocity profiles from ship-board ADCP and the velocity shears by the hydrographical data. We tested setting bins to 16m long in the tropical region. By this setting referred in Visbeck (2002), we will investigate whether the reliable velocity profile can be obtained in the subtropical region.

Reference

Fischer, J., and M. Visbeck (1993): Deep velocity profiling with self-contained ADCPs., *J. Atmos. Oceanic Technol.*, 10, 764-773.

Visbeck, M. (2002): Deep velocity profiling using Lowered Acoustic Doppler Current Profilers: Bottom track and inverse solutions. *J. Atmos. Oceanic Technol.*, 19, 794-807.

Figure 3.8.1

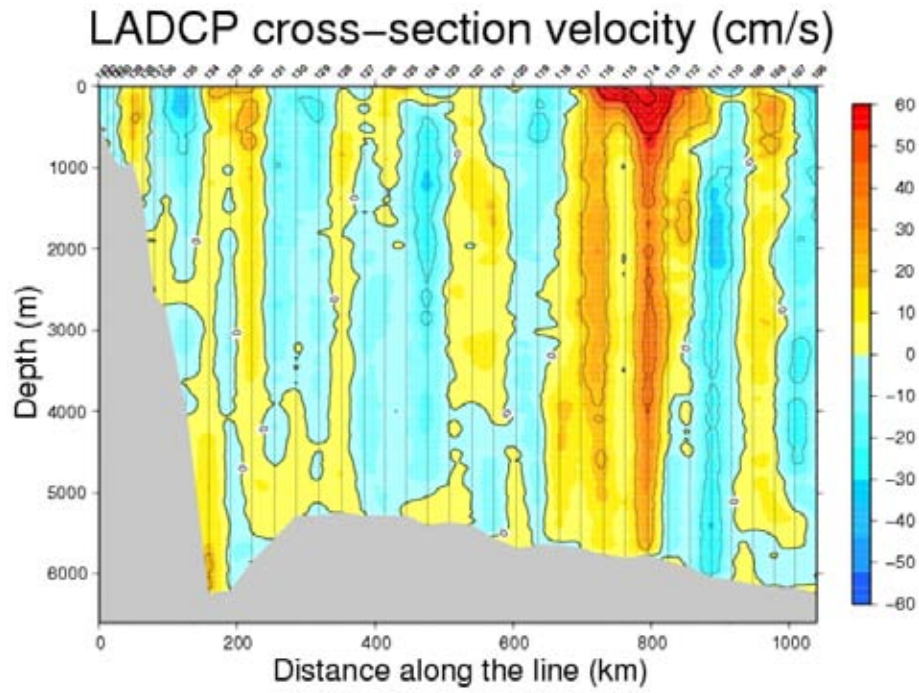


Figure 3.8.2

