

MR03-K04 Leg 2
Papeete (Tahiti)- Valparaiso (Chile)
September 6th - October 16th, 2003

Preliminary
Cruise Report

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1. Cruise Narrative

1.1 Highlights

Cruise Summary Information

WOCE line designation	P06C and P06E
Expedition designation	MR03-K01 leg 2
Chief scientist and affiliation	Shuichi Watanabe/JAMSTEC *
Ship	Mirai
Cruise dates	2003.Sept.09 to 2003.Oct.16
Ports of call Casey	Tahiti to Valparaiso
Number of stations	116 CTD/rosette
Geographic boundaries	149° 49.49' W to 71° 29.94' W 32° 40.03' S to 32° 10.17' S
Floats and drifters deployed	19 ALGO floats
Moorings deployed or recovered moorings	none

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1.2 Cruise summary

1.2.1 Geographic boundaries:

MR03-K04 Leg 2 occupied stations along 32°30' S from 149°50' W to 71°30' W. Two stations, No. 125 and 127, was revisited to be compared with Leg 1.

1.2.2 Stations occupied:

Leg2: 118 CTD/rosette. A track line of MR03-K04 Leg 2 is shown in Figure 1.2.1. The bottle depth diagram is shown in Figure 1.2.2.

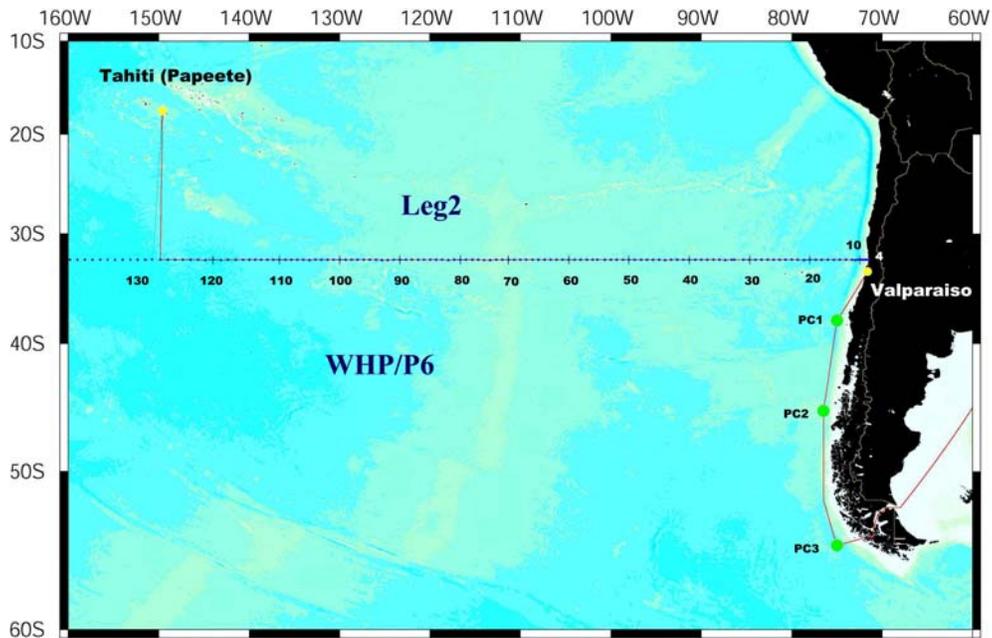


Figure 1.2.1 A track line of MR03-K04 Leg 2

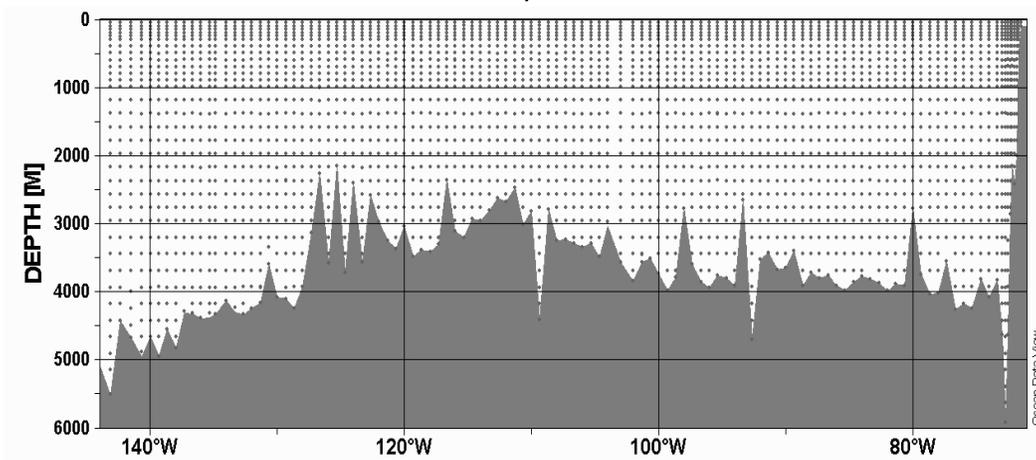


Figure 1.2.2 The bottle depth diagram of MR03-K04 Leg 2

1.2.3 Items and stations:

Seawater samples for analyzing salinity, dissolved oxygen and nutrients were collected at all CTD stations. CFCs, total carbon, alkalinity were determined at 59 stations named C-station. Samples for total organic carbon, radiocarbon, Ar/N₂, N₂O and chlorophyll-a took from the selected C stations. He samples were obtained at only 4 stations. Detail sample information and locations are listed up in the sum-file.

1.2.4 Floats and drifters deployed:

Nineteen ARGO floats, which were conducted by JAMSTEC and SIO, were launched along section P6 in this leg. Launched positions of their ARGO floats were listed in Table 4.1 in the chapter 4: Argo float.

1.2.5 Moorings deployed or recovered:

No mooring was deployed or recovered during this cruise.

1.3 List of PI and Person in charge on the ship (Table 1.3.1)

Chief Scientist : Shuichi Watanabe

Chief Technologist : Hideki Yamamoto

Item	Principal Scientists	Person in Charge on the Ship
Hydrography		
CTD-DO	Hiroshi Uchida Masao Fukasawa	Hiroshi Matsunaga Hiroshi Uchida
LADCP	Yasushi Yoshikawa	Hiroshi Matsunaga
BTL Salinity	Takeshi Kawano	Takeo Matsumoto
BTL Oxygen	Shuichi Watanabe	Tomoko Miyashita
Nutrients	Michio Aoyama	Ken-ichiro Sato
DIC	Akihiko Murata	Mikio Kitada
Alkalinity	Akihiko Murata	Taeko Ohama
pH	Akihiko Murata	Masaki Moro
CFCs	Yutaka Watanabe	Masahide Wakita
$\Delta^{14}\text{C}$, $\delta^{13}\text{C}$	Yuichiro Kumamoto	Same as PI (collection only)
TOC	Akihiko Murata	Same as PI (collection only)
$^3\text{He}/^4\text{He}$	Shuichi Watanabe	S. Watanabe(collection only)
Cs,Pu, ^3H ,Sr	Michio Aoyama	A. Takeuchi (collection only)
Ar/N ₂	Yutaka Watanabe	S. Tanaka (collection only)
N ₂ O	Laura Farias	Mauricio Gallegos
Primary Productivity	Gadiel Alarcon	Gadiel Alarcon
Chlorophyll-a	Gadiel Alarcon	Gadiel Alarcon
Underway		
ADCP	Yasushi Yoshikawa	Satoshi Okumura
Bathymetry	Sou-ichiro Sueyoshi	Satoshi Okumura
Meteorology	Kunio Yoneyama	Satoshi Okumura
Thermo-Salino.	Masao Fukasawa	Tomoko Miyashita
pCO ₂	Akihiko Murata	Mikio Kitada
pN ₂ O	Laura Farias	Mauricio Gallegos
Fluorescence	Gadiel Alarcon	Tomoko Miyashita
Argo float	Kensuke Takeuchi Dean Roemmich	Takeo Matsumoto Masao Fukasawa

1.4 Scientific Programme and Methods

1.4.1 Nature and objectives of MR03-K04 cruise project

It has been a decade since WOCE (World Ocean Circulation Experiment under WCRP) Hydrographic Program (WHP) was carried out in the world ocean. Not only accurate hydrographic sections but also mass transports and their divergence/convergence have been clarified on a basin scale. On the other hand, skills of measurements, especially those for carbon and CFC parameters, have been developed remarkably since the WOCE period. Thus, repeated land-to-land hydrography is recommended by CLIVAR and JGOFS strongly. At the same time, the repeated hydrography or WHP revisit is desirable to investigate long term changes in inventories of heat, water mass, materials and their transports; in fact, revisit of a WHP line in the North Pacific found a bottom water warming, which can be attributed to changes in the water column in the southern ocean. The magnitude of the warming was significant along its path way although very small.

Ocean Observation and Research Department of JAMSTEC plans to revisit WHP lines in the Southern Hemisphere as one of research actions of their project TAV-PI (Transport And Variability in the Pacific and the Indian) to detect long term changes in the hydrographic structure and the Antarctic overturn by surveying WHP lines in the Pacific, the Atlantic and the Indian at one cruise. This Southern Hemispheric circum navigation was highlighted at POGO-3 (December, 2001) as a following-up of the Sao Paulo Declaration of POGO-2 (January, 2001) that encourages and promotes both oceanographic studies and scientific capacity building in the Southern Hemisphere.

The main purpose of Leg2 of this research cruise is to detect and quantify temporal changes in the Antarctic overturn System corresponding to the global ocean and the Southern Ocean warming during the last decade through high quality and spatially dense observation along old WHP (WOCE Hydrographic Program: 1991-2002) lines. Scientific priorities, which lead to the above interest, are (1) changes in inventories of heat and freshwater, (2) changes in production rate, mass and pathway, (3) carbon and nutrients transport, (4) data base for model validation, and (5) ARGO sensor calibration.

The other purposes of this cruise are (1) to observe surface meteorological and hydrological parameters as a basic dataset of the meteorology and oceanography, (2) to launch ARGO floats in order to monitor the changes of sub-surface temperature and salinity, (3) to observe global warming gas distribution, (4) to observe sea bottom topography, gravity and magnetic fields along the cruise track in order to understand the dynamics of ocean plate and the accompanying geophysical activities, (5) to obtain data on global distribution and optical characteristics of aerosols and clouds for the climatology and for study of the feasibility of the satellite observations, (6) to construct a model to predict a primary production from satellite observation and (7) to observe concentration of cloud droplets for verification of satellite observation.

1.4.2 Leg 2 Overview

R/V Mirai cruise MR03-K04 Leg 2 is the re-visiting observation cruise in the eastern side of the transpacific WOCE Hydrographic Program section P6. That in the western side was observed in the previous cruise. The previous segment in the MR03-K04 leg 1 obtained measurements along latitude 32° 30'S between Australia coast and the west side of longitude 144°W. This leg's segment was planned to occupy measurements from the east side of 144°W to Chilean coast.

The sampling plan for this leg was made to obtain measurement at the 1990s WOCE hydrographic observation stations. Two stations, P06C125 and P06C127, were selected from those observed in the MR03-K04 Leg 1 to be compared with first leg data. A total of 116 stations included two comparison stations was occupied. Casts were to be done using 36-position, 10 liter Niskin bottles carousel system and SBE CTD-DO system attached LADCP. Water samples were obtained from fixed depth shallower bottom. The fixed depth layers were 10, 50, 100, 150, 200, 150, 200, 250, 300, 400, 500, 600, 700, 800, 900, 1000, 1200, 1400, 1600, 1800, 2000, 2200, 2400, 2600, 2800, 3000, 3250, 3500, 3750, 4000, 4250, 4500, 4750, 5000, 5250, 5500, 5750m and about 10m upper bottom. JAMSTEC scientists and MWJ (Marine Work Japan Co. Ltd.) technician Group was responsible for analyzing water sample for salinity, dissolved oxygen, nutrients, CFCs, total carbon contents, alkalinity and pH. They also contributed sampling for total organic carbon, radiocarbon and He. A student of Hokkaido University joined CFCs measurement. A technician in KANSO Co. Ltd collected sea water for radionuclide and took part in other sampling. Professor, students and technicians in University of Concepcion, POGO trainees who come from Peru, Colombia and Turkey participated in this cruise and contributed water sampling and/or operation of CTD system. POGO group also analyzed Chlorophyll-a contents and bioactivity in seawater. A part of Chilean group brought p N₂O system and collected seawater samples for N₂O analysis.

GODI (Global Ocean Development Inc.) technicians group undertook responsibility for underway ocean velocity

measurements using an Acoustic Current Profiler (ADCP), geological measurements (topography, geo-magnetic field and gravity), and collecting meteorological data. Finally, ARGO floats prepared by JAMSTEC and SIO were launched by MWJ technicians and ship crew.

Cruise Personnel

This investigate team was organized by JAMSTEC scientists, its research fellows, technicians from MWJ, GODI, KANSO and University of Concepcion, students from universities in Japan and Chile, and POGO trainees. Program leader of this cruise program, Dr. M. Fukasawa, also participated in this cruise and controlled CTD data and others. Staffs of JAMSTEC supported on land to predict weather.

Dr. M. Aoyama, JMA, was calibrated nutrient concentrations. Dr. Shubha let POGO trainees to get on board to learn how to measure biological activities. Member of University of Concepcion in Chile joined to measure pN_2O , to control CTD system, and to teach POGO trainees.

Cruise Narrative

R/V Mirai arrived at Papeete, Tahiti on 5th September after finishing MR03-K04 Leg 1 observation. Several scientists, Drs. Fukasawa, Murata, Kumamoto, Mr. Takeuchi, and Mr. Tanaka stayed onboard to join this leg. Other scientists and technicians took a ship on 7th or 8th Sept. Chilean participants and POGO trainees embarked on leaving day. During a short stay in Tahiti, this cruise member succeeded the procedure of previous cruise from participants of leg 1.

R/V Mirai left from Tahiti on 9th morning to go to observed area. The observation was started on 12th September (GMT) at P06C127 station, that is one to be compared with data obtained in Leg 1.

CTD system had communication trouble between systems under water and sensors. DO sensor was also replaced on the way of this leg. Instruments for analysis of chemical components without CFCs analyzing system was almost well working during this leg. One of CFCs instruments was working after half of way.

The first station, P06C119, during this leg was done on 13th (GMT). CTD observations in 116 stations were done during 31 days included no observation days (3days). R/V Mirai entered to Chilean EEZ area on 4th October (GMT). After finished CTD cast, summarized data and preparing for next cruise were carried out. R/V Mirai arrived at Valparaiso, Chile on 16th Oct.

During cruise, we had communication with land using e-mail, Fax and telephone. Effort of researchers on land, especially Dr. Aoyama, was helpful and useful. Finally, the effort of R/V Mirai's officers and crew are to be commended. I also thank everyone in the science party had good works.

Summary of observations

A total of 116 CTD stations were obtained on this leg, 114 stations contributing to the pone-time P6 section revisit. Two stations were selected to be compared with first leg. SBE CTD-DO system attached LADCP was used during cruise. Approximately 3,500 seawater samples were collected along this section. All seawater samples were analyzed for salinity, dissolved oxygen and nutrient (nitrate, nitrite, phosphate, silica) concentrations. Nutrients were calibrated with seawater standards made by KANSO which are under the international comparison conducted by Dr. Aoyama (JMA). Dissolved oxygen was determined using KIMOTO titrator that developed for this programme. This instrument had small trouble. However, high quality value was obtained during this cruise.

The dissolved chlorofluorocarbons (CFCs) measurements along this leg were carried out by Dr. S. Watanabe (JAMSTEC), M. Wakita (JAMSTEC), Mr. Tanaka (Hokkaido Univ.), H. Yamamoto (MWJ) and Y. Sonoyama (MWJ) using two JAMSTEC analytical systems modified the SIO system. Approximately 1,400 samples from 59 stations were analyzed for CFC-11, 12 and 113. Duplicate samples were obtained from 10 liter Niskin bottle of 250 and 1000 m depths at each station. Two analytical systems were not under the good condition. These precisions were more than 1%. Some small peaks around CFC-11 were not removed. The values obtained on board have to recalculate to remove the effect from small peaks.

Seawater samples for CO_2 species were collected from 59 stations. These water samples were analyzed for total carbon dioxide (TCO_2), alkalinity and pH by Dr. A. Murata (JAMSTEC) and his colleagues. The TCO_2 and alkalinity analysis were made on the automated system modified by Dr. Murata. These analytical methods were based on DOE Handbook written by Dickson and Goyet. These values were calibrated with CRM made by SIO. The pH was analyzed with photometric method using pH dye.

Surface sweater underway observations were carried out using pCO_2 measurement system and the SEACAT thermosalinograph. The pCO_2 measurement in surface seawater and the atmosphere were operated with Dr. Murata and his colleagues. Precision of pCO_2 in surface seawater was about 2 ppm. Surface seawater for calibration of thermosalinograph was collected with a bucket.

Samples for total organic carbon (TOC), C-14, Ar/N₂ and radionuclide were collected from selected stations (TOC: 28 stations, C-14: 27 stations, Ar/N₂: 15 stations, radionuclide: 28 stations). TOC and C-14 will be analyzed by JAMSTEC. Ar/N₂ will be measured by Dr. Y. Watanabe (Hokkaido Univ.). Radionuclide analysis is a co-operated work between Dr. Aoyama (JMA) and IAEA.

ADCP (VM-75, RD Inst., Inc.), meteorology and ship navigation data were collected by GODI technician (S. Okumura, W. Tokunaga and R. Kimura). The bottom topographical data were obtained using a multi narrow beam echo sounding system. Geographic measurement (gravity and three component geo-magnetic field vectors) were carried out along P06 section.

A total of 19 ALGO floats prepared by JAMSTEC and SIO was launched at the stations along P06 section. Data files containing the preliminary hydrographic observations were shared among the cruise participants at the completion of the cruise. Observed data inside the Chilean jurisdictional water was delivered to the Navy Hydrographic and Oceanographic Service through the national observer.

1.5 Major Problems and Goals not Achieved

An Instrument for measurement of CFCs didn't work during a half of this leg. Seawater samples for CFCs measurement could collect at the selected layers of C stations.

1.6 Other Incidents of Note

None.

1.7 List of Participants (Table 1.7.1)

Name	Responsibilities	Affiliation
Shuichi WATANABE	Chief Scientist CFCs, Helium isotopes	Japan Marine Science & Technology Center (JAMSTEC)
Masao FUKASAWA	Data Management, LADCP	JAMSTEC
Akihiko MURATA	Alkalinity, pH	JAMSTEC
Yuichiro KUMAMOTO	Bottle Oxygen, Water Sampling	JAMSTEC
Masahide WAKITA	CFCs	JAMSTEC
Hirofumi YAMAMOTO	Water sampling	JAMSTEC
Hiroshi UCHIDA	CTD operations	JAMSTEC
On SUGIMOTO	Water sampling	JAMSTEC
Akira TAKEUCHI	Radionuclides	Kansai Environment Engineering Center (KANSO)
Shinichi TANAKA	CFCs, Argon	Hokkaido Univ.
Jose Mauricio Gallegos Oieda	Nitrous Oxide	Regional Program of Physical Oceanographic and Climate
Susana Giglio Munoz	Observer (Chile)	Servicio Hidrografico y Oceanografico de la Armada de Chile
Wolfgang Schneider	CTD operations	Univ. of Concepcion
Rosalino del Carmen Fuenzalida Fuenzalida	Water sampling	Univ. of Concepcion
Victor Villagran	Elec. Engineer	Univ. of Concepcion
Gadiel Alarcon	Bio Optical	Univ. of Concepcion
Alexander Galan Mejia	Bio Optical	Univ. of Concepcion
Dante Benjamin Matellini	Bio Optical	Peruvian Marine Research Institute
Serkan Sancak	Bio Optical	Middle East Technical University
Miki YOSHIIKE	ARGO float, CTD operations	Marine Works Japan Ltd. (MWJ)
Yuki OTSUBO	Nutrients	MWJ
Masashi MORO	DIC	MWJ
Yuichi SONOYAMA	CFC	MWJ
Taeko OHAMA	Alkalinity, pH	MWJ
Ai YASUDA	Nutrients	MWJ
Tomoko MIYASHITA	Thermo-Salino, Bottle Oxygen	MWJ
Kenichiro SATO	Nutrients	MWJ
Mikio KITADA	DIC, pCO ₂	MWJ
Hideki YAMAMOTO	Data Management, LADCP, CFCs	MWJ
Noburaru KOMAI	Bottle Oxygen	MWJ
Kenichi KATAYAMA	ARGO float, Bottle Salinity	MWJ
Hiroshi MATSUNAGA	CTD operations	MWJ
Takeo MATSUMOTO	Bottle Salinity	MWJ
Keisuke MATSUMOTO	Water sampling	MWJ
Tokuya CHIHARA	Water sampling	MWJ
Tomomi WATANABE	Water sampling	MWJ
Satoshi OKUMURA	ADCP, Bathymetry, Meteorology	Global Ocean Development, Inc. (GODI)
Wataru TOKUNAGA	ADCP, Bathymetry, Meteorology	GODI
Ryo KIMURA	ADCP, Bathymetry, Meteorology	GODI

2. Underway Measurements

2.1 Navigation and Bathymetry

Satoshi Okumora (GODI)
Wataru Tokunaga (GODI)
Ryo Kimura (GODI)

Navigation

Ship's position and velocity was provided from Radio Navigation System to some equipment that required fixed position throughout the cruise. This system integrates GPS position data (from Leica MX9400N GPS receiver), log speed (from Furuno DS-300, Doppler sonar), gyro heading (from Tokimec TG-6000, ship's main gyrocompass) and other basic data for navigation, and calculate and distribute speed over ground and course over ground. These data were logged on network server as "SOJ" data every 1-minute. To keep the system clock correct, SUN workstation operating this system synchronized to GPS time-server, Datum Tymserv2100, frequently.

The differential GPS system, THALES Geosolutions SkyFix, has also installed, but we had few chances to use this system because it needs reference stations within 2,000 km from the ship, so that differential corrections became available just before the end of this cruise. Two antennas for Leica GPS receiver located on the navigation deck, offset to starboard and portside, respectively. We switched them to choose better state of receiving when the number of satellites decreased or HDOP increased. But the system sometimes lost the position while the receiving status became worth. The periods of losing the position are described in "Readme" file attached to SOJ data.

Swath Bathymetry

Continuous survey of swath bathymetry was performed along ship's track during MR03-K04 Leg2 Cruise. The multi-beam system equipped on R/V Mirai is SeaBeam 2112, that has max 150 degrees swath and 1 degree receiving beam spacing athwart ship operating at 12 kHz. The depth range of the system 100 m to 11,000 m, and its accuracy is within 0.5 % of depth, especially greater for nadir beam is from within 0.2 % of depth. Data interval along ship's track was max 16 seconds at 6,000 m.

For primary data quality management, applying proper sound velocity profile is the most important. Sound velocity profiles were calculated using temperature and salinity data of the proximate CTD cast by the equation in Mackenzie (1981). Variations of sound velocity at transducer face have a large influence on depth, especially side beams, so that this system has Surface Sound Velocimeter, which measuring sound velocity in the surface intake water continuously. Obvious bad data was flagged automatically by real-time data screening function of the system.

Post-processing will advance in following steps,

- Checking the navigation data to identify outliers and interpolate over them.
- Recalculating all data with sound velocity profile from immediate CTD station.
- Checking the bathymetry data to identify and flag of anomalous beams.
- Quality controlled bathymetry data will be converted to grid data in netCDF format as a final product.

2.2 Acoustic Doppler Current Profiler (ADCP)

Satoshi Okumora (GODI)
Wataru Tokunaga (GODI)
Ryo Kimura (GODI)

Continuous upper ocean current measurement along ship's track were made using hull-mounted Acoustic Doppler Current Profiler, RD Instruments VM-75 system installed on the centerline and approximately 28 m aft from the bow. The firmware version was 5.59 and the data acquisition software was VmDas Ver.1.3. For most of its operation, the instrument was configured for water-tracking mode recording each ping as the raw data in 8 m x 100 bins from 16.4 m to 816.4 m. Bottom-tracking mode, interleaved bottom-ping with water-ping, was made in shallower water region between last two CTD stations to get the calibration data for evaluating transducer misalignment angle. Raw data was recorded in beam coordinate, and then converted to earth coordinate using ship's heading data from ship's main gyrocompass, Tokimec TG-6000. The position fix data from ship's navigation system was also recorded in NMEA0183 format and merged with ensemble data in the VmDas. Additional heading data, measured by Inertial Navigation Unit, was also recorded for post-processing. Its accuracy is within 1.0 mil, about 0.056 degree and had already set on zero bias.

The system performed well throughout the cruise. The profile range while steaming exceeded 500 m, sometimes reached 600 m under calm weather. But the rough sea condition made this range shorter, less than 300 m. Bubbles from bow-thruster obstructed the beam and also made this range shorter on CTD station.

ADCP data will process following steps,

1. Estimating transducer misalignment and current magnitude scale factor from bottom tracking data and applying them to all data. Heading data from INU and ship's roll/pitch data will be used in the estimation.
2. Screening and editing bad profile.

Roughly estimated on board, misalignment error and scale factor value were as follows;

Transducer misalignment error vs. ship's main Gyro = 1.06 deg

Scale factor: Bottom track magnitude/Delta nav position = 1.03

This means that current speed should reduce about 3% from detected by ADCP during this cruise. These estimation was made using bottom track data obtained between Stn. 5 and Stn. 4. Data quality of heading were not good because the INU data had not been merged with gyro data.

2.3 Thermo-Salino Meter

Tomoko Miyashita (MWJ)
Nobuharu Komai (MWJ)
Masao FUKASAWA (JAMSTEC)

2.3.1 Objective

To measure salinity, temperature, dissolved oxygen, and fluorescence of near-sea surface water.

2.3.2 Methods

Surface sea water monitoring system (Nippon Kaiyo co.,Ltd.) has five kind of sensors and fluorescence photometer. Salinity, temperature, dissolved oxygen, fluorescence and particle size of plankton near surface sea water are continuously measured every 1-minute. This system is set up in the “*sea surface monitoring laboratory*” on R/V Mirai. This system is connected to shipboard LAN-system. Measured data are stored in a hard disk of PC machine every 1-minute together with time and position of ship, and displayed in the data management PC machine.

Surface sea water is continuously pumped up to the laboratory and flowed into the system. The flow rate is controlled 12L/min except with fluorometer (about 0.3L/min). The flow rate is measured with two flow meters and each values were checked everyday.

Specification of the each sensor in this system is listed below.

a) Temperature and Salinity sensor

SEACAT THERMOSALINOGRAPH

Model: SBE-21, SEA-BIRD ELECTRONICS, INC.

Serial number: 2118859-2641

Measurement range: Temperature -5 to +35 , Salinity 0 to 6.5 S m⁻¹

Accuracy: Temperature 0.01 6month⁻¹, Salinity 0.001 S m⁻¹ month⁻¹

Resolution: Temperatures 0.001 , Salinity 0.0001 S m⁻¹

b) Bottom of ship thermometer

Model: SBE 3S, SEA-BIRD ELECTRONICS, INC.

Serial number: 032175

Measurement range: -5 to +35

Resolution: ± 0.001

Stability: 0.002 year⁻¹

c) Dissolved oxygen sensor

Model: 2127A, Orbisphere Laboratories Japan INC.

Serial number: 44733

Measurement range: 0 to 14 ppm

Accuracy: ± 1% at 5 of correction range

Stability: 1% month⁻¹

d) Fluorometer

Model: 10-AU-005, TURNER DESIGNS

Serial number: 5562 FRXX

Detection limit: 5 ppt or less for chlorophyll a

Stability: 0.5% month⁻¹ of full scale

e) Particle Size sensor

Model: P-05, Nippon Kaiyo LTD.

Serial number: P5024

Measurement range: 0.02681 mmt to 6.666 mm

Accuracy: ± 10% of range

Reproducibility: ± 5%

Stability: 5% week⁻¹

f) Flow meter

Model: EMARG2W, Aichi Watch Electronics LTD.
Serial number: 8672
Measurement range: 0 to 30 l min⁻¹
Accuracy: ± 1%
Stability: ± 1% day⁻¹

The monitoring Periods (UTC) during this cruise are listed below.
11-Sep.-'03 23:30 to 13-Oct.-'03 14:00

2.3.3 Preliminary Result

We sampled about three times every day for salinity sensor calibration. All salinity samples were collected from the course of the system while on station or from regions with weak horizontal gradients. All samples were analyzed on the Guildline 8400B. The results were shown in Table 2.3.1.

2.3.4 Data archive

The data were stored on a magnetic optical disk, which will be submitted to the Data Management Office (DMO) JAMSTEC, and will be opened to public via " R/V MIRAI Data Web Page " in JAMSTEC homepage.

Table.2.3.1 Comparison between salinity data from *Continuous Sea Surface Water Monitoring* and bottle salinity.

Date[UTC]	Time[UTC]	Salinity data	Bottle Salinity[PSS-78]
2003/9/12	0:04	35.4439	35.4388
2003/9/12	4:50	35.3963	35.3872
2003/9/12	13:57	35.4003	35.3969
2003/9/12	21:53	35.3118	35.3038
2003/9/13	5:50	35.4051	35.3944
2003/9/13	14:12	35.3712	35.3756
2003/9/13	21:49	35.3911	35.3844
2003/9/14	5:55	35.3108	35.3050
2003/9/14	13:57	35.3014	35.2981
2003/9/14	21:54	35.3744	35.3707
2003/9/15	6:06	35.2835	35.2799
2003/9/15	13:58	35.1876	35.1810
2003/9/15	21:51	35.1790	35.1674
2003/9/16	6:14	34.9382	34.9259
2003/9/16	12:41	35.0919	35.0850
2003/9/16	20:51	35.1629	35.1564
2003/9/17	4:51	35.0098	35.0148
2003/9/17	13:00	35.0033	34.9987
2003/9/17	20:51	35.0895	35.0844
2003/9/18	5:08	35.1236	35.0788
2003/9/18	13:04	35.1737	35.1689
2003/9/18	20:57	34.9896	34.9934
2003/9/19	5:05	35.1949	35.1894
2003/9/19	13:45	35.1500	35.1461
2003/9/19	20:49	34.9999	34.9976
2003/9/20	4:54	34.8266	34.8203
2003/9/20	12:04	35.0261	35.0190
2003/9/20	19:50	34.9281	34.9238
2003/9/21	15:52	35.1231	35.1174
2003/9/21	20:12	35.1562	35.1505
2003/9/22	12:01	34.7262	34.7236
2003/9/22	19:47	34.6572	34.6524
2003/9/23	3:54	34.5923	34.5870
2003/9/23	11:54	34.6121	34.6025
2003/9/23	19:44	34.7548	34.7495
2003/9/24	3:28	34.6148	34.5793
2003/9/24	11:52	34.6804	34.6772
2003/9/24	19:56	34.6641	34.7457
2003/9/25	3:24	35.1447	35.1417

Table 2.3.1 (continued)

Date[UTC]	Time[UTC]	Salinity data	Bottle Salinity[PSS-78]
2003/9/25	11:54	34.9619	34.9601
2003/9/25	19:53	34.7201	34.7183
2003/9/26	3:47	34.8324	34.8302
2003/9/26	11:52	34.5981	34.5895
2003/9/26	19:51	34.6506	34.6458
2003/9/27	3:29	34.7590	34.7481
2003/9/27	10:46	34.5932	34.5780
2003/9/27	18:53	34.7409	34.7540
2003/9/28	2:42	34.5840	34.5791
2003/9/28	10:54	34.2848	34.2899
2003/9/28	18:54	34.3686	34.3644
2003/9/29	3:09	34.4975	34.4959
2003/9/29	10:58	34.8530	34.8501
2003/9/29	18:57	34.8608	34.8580
2003/9/30	14:52	34.8546	34.8509
2003/9/30	18:50	34.7904	34.7903
2003/10/1	2:39	34.6251	34.6164
2003/10/1	10:54	34.8408	34.8399
2003/10/1	18:53	34.8261	34.8265
2003/10/2	2:10	34.6571	34.6547
2003/10/2	10:53	34.9884	34.9745
2003/10/2	18:54	34.4697	34.4692
2003/10/3	2:50	34.2944	34.2984
2003/10/3	10:00	34.2395	34.2355
2003/10/3	17:48	34.2884	34.2893
2003/10/4	1:11	34.3806	34.3789
2003/10/4	9:55	34.4391	34.4373
2003/10/4	17:50	34.4851	34.4850
2003/10/5	2:00	34.2875	34.2835
2003/10/5	10:01	34.3031	34.3025
2003/10/5	17:50	34.4102	34.4096
2003/10/6	1:27	34.4638	34.4738
2003/10/6	9:56	34.5224	34.5197
2003/10/6	17:49	34.5731	34.5723
2003/10/7	0:34	34.4679	34.4655
2003/10/7	10:11	34.4325	34.4312
2003/10/7	17:50	34.4260	34.4274
2003/10/8	12:54	34.4017	34.4126

Table 2.3.1 (continued)

Date[UTC]	Time[UTC]	Salinity data	Bottle Salinity[PSS-78]
2003/10/8	17:06	34.4433	34.4455
2003/10/9	0:04	34.2978	34.3073
2003/10/9	8:49	34.3004	34.2992
2003/10/9	16:55	34.2764	34.2782
2003/10/10	0:27	34.1796	34.1775
2003/10/10	8:56	34.1458	34.1464
2003/10/10	16:50	34.2664	34.2686
2003/10/11	0:11	34.2401	34.2395
2003/10/11	8:58	34.2382	34.2358
2003/10/11	16:49	34.2659	34.2650
2003/10/11	23:26	34.6082	34.6093

2. 4 pCO₂

Akihiko Murata (JAMSTEC)
Mikio Kitada (MWJ)
Masaki Moro (MWJ)

2.4.1 Objective

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 are aimed at quantifying how much anthropogenic CO₂ absorbed in the surface ocean in the Southern Hemisphere, where data for CO₂ are sparse. For the purpose, we measured pCO₂ (partial pressure of CO₂) in the atmosphere and surface seawater.

2.4.2 Apparatus and performance

Concentrations of CO₂ in the atmosphere and the sea surface were measured continuously during the cruise using an automated system with a non-dispersive infrared (NDIR) analyzer (BINOSTM). The automated system was operated by on one and a half hour cycle. In one cycle, standard gasses, marine air and an air in a headspace of an equilibrator were analyzed subsequently. The concentrations of the standard gas were 270.09, 328.86, 359.10 and 409.22 ppm. The standard gases will be recalibrated after the cruise.

The marine air taken from the bow was introduced into the NDIR by passing through a mass flow controller which controlled the air flow rate at about 0.5 L/min, a cooling unit, a perma-pure dryer (GL Sciences Inc.) and a desiccant holder containing Mg(ClO₄)₂.

A fixed volume of the marine air taken from the bow was equilibrated with a stream of seawater that flowed at a rate of 5-6L/min in the equilibrator. The air in the equilibrator was circulated with a pump at 0.7-0.8L/min in a closed loop passing through two cooling units, a perma-pure dryer (GL Science Inc.) and a desiccant holder containing Mg(ClO₄)₂.

2.4.3 Results

Concentrations of CO₂ (xCO₂) of marine air and surface seawater are shown in Fig. 2.4.1. From this figure, it is found that the area acted as a sink for atmospheric CO₂, except for the eastern end.

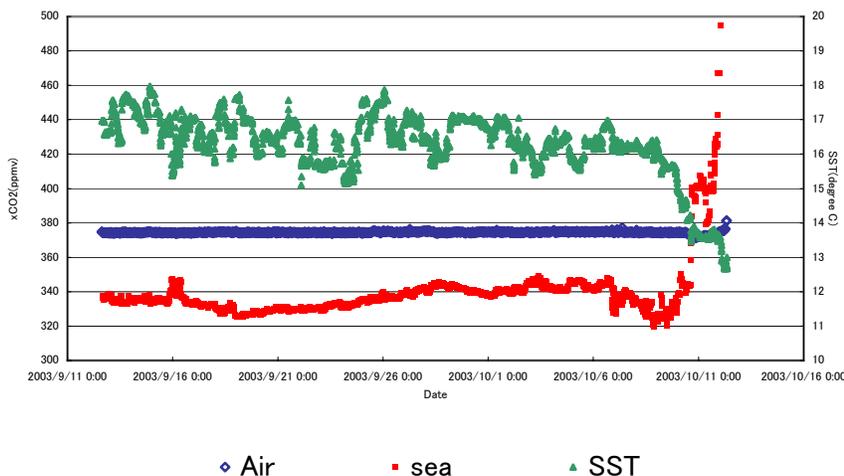


Figure 2.4.1. Concentrations of CO₂ (xCO₂) in atmosphere and surface

2.5 Meteorological observation

Satoshi Okumora (GODI)
Wataru Tokunaga (GODI)
Ryo Kimura (GODI)

2.5.1 Objective

The surface meteorological parameters are observed as a basic dataset of the meteorology. Accurate and continuous measurements are crucial to understand the air-sea interaction quantitatively. These parameters are used to study the temporal and spatial distribution of the exchange of heat, momentum, and radiation through the sea surface. These parameters were observed throughout the MR03-K04 Leg2 cruise from the 32-30S, 150-00W, 12 September 2003 to 32-30S, 71-30W, 12 October 2003.

2.5.2 Apparatus and Performance

R/V MIRAI had two systems for the surface meteorological observation. At this cruise, we used both systems.

- (1) MIRAI Surface Meteorological observation (SMet) system
- (2) Shipboard Oceanographic and Atmospheric Radiation (SOAR) system

(1)MIRAI Surface Meteorological observation (SMet) system

SMet is basic meteorological observation system designed by Koshin-Denki, Japan. Data was collected and processed by KOAC-7800 (Koshin-Denki).

Sensor	Type, Manufacturer	Location(altitude from surface)
Anemometer	KE-500, Koshin-Denki	foremast (24m) aftmast (37m)
Thermometer (sea water)	RFN1-0, Koshin-Denki	4th deck (-1m, inlet -5m)
Thermometer (air temperature and relative humidity)	HMP45A, VAISALA, Finland with 43408 Gill aspirated shield (R.M.Young, USA)	compass deck (21m)
Barometer	F-451, Yokogawa, Japan	weather observation room captain deck (13m)
Rain gauge	50202, R.M.Young	compass deck (19m)
Optical rain gauge	ORG-115DR, Osi, USA	compass deck (19m)
Radiometer		
Short wave	MS-801, Eiko-Seiki, Japan	radar mast (28m)
Long wave	MS-202, Eiko-Seiki	radar mast (28m)
Wave height meter	MW-2, Tsurumi-Seiki, Japan	bow (10m) portside quarter (8m)

(2)Shipboard Oceanographic and Atmospheric Radiation (SOAR) system

SOAR is designed by BNL (Brookhaven National Laboratory, USA), radiation measurement for the subject. Users are able to construct variability. MIRAI's SOAR consists of major 3 parts.

- i) Portable Radiation Package (PRP) system designed by BNL – short and long wave downward radiation.
- ii) Zeno meteorological system designed by BNL – wind, air temperature, relative humidity, pressure, and rainfall measurement.
- iii) Scientific Computer System (SCS) designed by NOAA (National Oceanic and Atmospheric Administration, USA)- centralized data acquisition and logging of all data sets.

Sensors	Type, Manufacturer	Location (altitude form surface)
i) PRP		
Radiometer		
	Short wave	PSP, Eppley labs, USA
	Long wave	PIR, Eppley labs
Fast rotating shadowband radiometer	Yankee, USA	foremast (25m)
ii) Zeno meteorological		
Anemometer	5106, R.M.Young	foremast (25m)
Thermometer (air temperature and relative humidity)	HMP45A, VAISALA, Finland with 43408 Gill aspirated shield (R.M.Young, USA)	compass deck (21m)
Barometer	61201, R.M.Young with 61002 Gill pressure (R.M.Young)	foremast (24m)
Rain gauge	50202, R.M.Young	foremast (24m)
Optical rain gauge	ORG-815DA, Osi, USA	foremast (24m)

2.5.3 Calibration

We have carried out inspecting and comparing about following three sensors, before and after the cruise.

- (1) Rain gauge (SMet and SOAR)
Inspecting the linearity of output value from the rain gauge sensor to change input value by adding fixed quantity of test water.
- (2) Barometer (SMet and SOAR)
Comparing with the portable barometer value, PTB220CASE, VAISALA.
- (3) Thermometer (air temperature and relative humidity) (SMet and SOAR)
Comparing with the portable thermometer value, HMP41/45, VAISALA.

2.5.4 Preliminary results

Original data are taken every 6 seconds for SMet and SOAR, during the cruise. Time series plots of basic surface meteorology every one minutes are shown in Figure 2.5.1. SST (Sea Surface Temperature) and SWH (Significant Wave Height) data form SMet, the others from SOAR.

2.5.5 Data archives

The raw data obtained during this cruise will be submitted to JAMSTEC Data Management Division. Corrected data sets will also be available from K. Yoneyama of JAMSTEC.

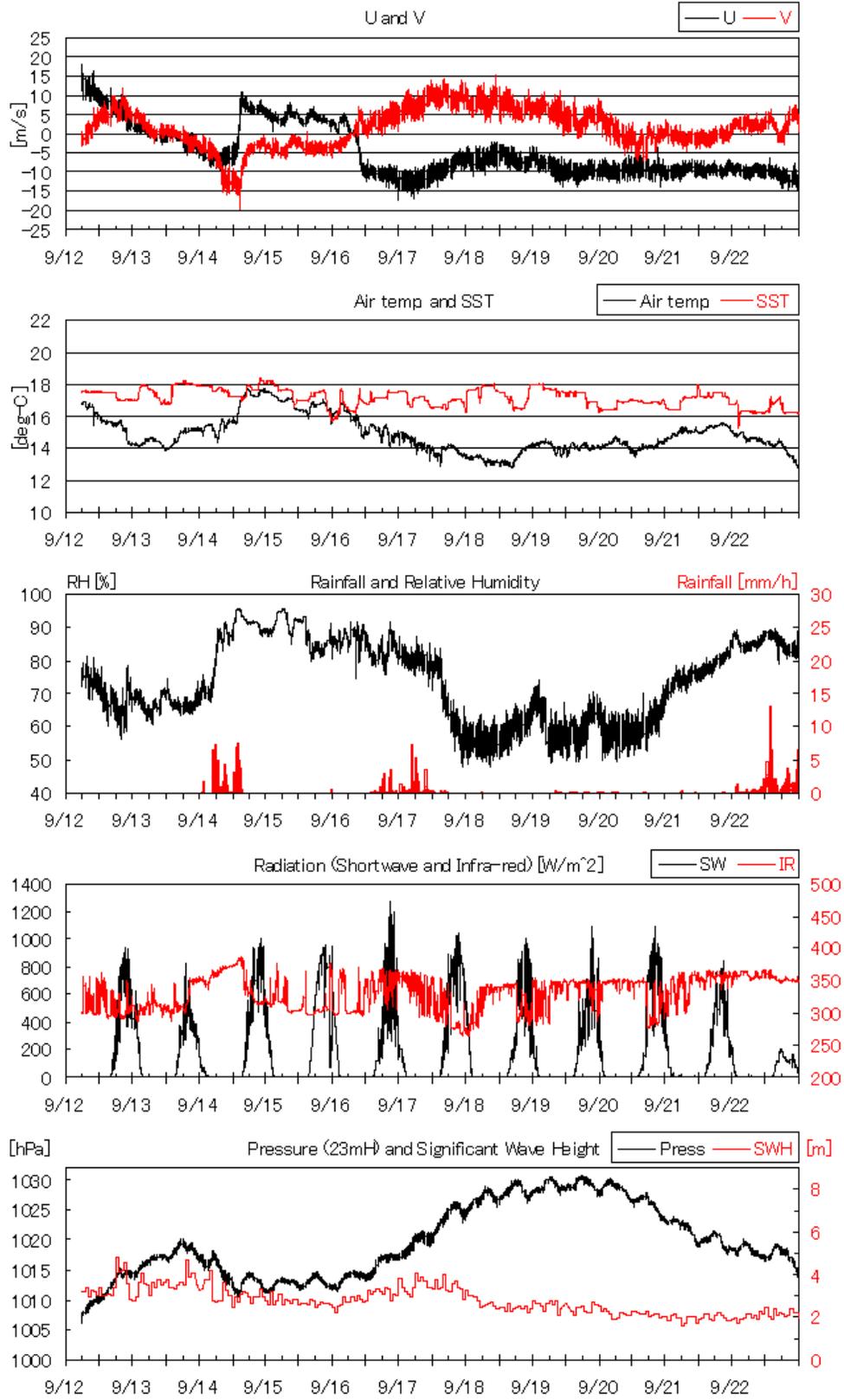


Figure 2.5.1

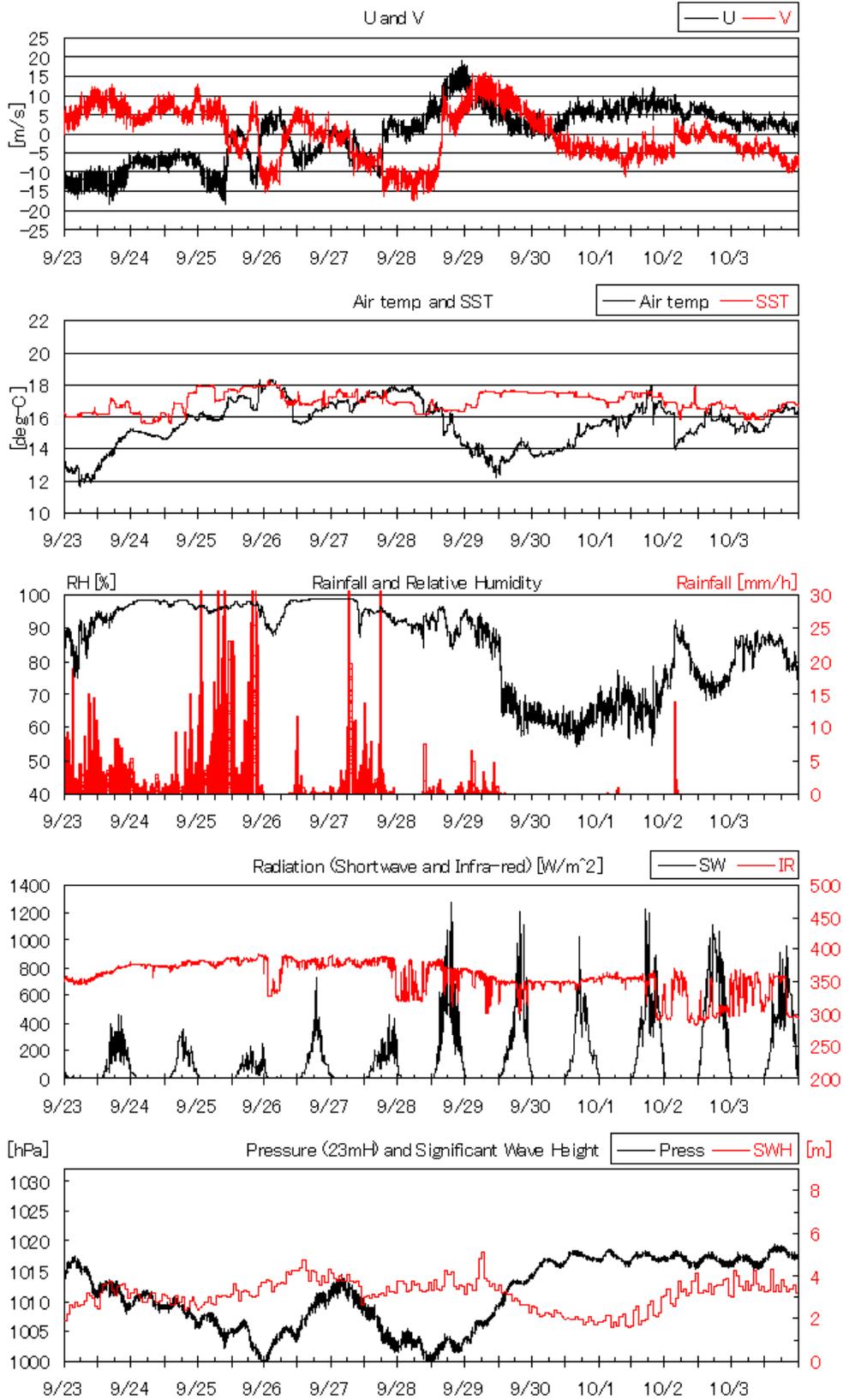


Figure 2.5.1 (continued)

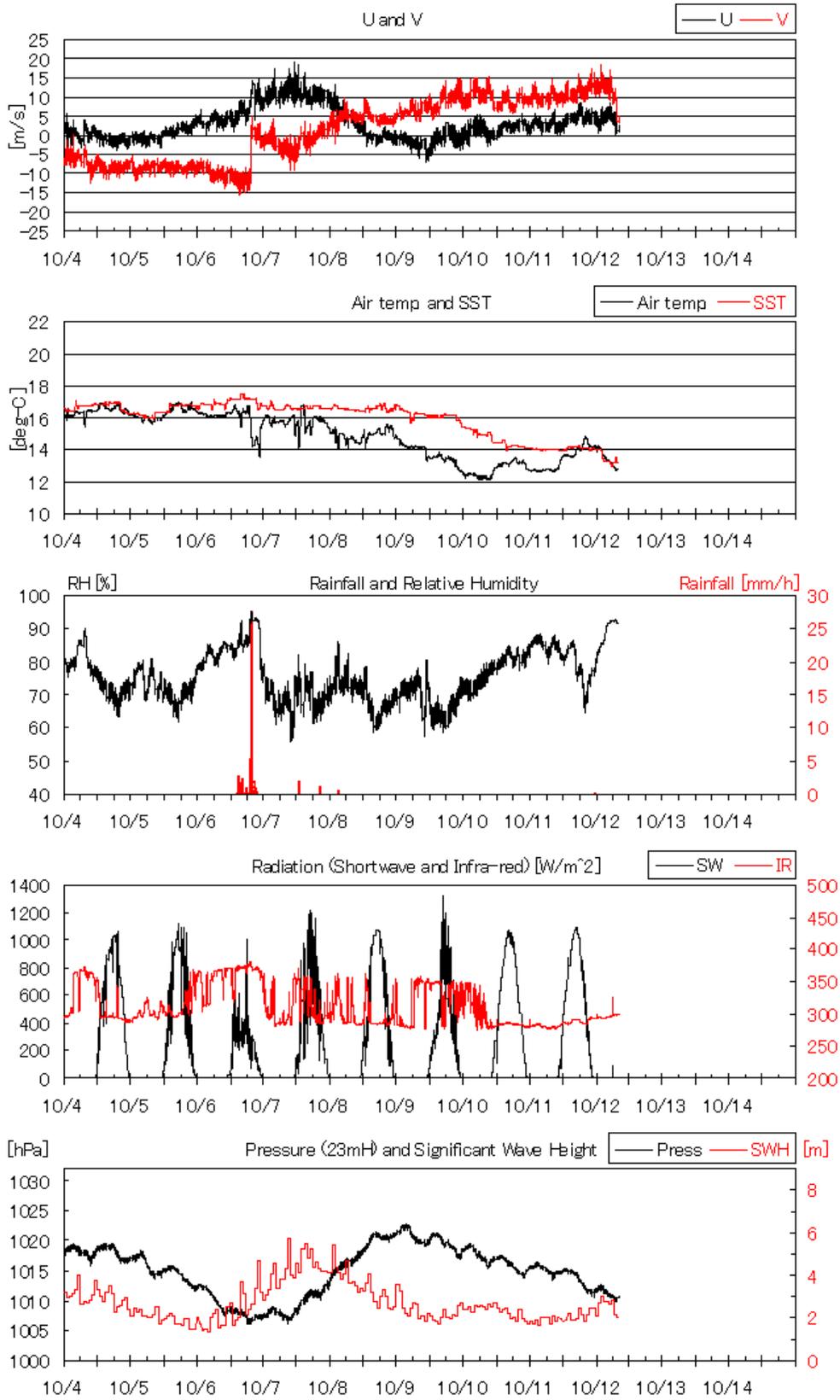


Figure 2.5.1 (continued)

2.6 Ceilometer Observation

Satoshi Okumora (GODI)
Wataru Tokunaga (GODI)
Ryo Kimura (GODI)

2.6.1 Objectives

The information of cloud base height and the liquid water amount around cloud base is important to understand the process on formation of the cloud. As one of the methods to measure them, the ceilometer observation was carried out.

2.6.2 Parameters

Cloud base height [m].

Backscatter profile, sensitivity and range normalized at 30 m resolution.

Estimated cloud amount [oktas] and height [m]; Sky Condition Algorithm.

2.6.3 Methods

We measured cloud base height and backscatter profile using ceilometer (CT-25K, VAISALA, Finland) throughout the MR03-K04 Leg.2 cruise.

Major parameters for the measurement configuration are as follows;

Laser source:	Indium Gallium Arsenide (InGaAs) Diode
Transmitting wavelength:	905±5 nm at 25 degC
Transmitting average power:	8.9 mW
Repetition rate:	5.57 kHz
Detector:	Silicon avalanche photodiode (APD)
	Responsibility at 905 nm: 65 A/W
Measurement range:	0 ~ 7.5 km
Resolution:	50 ft in full range
Sampling rate:	60 sec
Sky Condition	0, 1, 3, 5, 7, 8 oktas (9: Vertical Visibility)
	(0: Sky Clear, 1:Few, 3:Scattered, 5-7: Broken, 8: Overcast)

On the archive dataset, cloud base height and backscatter profile are recorded with the resolution of 30 m (100 ft).

2.6.4 Data archives

The raw data obtained during this cruise will be submitted to JAMSTEC Data Management Division.

2.7 Surface atmospheric turbulent flux measurement

Kunio Yoneyama (JAMSTEC)

Osamu Tsukamoto (Okayama Univ.)

Hiroshi Ishida (Kobe Univ. of Mercantile Marine)

2.7.1 Objective

To better understand the air-sea interaction, accurate measurements of surface heat and fresh water budgets are necessary as well as momentum exchange through the sea surface. In addition, the evaluation of surface flux of carbon dioxide is also indispensable for the study of global warming. Sea surface turbulent fluxes of momentum, sensible heat, latent heat, and carbon dioxide were measured by using the eddy correlation method that is thought to be most accurate and free from assumptions. These surface heat flux data are combined with radiation fluxes and water temperature profiles to derive the surface energy budget.

2.7.2 Apparatus and Performance

The surface turbulent flux measurement system consists of turbulence instruments (Kaijo Co., Ltd.) and ship motion sensors (Kanto Aircraft Instrument Co., Ltd.). Details of each sensor are as follows. All sensors are equipped at 25 m height from sea surface.

Sensor	Type / Manufacturer
Three-dimensional sonic anemometer-thermometer	Kaijo, DA-600
Infrared hygrometer	LICOR, LI-7500
Two-axis inclinometer	Applied Geomechanics, MD-900-T
Three-axis accelerometer	Applied Signal Inc., QA-700-020
Three-axis rate gyro	Systron Donner, QRS-0050-100

These signals are sampled at 10 Hz by a PC-based data logging system (Labview, National Instruments Co., Ltd.). By obtaining the ship speed and heading information through the Mirai network system it yields the absolute wind components relative to the ground. Combining wind data with the turbulence data, turbulent fluxes and statistics are calculated in a real-time basis.

2.7.3 Calibration

All sensors were calibrated at the manufacturer (Kaijo Co. Ltd.) in April 2003. After the cruise, these data will be compared with surface meteorological data obtained by another system (SOAR) to exclude unreliable data.

2.7.4 Preliminary results

Data will be processed after the cruise at Okayama University.

2.7.5 Data Archive

All data are archived at Okayama University, and will be open to public after quality checks and corrections. Corrected data will be submitted to JAMSTEC Data Management Division.

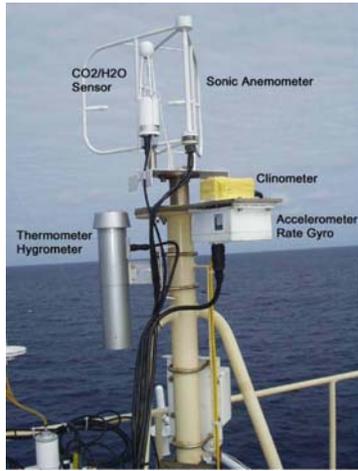


Figure 2.7.1 Turbulent flux measurement system on the top deck of the foremast.

2.8 N₂O

See section 3.12

3. Hydrographic Measurements

3.1 CTDO-Sampler

Hiroshi Uchida (JAMSTEC)
Masao Fukasawa (JAMSTEC)
Wolfgang Schneider (University of Concepcion)
Hiroshi Matsunaga (MWJ)
Miki Yoshiike (MWJ)

3.1.1 Winch arrangements

The CTD package was deployed using a 4.5 Ton Traction Winch System (Dynacon, Inc., USA) which was installed on the R/V Mirai in April 2001 and moved its position several meters to stern side in April 2003. 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 8,200 m of 9.53 mm armored 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 34560 Hz carrier-modulated differential-phase-shift-keying (DPSK) telemetry link. The deck unit decodes the serial data and sends them to a personal computer (Hewlett Packard Vectra VL, Intel(r) Celeron(tm), Microsoft Windows98 2nd edition) 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 premium temperature (SBE 3plus) 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 (3000 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 2.3 m/s. SBE's dissolved oxygen sensor (SBE 43) was placed between the conductivity sensor module and the pump.

The system used in this cruise is summarized as follows:

Under water unit:

SBE, Inc., SBE 9plus, S/N 42423

Temperature sensor (primary):

SBE, Inc., SBE 3plus, S/N 031524 (station P06C-127)

Temperature sensor (primary):

SBE, Inc., SBE 3plus, S/N 03P4216 (from station P06C-125 to P06E-004)

Temperature sensor (secondary):
 SBE, Inc., SBE 3-04/F, S/N 03P2453

Conductivity sensor (primary):
 SBE, Inc., SBE 4-04/0, S/N 042240

Conductivity sensor (secondary):
 SBE, Inc., SBE 4-04/0, S/N 041206

Oxygen sensor (primary):
 SBE, Inc., SBE 43, S/N 430391

Oxygen sensor (secondary):
 SBE, Inc., SBE 43, S/N 430069 (from station P06C-127 to P06E-061)

Pump (primary):
 SBE, Inc., SBE 5T, S/N 053575

Pump (secondary):
 SBE, Inc., SBE 5T, S/N 050984

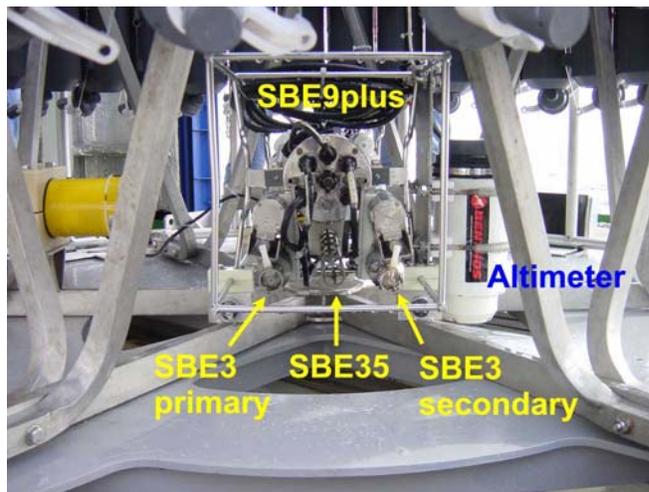
Altimeter:
 Benthos Inc., PSA-900D, S/N 1026

Deep Ocean Standards Thermometer:
 SBE, Inc., SBE 35, S/N 3528054-0022

Deck unit:
 SBE, Inc., SBE 11plus, S/N 11P7030-0272

Carousel Water Sampler:
 SBE, Inc., SBE 32, S/N 3221746-0278

Water sample bottle:
 General Oceanics, Inc., 12-litre Niskin-X



3.1.3 Pre-cruise calibration

3.1.3.1 Pressure

The Paroscientific series 4000 Digiquartz 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. in Bellevue, Washington, USA. The following coefficients were used in the SEASOFT:

S/N 42423 May 17, 1994

c1 = -69582.91
c2 = -1.619244
c3 = 2.34327e-02
d1 = 0.029679
d2 = 0
t1 = 28.12082
t2 = -4.595919e-04
t3 = 3.89464e-06
t4 = 0
t5 = 0

Pressure coefficients are first formulated into

$c = c1 + c2 * U + c3 * U^2$
 $d = d1 + d2 * U$
 $t0 = t1 + t2 * U + t3 * U^2 + t4 * U^3 + t5 * U^4$

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

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

The following coefficients were used in SEASOFT:

M = 0.01161
B = -8.32759

(in the underwater unit system configuration sheet dated on May 24, 1994)

Finally, pressure is computed as

$P \text{ (psi)} = c * [1 - (t0^2 / t^2)] * \{1 - d * [1 - (t0^2 / t^2)]\}$

where t is pressure period (microsec). 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 are performed at Marine Works Japan Ltd. in Yokosuka, Kanagawa, JAPAN, 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 42423 April 18, 2003
slope = 0.9999112
offset = -0.0295469

The drift-corrected pressure is computed as

$\text{Drift-corrected pressure (dbar)} = \text{slope} * (\text{computed pressure in dbar}) + \text{offset}$

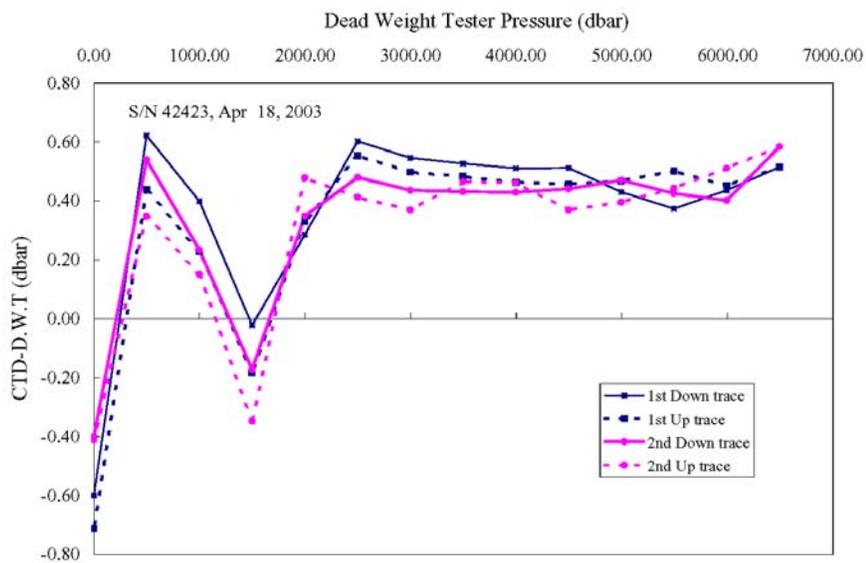


Figure 3.1.1 The residual pressures between the Dead Weight Tester and the CTD.

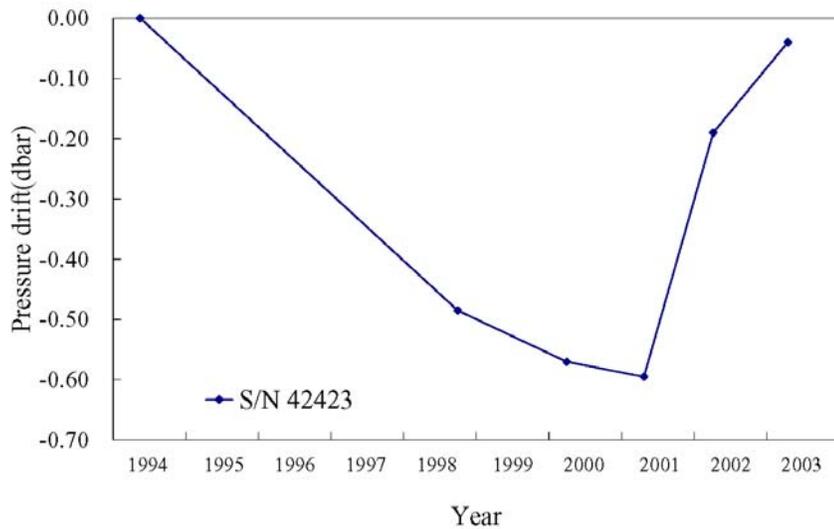


Figure 3.1.2 Drift of the pressure sensor (offset) measured by the Dead Weight Tester.

3.1.3.2 Temperature (SBE 3plus and 3F)

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 meters. The sensor output frequency ranges from approximately 5 to 13 kHz corresponding to temperature from -5 to 35 degC. 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 3F thermometer has a nominal accuracy of 0.001 degC, typical stability of 0.0002 degC/month and resolution of 0.0002 degC at 24 samples per second. The premium temperature sensor, SBE 3plus, is a more rigorously tested and calibrated version of standard temperature sensor (SBE 3F). A sensor is designated as an SBE 3plus only after demonstrating drift of less than 0.001 degC 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. in Bellevue, Washington, USA. The following coefficients were used in SEASOFT:

S/N 03P4216 (primary) July 29 , 2003

$$g = 4.35956769e-03$$

$$h = 6.45664029e-04$$

$$i = 2.25867675e-05$$

$$j = 1.88325427e-06$$

$$f_0 = 1000.000$$

S/N 03P2453 (secondary) July 25, 2003

$$g = 4.4010773e-03$$

$$h = 6.47307314e-04$$

$$i = 2.32721826e-05$$

$$j = 2.09881293e-06$$

$$f_0 = 1000.000$$

S/N 031524 (primary for station P06C-127) April 15 , 2003

$$g = 4.85928482e-03$$

$$h = 6.85560499e-04$$

$$i = 2.72682203e-05$$

$$j = 2.04591608e-06$$

$$f_0 = 1000.000$$

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).

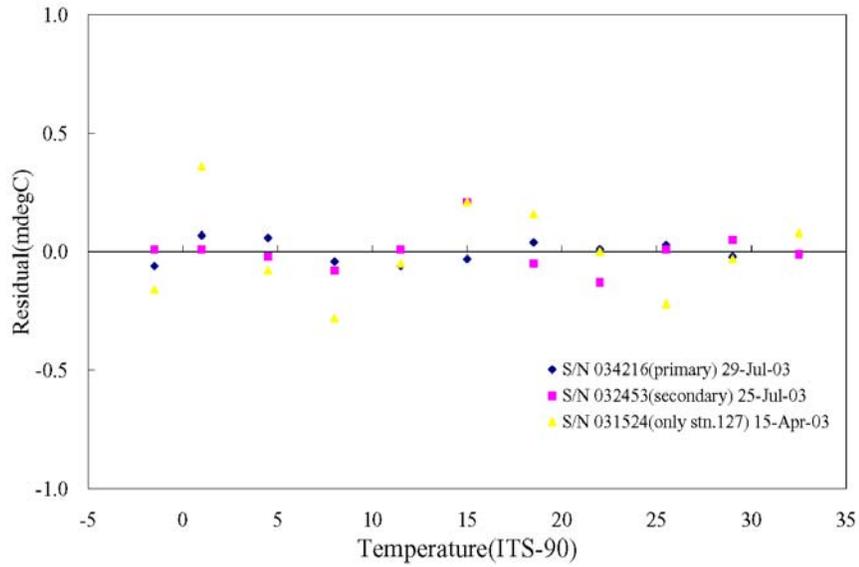


Figure 3.1.3 Residual temperature between bath and instrument temperatures.

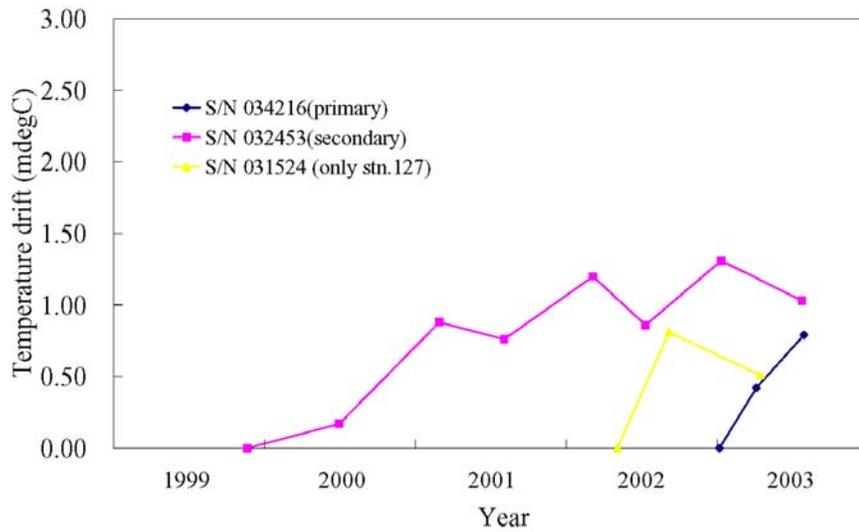


Figure 3.1.4 Drift of the temperature sensors based on laboratory calibrations.

3.1.3.3 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. in Bellevue, Washington, USA. The following coefficients were used in SEASOFT:

S/N 042240 (primary) July 30, 2003

g = -1.06122361e+01
h = 1.51071990e+00
i = -2.24813805e-03
j = 2.43876786e-04
CPcor = -9.57e-08 (nominal)
CTcor = 3.25e-06 (nominal)

S/N 041206 (secondary) July 30, 2003

g = -4.29002369+00
h = 5.03379521e-01
i = 1.18152789e-04
j = 2.02164093e-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 (degC) and p is the water pressure (dbar). The value of conductivity at salinity of 35, temperature of 15 degC (IPTS-68) and pressure of 0 dbar is 4.2914 S/m.

3.1.3.4 Deep Ocean Standards Thermometer

The 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. 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.

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. 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. in Bellevue, Washington, USA. The following coefficients were stored in EEPROM:

S/N 022 October 12, 1999 (1st step: linearization)

a0 = 4.320725498e-3
a1 = -1.189839279e-3
a2 = 1.836299593e-3

$$a3 = -1.032916769e-5$$

$$a4 = 2.225491125e-7$$

Temperature (ITS-90) is computed according to

$$\text{Temperature (ITS-90)} = \frac{1}{\{a0 + a1 * [\ln(n)] + a2 * [\ln^2(n)] + a3 * [\ln^3(n)] + a4 * [\ln^4(n)]\}} - 273.15$$

where n is the instrument output.

S/N 022 26 March, 2003 (2nd step: fixed point calibration)

$$\text{Slope} = 1.000012$$

$$\text{Offset} = 0.000052$$

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. RMS temperature noise for an SBE 35 in a Triple Point of Water cell is typically expressed as $82 / \sqrt{\text{NCYCLES}}$ in micro K. In this cruise NCYCLES was set to 4 (acquisition time was 4.4 seconds) and the RMS noise was 0.000041 degrees C.

3.1.3.5 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 (1000 m). Continuous polarization eliminates the wait-time for stabilization after power-up. Signal resolution is increased by on-board temperature compensation. This 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 through almost the same way as for the case of the SBE 13. 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 1000 hours.

The following coefficients were used in SEASOFT:

S/N 430391(primary) July 17, 2003

$$\text{Soc} = 0.4108$$

$$\text{Boc} = 0.0000$$

$$\text{TCor} = 0.0012$$

$$\text{PCor} = 1.350e-04$$

$$\text{Offset} = -0.4851$$

$$\text{tau} = 0$$

S/N 430069(secondary) August 07, 2003

$$\text{Soc} = 0.3001$$

$$\text{Boc} = 0.0000$$

$$\text{TCor} = 0.0009$$

$$\text{PCor} = 1.350e-04$$

$$\text{Offset} = 0.5984$$

$$\text{tau} = 0$$

Oxygen (ml/l) is computed as

$$\text{Oxygen (ml/l)} = [\text{Soc} * \{(v + \text{offset}) + (\text{tau} * \text{doc/dt})\} + \text{Boc} * \exp(-0.03 * t)] * \exp(\text{TCor} * t + \text{PCor} * p) * \text{Oxsat}(t, s)$$

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

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. Its coefficients are as follows.

$$\begin{aligned} A1 &= -173.4292 \\ A2 &= 249.6339 \\ A3 &= 143.3483 \\ A4 &= -21.8482 \\ B1 &= -0.033096 \\ B2 &= -0.00170 \end{aligned}$$

3.1.3.6 Altimeter

The Benthos PSA-900 Programmable Sonar Altimeter (Benthos, Inc., USA) determines the distance of the target from the unit in almost the same way as the Benthos 2110. PSA-900 also uses the nominal speed of sound of 1500 m/s. But, PSA-900 compensates for sound velocity errors due to temperature. In a PSA-900 operating at a 350 microsecond pulse at 200 kHz, the jitter of the detectors can be as small as 5 microseconds or approximately 0.4 centimeters total distance. Since the total travel time is divided by two, the jitter error is 0.25 centimeters. The unit (PSA-900D) is rated to a depth of 6,000 meters.

The following scale factors were used in SEASOFT:

$$\begin{aligned} \text{FSVolt} * 300 / \text{FSRange} &= 10 \\ \text{Offset} &= 0.0 \end{aligned}$$

3.1.4 Data collection and processing

3.1.4.1 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. The SBE 9plus CTD (sampling rate of 24 Hz) was mounted horizontally in a 36-position carousel frame. Auxiliary sensors included altimeter, dissolved oxygen sensors and Deep Ocean Standards Thermometer.

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 0.5 m/s to 100 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 multibeam sounder on board. For the up cast, the package was lifted at a rate of 1.2 m/s except for bottle firing stops. At each bottle firing stops, the bottle was fired after waiting 30 seconds and the package was stayed 7 seconds in order to sample temperature by the Deep Ocean Standards Thermometer. At 100 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. Niskin-X bottle samples were taken water for analysis of salinity, dissolved oxygen, nutrients, DIC, TOC, pH, total alkalinity, CFCs, radio nuclear, ¹⁴C, N/Argon, ³H, ³He/⁴He, chlorophyll-a and primary productivity. 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 module of the SEASOFT acquisition and processing software, version 4.25b. Temperature, conductivity, salinity, oxygen and descent rate profiles were displayed in real-time with the package depth and altimeter reading.

3.1.4.2 Data collection problems

At station P06C-127 second cast (first cast of this leg), frequent noise in primary temperature (its magnitude was about one to two degrees C) was found during 400 to 900 m depths in the down cast. So the cast was aborted and the CTD package was lifted to the deck. Primary temperature sensor was replaced from S/N 03P4216 to S/N 031524 and the connection cable was also replaced. A third cast was done at the site. But similar noise in primary temperature was found around 600 m depths in the down cast. So the cast was aborted. After replacing

SBE 9plus from S/N 0575 to S/N 0357 and all of the connection cables used, a fourth cast was done at the site. After the cast primary temperature sensor was replaced again from S/N 031524 to 03P4216 because it found that the cause of the noise was not the temperature sensor.

At station P06C-X17, the personal computer, which displays and stores the serial data from the deck unit, was rebooted at about 1,500 m in the down cast. So the cast was aborted and the CTD package was lifted to the deck. Connection of the AC power cable was checked and an AC power supply, CVFT1-500H (TOKYO SEIDEN Co., JAPAN), was used in order to remove voltage fluctuations and irregularities in power lines. A second cast was done at the site.

After the cast of station P06C-102, Niskin-X bottle #9 (NX(NC)12021) was replaced with bottle #3 (NX(NC)12015) in order to check leakage or miss-trip of the bottle #9 that was guessed from analyzed values of salinity, oxygen and nutrients at station P06C-114.

When the CTD package was lifted to the deck after the up-cast of P06C-101, a hook that was connecting top and bottom caps of Niskin-X bottle #9 by nylon line was away from the bottom cap. So the bottle #9 was replaced from NX(NC)12015 to NX(NC)12012 after the cast.

At station P06E-061, output from secondary dissolved oxygen sensor (S/N 430069) showed unusual (negative) value. The secondary sensor was removed after the cast.

When operating the SBE 911 system with SBE 35, it was found that the deck unit (SBE 11plus) had received incorrect signal for confirmation of firing bottle #16. During this leg a module (Yoshi Ver. 1, EMS Co. Ltd., JAPAN) to correct the signal was used between the underwater unit and the deck unit. At the beginning of the down cast of station P06E-044, the module continued to display unusual signal while the package was lifting from 10 m beneath the surface after activating the pump (although the status lamp was green). The status lamp did not change from red to green though the module was turned on again. So the SEASAVE software was re-started from the surface in order to acquire the data in a new file, 044M02.

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

Frequently date and time of the SBE 35 did not change from "01 Jan 1980 00:00:-1" by the setup commands "ddmmyy" and "hhmmss". In such a case, test command (*rtctest) to reset date and time to default (01 Jan 1980 00:00:00) did not work and date and time of the samples in the data file did not change from "01 Jan 1980 00:00:-1". This problem was found at station P06C-126 of the previous leg for the first time. In this leg CTD stations that encountered this problem were as follows: P06C-119, 118, 117, 109, 108, X17, 106, 105, 104, 103, 102, 101, 100, 099, 098, 097, 096, 095, 094, 091, 089, 087, 086, 085, 084, 083, 082, 081, 080, 078, 077, 076, P06E-069, 056, 055, 054, 053, 052, 050, 049, 045, 036, 031, 028, 027, 024, 023, 022, 021, 019, 016, 015, 014, 013, 012, 011, 010, 009, 008, 007, 006 and 005. This problem was found at about half stations of this leg.

3.1.4.3 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-Win32 (Ver. 5.27b) processing module sequence and specifications used in the reduction of CTD data in this cruise. Some modules are originally developed for additional processing and post-cruise calibration.

DATCNV converted the raw data to scan number, pressure, depth, temperatures, conductivities, oxygen, oxygen voltage. 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, and altitude were averaged over 4.4 seconds.

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 3000 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 conductivity for 1.73 scans ($1.75/24 = 0.073$ seconds). As a result, the secondary conductivity was advanced 0.073 seconds relative to the temperature. 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 pressure.

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 pressure, temperatures, conductivities, oxygen voltage and altimeter outputs.

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.

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 starting 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 sigma-theta.

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

3.1.5 Post-cruise calibration

3.1.5.1 Pressure

The CTD pressure sensor drift in the period of this 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 pressure. The atmospheric pressure was measured at the captain deck (20 m high from the base line) and averaged over one minute for a meteorological data.

The CTD pressure sensor drift is estimated from the deck pressure obtained above. An average of the pre- and the post-casts data over the whole period of this cruise gave an estimation of -0.71 dbar and the root-mean-square difference of 0.10 dbar. And the pre-cruise calibration (April 2003) shows that residual pressure between the Dead Weight Tester and the drift corrected CTD data at 0 dbar was -0.57 dbar. Therefore the pressure sensor drift from the pre-cruise calibration is estimated as -0.14 dbar. So the post-cruise calibration is not deemed necessary for this pressure sensor.

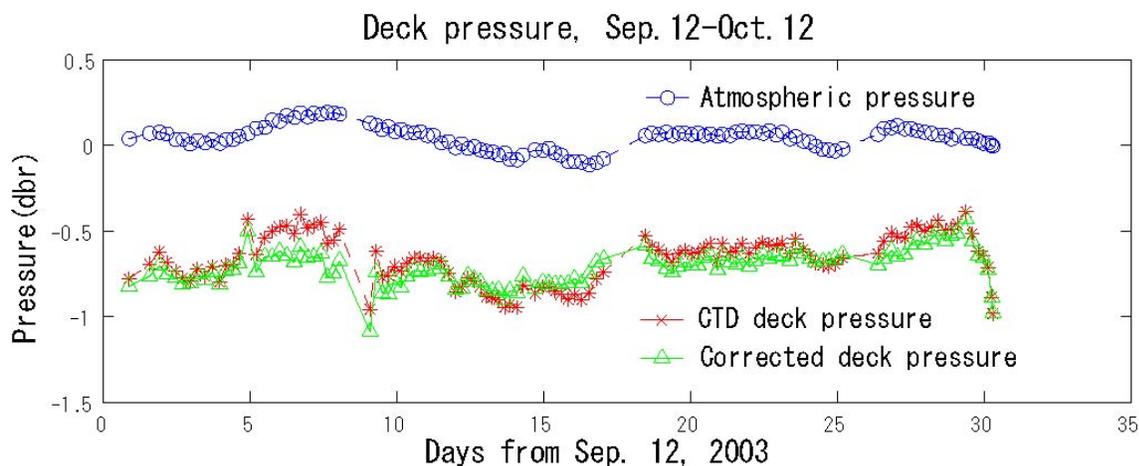


Figure 3.1.5 Time series of the CTD deck pressure.

3.1.5.2 Temperature

Post-cruise sensor calibrations are going to be performed at SBE, Inc. in Bellevue, Washington, USA. SBE 3plus temperature sensors (S/N 03P4216 and 03P2453) and SBE 35 Deep Ocean Standards thermometer (S/N 022) are going to be sent to SBE immediately after the cruise. Using results of these calibrations and SBE 35 data, CTD temperature is going to be corrected.

SBE 3 sensors are 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. The pressure sensitivity for a SBE 3 sensor is usually less than +2 mK / 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 that occurs in a TC duct and does not occur for un-pumped SBE 35 measurements.

SBE 35 calibrations have some uncertainty (about 0.2 mK) and SBE 3 calibrations have some uncertainty (about 1 mK). So the best corrections for CTD temperature data can be made by using a SBE 35, correcting the SBE 3 data for viscous heating and then correcting the SBE 3 to agree with the SBE 35 (a linear pressure correction and an offset for drift and/or calibration uncertainty).

Comparison between the primary temperature sensor (S/N 03P4216) and SBE 35 readings showed an unusually large difference of +2 to +3 mK. Also secondary temperature sensor (S/N 03P2453) had an unusually large pressure effect of +5 mK / 6000 dbar. And the differences between SBE 3 and SBE 35 were drifting rapidly (order of 1 mK/month). Therefore the CTD temperature must be corrected carefully based on laboratory calibrations and in-situ comparisons with SBE 35.

3.1.5.3 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 CTD temperature is calibrated.

3.1.6 Preliminary results

Date, time and locations of the CTD casts are listed in SUM (station summary) file. In total 116 CTD casts were carried out. T-S (temperature vs salinity) diagram and vertical section of temperature, salinity and dissolved oxygen are shown in Plate 3.1.1. Uncorrected CTD data are used in Plate 3.1.1.

3.1.7 Data archive

All raw and processed CTD data files will be submitted to JAMSTEC Data Management Office (DMO).

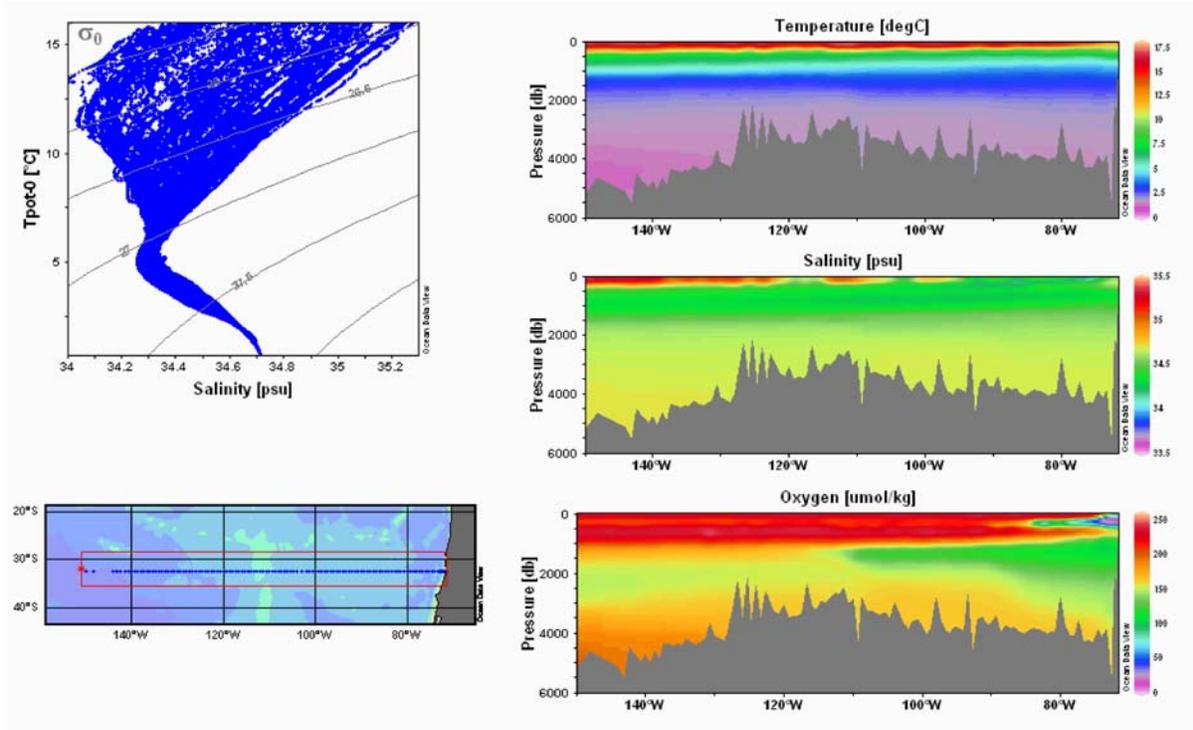


Plate 3.1.1 (a) T-S diagram, (b) station locations, vertical section of (c) temperature, (d) salinity and (e) dissolved oxygen.

3.2 Bottle Salinity

Takeshi Kawano (JAMSTEC)
Takeo Matsumoto (MWJ)
Kenichi Katayama (MWJ)

3.2.1 Objectives

Bottle salinities were measured in order to be compared with CTD salinities to identify leaking bottles and calibrate CTD salinities.

3.2.2 Instrument and Method

3.2.2.1 Salinity Sample Collection

The bottles in which the salinity samples are collected and stored are 250 ml Phoenix brown glass bottles with screw caps. Each bottle was rinsed three times with sample water and was filled to the shoulder of the bottle. The caps were also thoroughly rinsed. Salinity samples were stored for about 24 hours in the same laboratory as the salinity measurement was made.

3.2.2.2 Instruments and Method

The salinity analysis was carried out on Guildline Autosol salinometer model 8400B (S/N 62827), which was modified by addition of an Ocean Science International peristaltic-type sample intake pump and two Guildline platinum thermometers model 9450. One thermometer monitored an ambient temperature and the other monitored a bath temperature. The resolution of the thermometers was 0.001 deg C. The measurement system was almost same as Aoyama et al (2003). The salinometer was operated in the air-conditioned ship's laboratory at a bath temperature of 24 deg C. An ambient temperature varied from approximately 20 deg C to 23 deg C, while a bath temperature is very stable and varied within +/- 0.002 deg C on rare occasion. A measure of a double conductivity ratio of a sample is taken as a median of thirty-one reading. Data collection was started after 5 seconds and it took about 10 seconds to collect 31 readings by a personal computer. Data were sampled for the sixth and seventh filling of the conductivity cell. In case the difference between the double conductivity ratio of these two fillings is smaller than 0.00002, the average value of the two double conductivity ratios 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 the 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 13hours per day (typically from 04:00 to 17:00 in the next day) and the cell was rinsed by pure water every day and sometime cleaned by ethanol or soap or both after the measurement of the day.

Besides the daily cleaning of the cell, the cell of Autosol was removed and washed thoroughly between the between station 94 and 95, since the standard deviation of SSWs is rather larger than the modern measurement precision (Aoyama et al, 2003).

3.2.3 Preliminary Result

3.2.3.1 Stand Seawater

Standardization control was set to 506 and all the measurements were done by this setting. During the whole measurement, the STANDBY was 6110 +/- 0001 and ZERO was -0.00001 to 0.00001. We used IAPSO Standard Seawater batch P142 which conductivity ratio was 0.99991 (double conductivity ratio is 1.99982) as the standard for salinity. We measured 157 ampoules of P142. Fig.3.2.1 shows the history of double conductivity ratio of the Standard Seawater batch P142.

The values are rather scattered during the period from the beginning to the serial number 47 (from station 127 to 95). The average of double conductivity ratio was 1.99976 and the standard deviation was 0.00018, which is equivalent to 0.0004 in salinity. We add 0.00006 to the measured double conductivity ratio during this period. As mentioned above, the cell of Autosol was removed and washed thoroughly between the serial number 47 and 48 (between station 94 and 95). The measurement system became stable after washing. The average became 1.99978 and the standard deviation became 0.00001, which is equivalent to 0.0002 in salinity. We add 0.00004 to the measured double conductivity ratio after station 94.

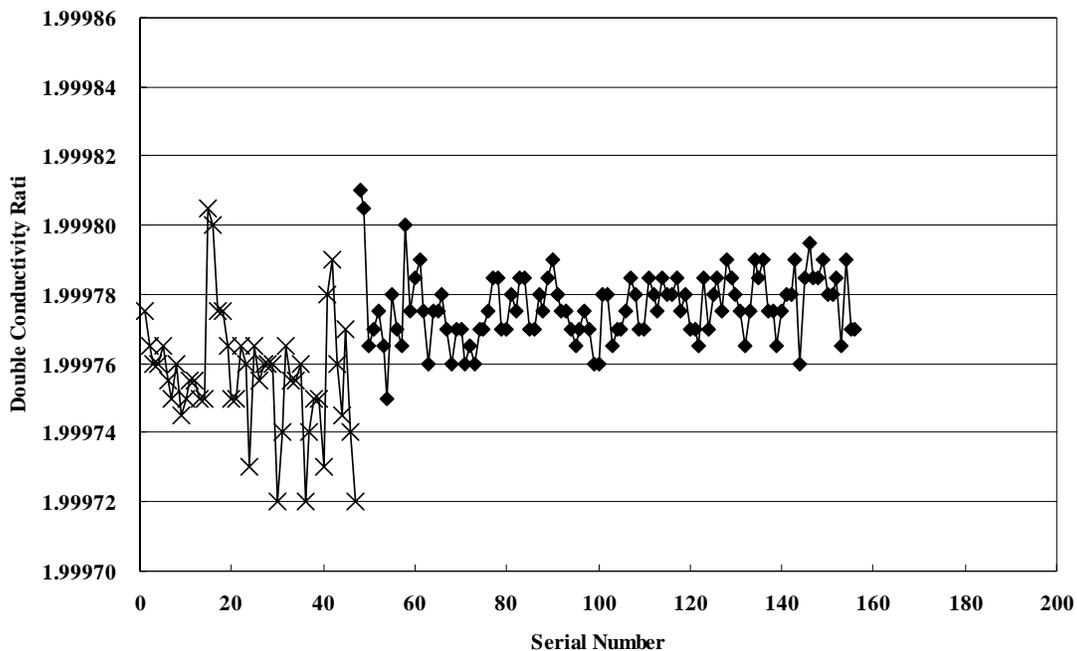


Fig.3.2.1 The history of double conductivity ratio of the Standard Seawater batch P142

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 and stored in a 20 liter cubitainer 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.

3.2.3.3 Replicate and Duplicate Samples

We took 685 pairs of replicate and 67 pairs of duplicate samples. Fig.3.2.2 (a) and (b) shows the histogram of the absolute difference between replicate samples and duplicate samples, respectively. There were 11 bad measurements and 7 questionable measurements of replicate samples. As for questionable measurements, one of the pairs is extremely high (more than 0.01 in salinity). This might be caused by insufficient seal of the sample bottles. Excluding these bad and questionable measurements, the standard deviation of the absolute difference of 667 pairs of replicate samples was 0.0002 in salinity and that of 67 pairs of duplicate samples was 0.0003 in salinity.

3.2.3.4 Figures

We measured about 3,952 samples in this leg. As a preliminary result, we will show several figures without any interpretation. Fig.3.2.3 shows a vertical section of bottle salinity, vertical profile of bottle salinity and Sigma4-Salinity diagram produced by Ocean Data View. The same section, P06W and P06C, was observed in 1992. Fig.3.2.4 shows a vertical profile of bottle salinity in 1992 plotted with the profile obtained during this cruise (Bad and questionable measurements are omitted).

3.2.4 Further data quality check

All the 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 Tech. Papers in Mar. Sci., 36, 25 pp., 1981

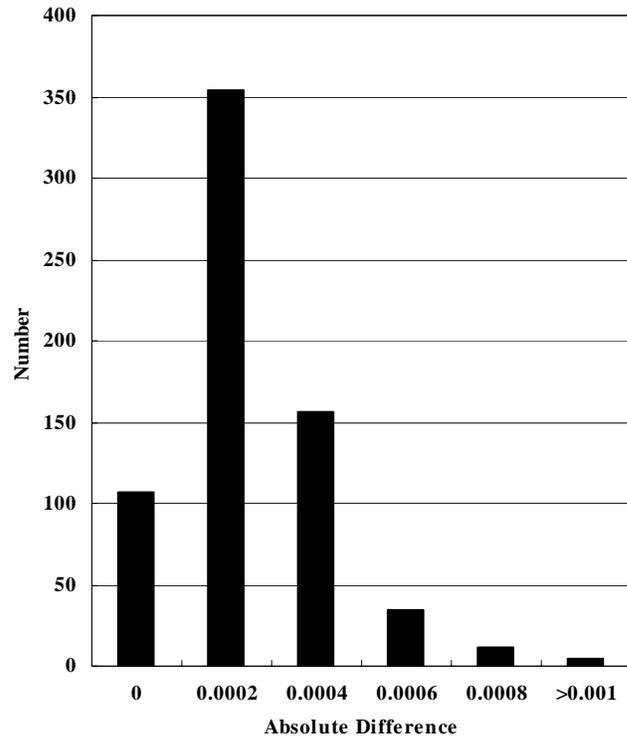


Fig.3.2.2 (a) The histogram of the absolute difference between replicate samples

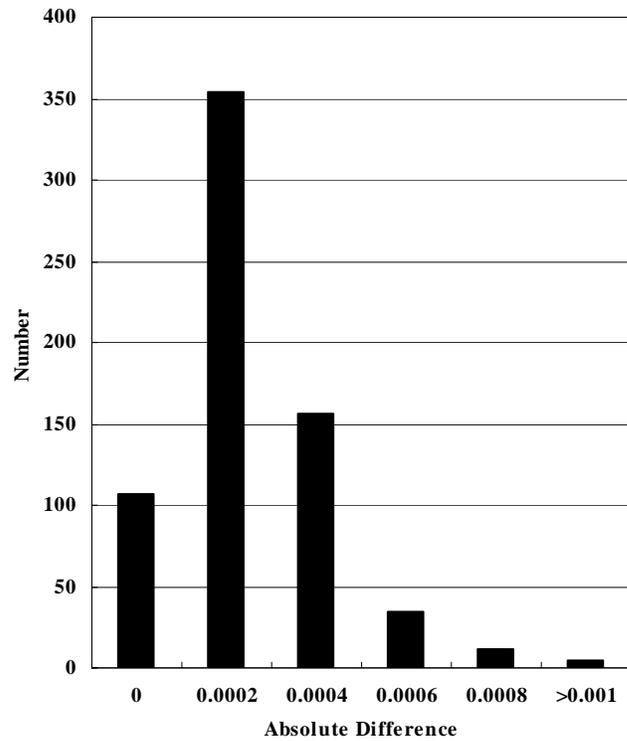


Fig.3.2.2 (b) The histogram of the absolute difference between duplicate samples.

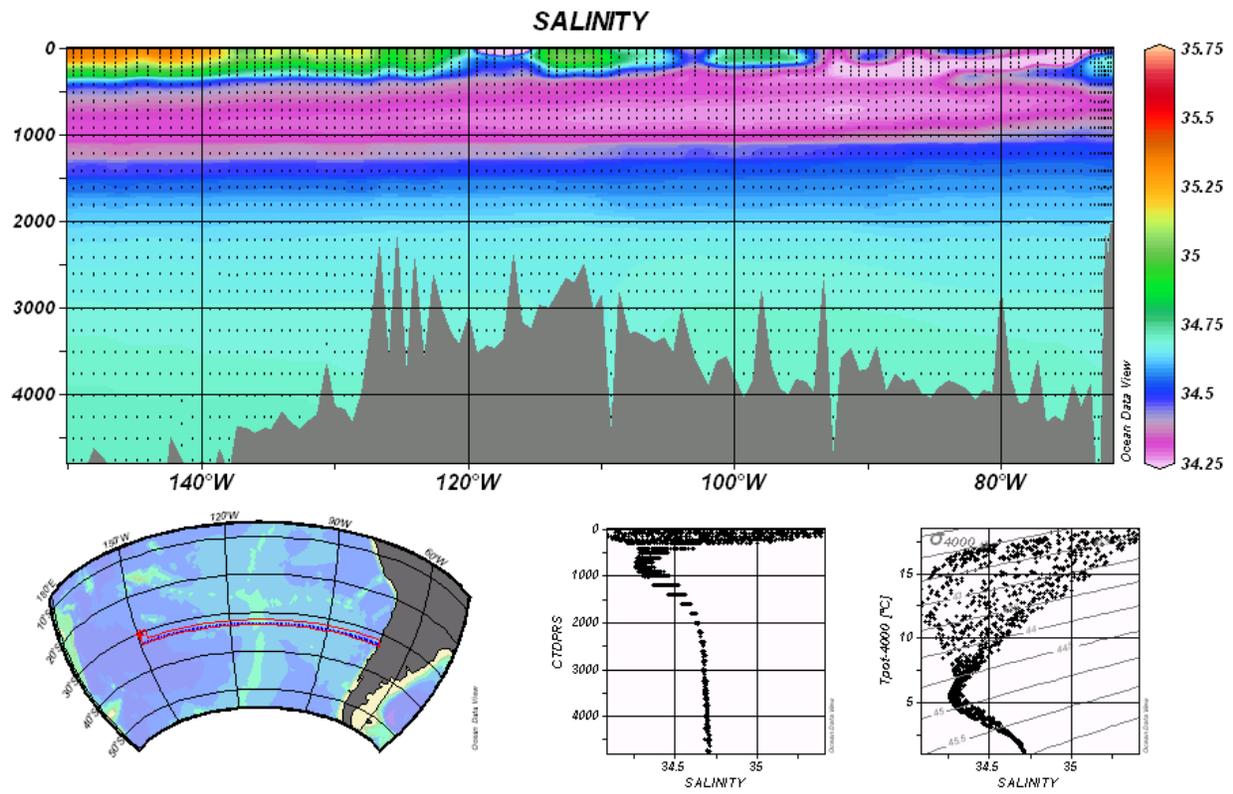


Fig.3.2.3 Vertical section, vertical profile of bottle salinity and Sigma4-Salinity diagram

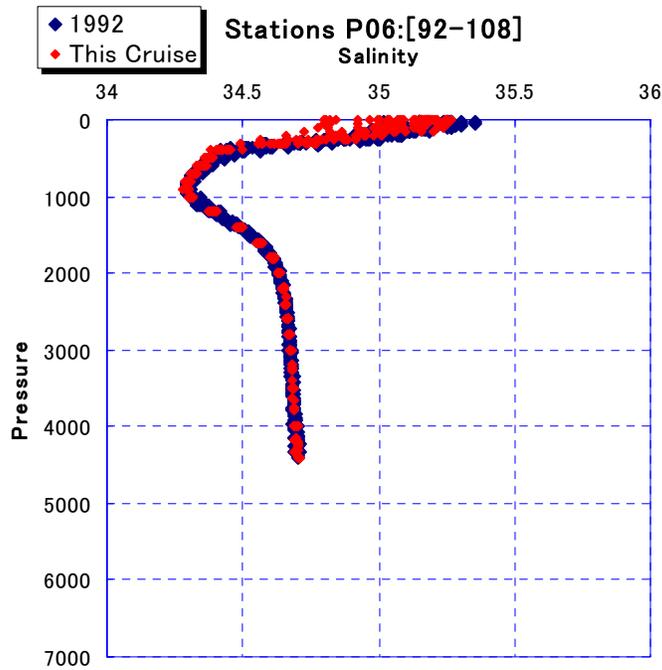
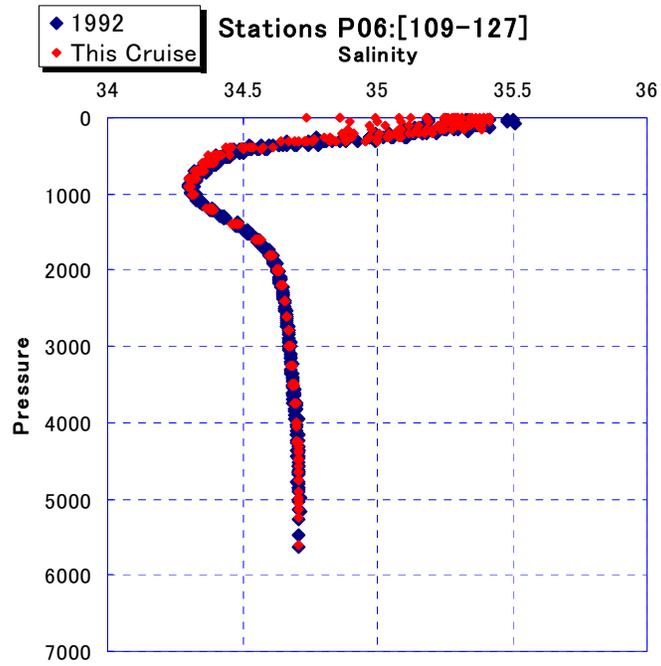


Fig.3.2.4 (a) Vertical Profile of salinity in 1992 () and this cruise ().

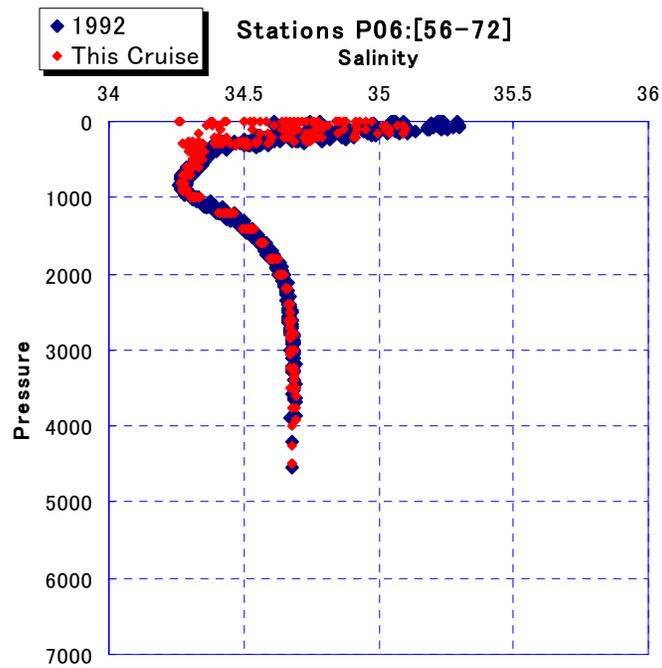
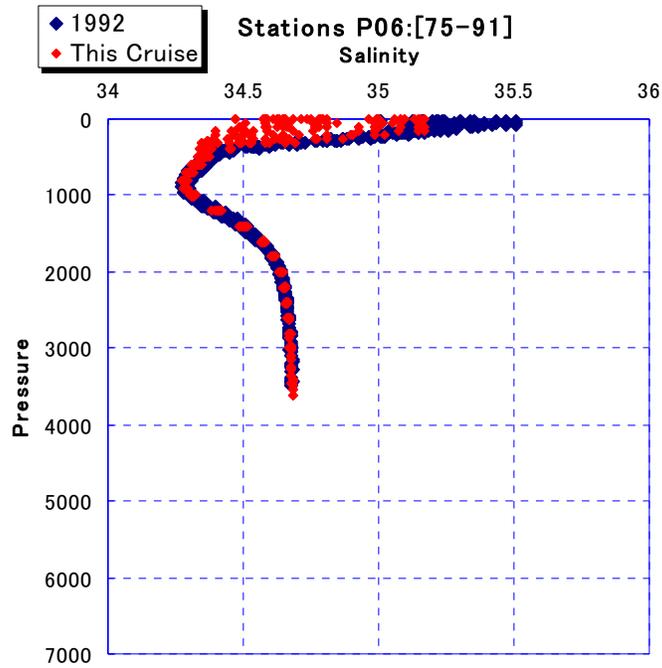


Fig.3.2.4 (b) Vertical Profile of salinity in 1992 () and this cruise ().

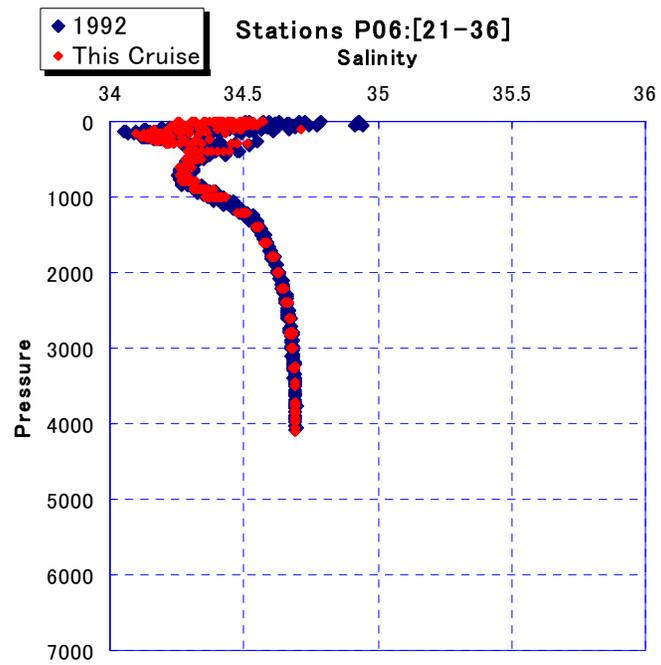
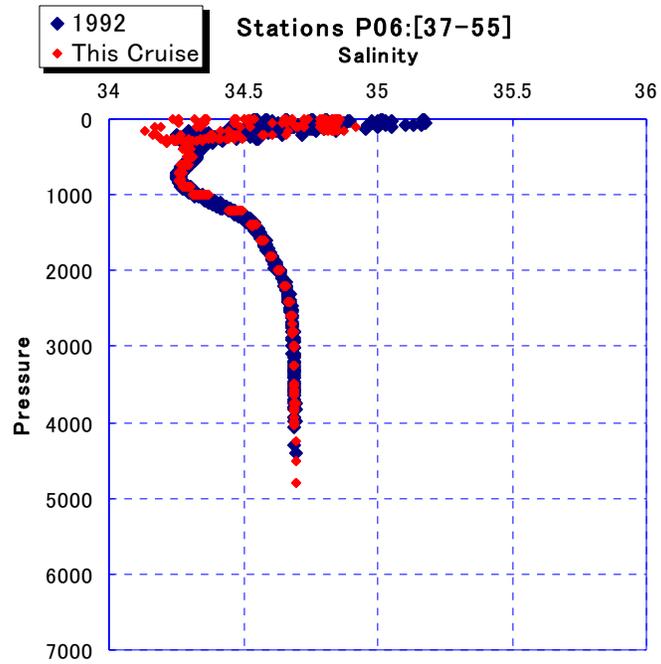


Fig.3.2.4 (c) Vertical Profile of salinity in 1992 () and this cruise ().

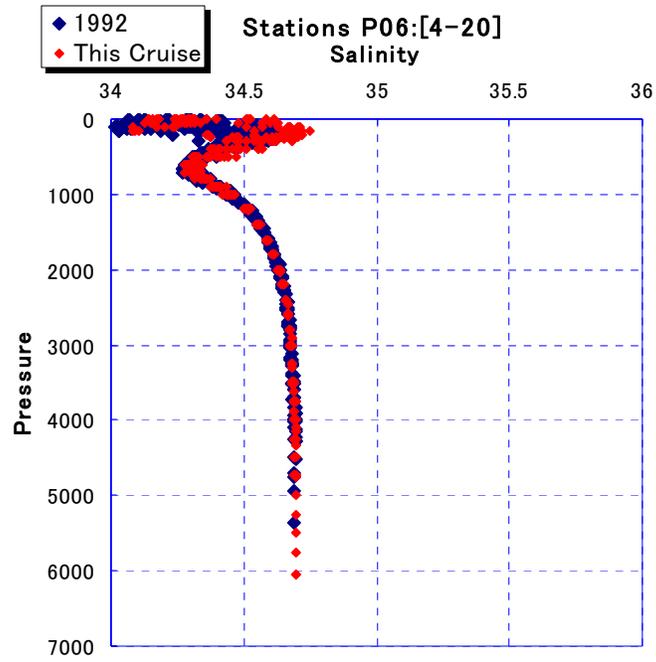


Fig.3.2.4 (d) Vertical Profile of salinity in 1992 () and this cruise ().

3.3 Bottle Oxygen

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3.3.1 Objectives

Dissolved oxygen is one of the most significant tracer for the ocean circulation study. During the past decades, dissolved oxygen concentration in intermediate layers has decreased in the North Pacific. The causes of the decrease, however, are still unclear. In this cruise (MR03-K04 Leg-2), we measured dissolved oxygen concentration at the stations along WHP P06C from 140.0°W to 113.3°W and P06E in the South Pacific. Our purposes are to compare our oxygen data in 2003 and those of WHP P06 in 1992.

3.3.2 Methods

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)

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 and Software; Automatic photometric titrator manufactured by Kimoto Electronic Co. Ltd.

Sampling

Following procedure is based on the WHP Operations and Methods (Dickson, 1996). Seawater samples were collected with Niskin bottle attached to the CTD-system. Seawater for oxygen measurement was transferred from Niskin sampler bottle to a volume calibrated flask (ca. 100 cm³). Three times volume of the flask of seawater was overflowed. Temperature was measured by digital 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.

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. Temperature of sodium thiosulfate during titration was recorded by a digital 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 sample temperature during seawater sampling, salinity of the sample, and titrated volume of sodium thiosulfate solution without the blank.

Standardization and determination of the blank

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 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 sodium thiosulfate titrated gave the molarity of sodium thiosulfate titrant.

The blank from the presence of redox species apart from oxygen in the reagents was determined as follows. 1

cm³ of the standard potassium iodate solution was added to a flask using a calibrated dispenser. 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 flask in order. Just after titration of the first potassium iodate, a further 1 cm³ of standard potassium iodate was added and titrated. The blank was determined by difference between the first and second titrated volumes of the sodium thiosulfate. 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). Table 3.3.1 shows results of the standardization and the blank determination during this cruise. The blank was less than 0.3 $\mu\text{mol/kg}$. Reproducibility (C.V.) of standardization was less than 0.08 % (n = 5).

3.3.3 Reproducibility of sample measurement

Replicate samples were taken at every CTD cast; usually these were 5 - 10 % of seawater samples of each cast during this cruise. Number of replicate sample pairs was 380 and the standard deviation was calculated to be 0.13 $\mu\text{mol/kg}$. The standard deviation was calculated by a procedure (SOP23) in DOE (1994).

3.3.4 Post-cruise calibrations

We will calibrate oxygen data that obtained on board using results of the CSK standard solution (potassium iodate solution, 0.001667M) and reassess the standardizations and the blank determinations.

3.3.5 Preliminary results

During this cruise we measured oxygen concentration in 3,560 seawater samples. Distribution of dissolved oxygen (32.5°S, 144°W ~ 71°W) were shown in Figure 3.3.1 that obviously shows three water mass; Antarctic Intermediate Water (AAIW), Pacific Deep Water (PDW), and Antarctic Bottom Water (ABW) in the west of 131°W. The oxygen concentration in PDW gradually decreased from 120°W to 71°W. Additionally, the subsurface oxygen minimum reached less than 10 $\mu\text{mol kg}^{-1}$ in the coastal area off Chile. These low-oxygen waters come from the eastern Equatorial Pacific. We compared our oxygen data in 2003 and those of WHP P06 in 1992. Below 4000 m depth, the oxygen concentration difference between two cruises is less than 1 $\mu\text{mol kg}^{-1}$ approximately. Thus we believe that there is not "offset" of oxygen measurements between the cruises in 1992 and 2003. In shallower depths including AAIW (400 – 1000 m depth), significant oxygen change between 1992 and 2003 was not found. This contrasts well with recent decrease of oxygen concentration in intermediate water in the North Pacific (Emerson et al., 2001; Watanabe et al., 2001). We found oxygen increase and decrease in the subsurface oxygen minimum layers (about 100-600 m depth) in the east of 71°W. However, it is unknown whether these changes are decadal change of oxygen concentration because the oxygen concentration changes steeply change with depth.

References

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- Emerson, S, S. Mecking and J.Abell (2001) The biological pump in the subtropical North Pacific Ocean: nutrient sources, redfield ratios, and recent changes. *Global Biogeochem. Cycles*, 15, 535-554.
- Watanabe, Y. W., T. Ono, A. Shimamoto, T. Sugimoto, M. Wakita and S. Watanabe (2001) Probability of a reduction in the formation rate of subsurface water in the North Pacific during the 1980s and 1990s. *Geophys. Res. Letts.*, 28, 3298-3292.

Table 3.3.1 Results of the standardization and the blank determinations during MR03-K04 Leg-2

Date (UTC)	Time (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	
09-12-03	05:11	# 7	030417-31	030828-4	3.960	0.004	030828-5	3.962	0.009	127,125
09-13-03	12:38		030417-32	030910-1	3.961	0.004	030910-2	3.964	0.010	120,119
09-14-03	11:22		030417-33	030910-1	3.959	0.004	030910-2	3.963	0.010	118,117,116
09-15-03	07:24		030417-45	030910-3	3.961	0.006	030910-4	3.963	0.011	115,114,113
09-15-03	20:23		030417-34	030910-3	3.961	0.005	030910-4	3.963	0.011	112,111,110
09-16-03	16:05		030417-35	030910-5	3.962	0.005	030910-6	3.961	0.012	109,108,X17
09-17-03	10:15		030417-36	030910-5	3.959	0.006	030910-5	3.962	0.012	106,105,104
09-18-03	08:31		030417-37	030916-1	3.961	0.006	030916-2	3.965	0.011	103,102,101
09-18-03	23:02		030417-38	030916-1	3.961	0.005	030916-2	3.963	0.010	100,099,098
09-19-03	17:34		030417-39	030916-3	3.962	0.005	030916-4	3.965	0.008	097,096,095,094
09-21-03	03:48	# 8	030418-1	030916-6	3.966	0.005	030916-7	3.970	0.012	093,092,091
09-21-03	21:40		030418-2	030916-6	3.966	0.005	030916-7	3.968	0.009	090,089,088,087
09-22-03	18:21		030418-3	030916-6	3.965	0.006	030916-7	3.965	0.009	086,085,084
09-23-03	11:27		030418-4	030921-1	3.966	0.006	030921-2	3.968	0.009	083,082,081
09-24-03	05:36		030418-5	030921-1	3.964	0.005	030921-2	3.969	0.011	080,079,078,077
09-25-03	07:20		030418-6	030921-3	3.965	0.006	030921-4	3.968	0.012	076,075,072,071
09-25-03	19:31		030418-7	030921-3	3.962	0.007	030921-4	3.963	0.012	070,069,068,067
09-26-03	18:45		030418-9	030921-6	3.964	0.005	030921-7	3.970	0.009	066,065,064
09-27-03	13:12		030418-10	030921-6	3.968	0.006	030921-7	3.971	0.011	063,062,061,060
09-28-03	12:29		030418-11	030925-1	3.967	0.006	030925-2	3.969	0.010	059,X18,056
09-29-03	10:52	030418-12	030925-1	3.964	0.005	030925-2	3.969	0.009	055	
09-30-03	16:58	030418-16	030925-1	3.961	-	030925-2	3.967	-	054,053	
10-01-03	05:09	# 9	030418-17	030925-3	3.964	0.006	030925-4	3.970	0.010	052,051,050
10-01-03	18:34		030418-18	030925-3	3.967	0.007	030925-4	3.967	0.010	049,048,047
10-02-03	11:46		030418-19	030925-6	3.963	0.004	030925-7	3.968	0.010	046,045,044
10-03-03	03:43		030418-20	030925-6	3.964	0.005	030925-7	3.970	0.013	043,042,041
10-03-03	19:06		030418-21	030930-1	3.963	0.005	030930-2	3.968	0.012	040,039,038
10-04-03	10:37		030418-22	030930-1	3.963	0.007	030930-2	3.965	0.009	037,036,X19
10-05-03	06:03		030418-23	030930-3	3.964	0.007	030930-4	3.970	0.009	034,033,032
10-05-03	18:54		030418-24	030930-3	3.961	0.007	030930-4	3.964	0.008	031,030,029
10-06-03	12:07		030418-25	030930-6	3.964	0.005	030930-7	3.966	0.009	028,027,026
10-07-03	05:19		030418-26	030930-6	3.965	0.005	030930-7	3.967	0.013	025,024
10-08-03	13:45	# 10	030418-32	031005-1	3.966	0.005	031005-2	3.971	0.011	023,022,021
10-09-03	08:02		030418-33	031005-1	3.968	0.006	031005-2	3.969	0.010	020,019,018
10-10-03	01:15		030418-34	031005-3	3.965	0.004	031005-4	3.969	0.009	017,016,015
10-10-03	15:13		030418-35	031005-3	3.966	0.004	031005-4	3.970	0.010	014,013,012
10-11-03	09:23		030418-36	031005-6	3.966	0.005	031005-7	3.969	0.009	011,010,009
10-11-03	23:31		030418-37	031005-6	3.966	0.007	031005-7	3.970	0.012	008,007,006,005,004

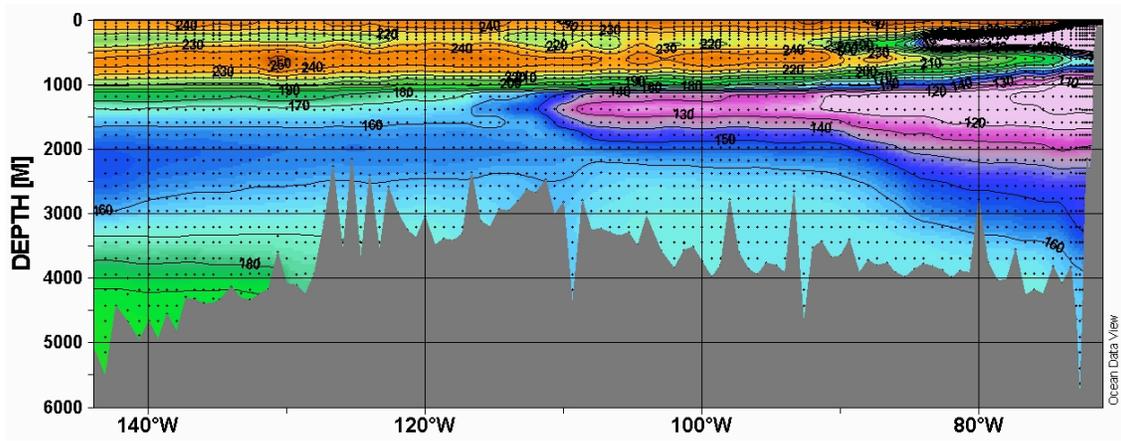


Figure 3.3.1 Dissolved oxygen concentration ($\mu\text{mol} / \text{kg}$) in 2003. This figure was drawn using Ocean Data View (R. Schlitzer, <http://www.awi-bremerhaven.de/GEO/ODV>, 2002).

3.4 Nutrients

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Yuki Otsubo (MWJ)

3.4.1 Objectives

The objectives of nutrients analyses during the R/V Mirai around the world cruises along ca. 30 deg. S in the Southern Hemisphere are as follows;

- (1) Describe the present status of nutrients in 2003-2004 in good traceability throughout the cruises. The target nutrients are nitrate, nitrite, phosphate and silicate (silicic acid?), respectively.
- (2) Study the temporal and spatial variation of nutrients based on the previous high quality experiments data of WOCE, GOESECS, IGY and so on.
- (3) Study of temporal and spatial variation of nitrate:phosphate ratio, so called Redfield ratio.
- (4) Obtain more accurate estimation of total amount of nitrate, phosphate and silicate silicic acid? in the interested area.
- (5) 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. N-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 silicic acid (hereafter 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 for each parameter are shown in Fig.3.4.1-3.4.4.

3.4.2.2 Sampling procedures

Sampling of nutrients followed that trace gases, oxygen 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.

No transfer was made and the vials were set an auto sampler tray directly. Samples were analyzed as rapidly as possible after collection, and then the samples were analyzed within 5 hours in average.

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-ware used were gravimetrically calibrated. Plastic volumetric flasks were gravimetrically calibrated at the temperature of use within 2-3 K

- (1) 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 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 2-3 K of the calibration temperature.

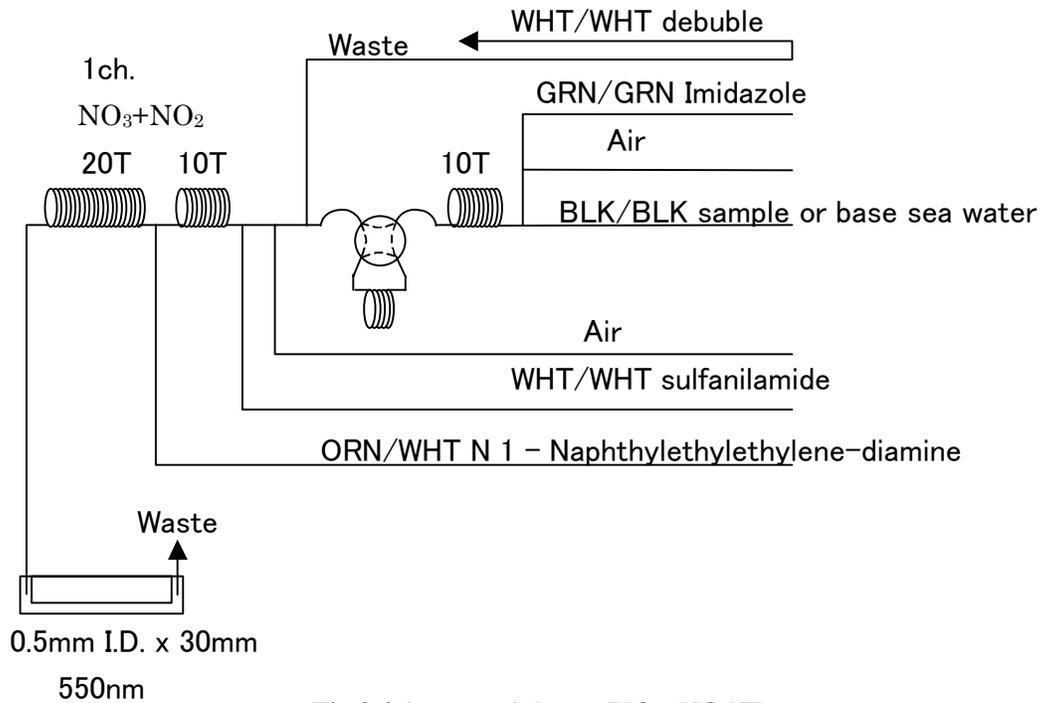


Fig.3.4.1 1ch. (NO₃+NO₂)Flow

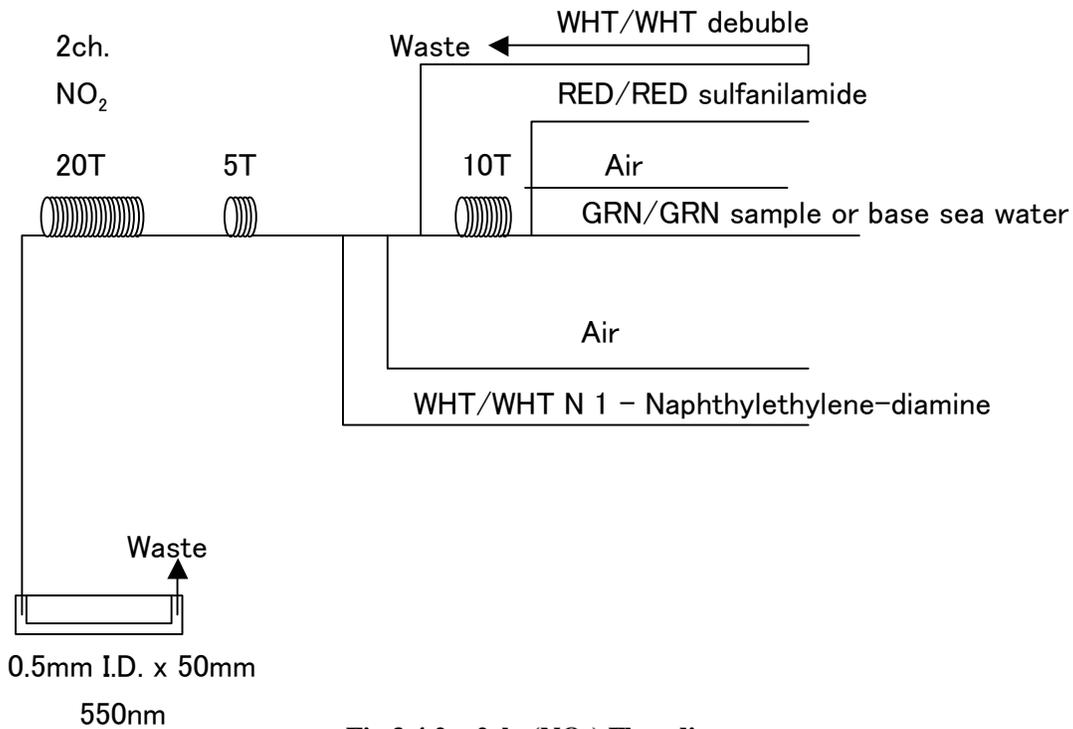


Fig.3.4.2 2ch. (NO₂) Flow diagram.

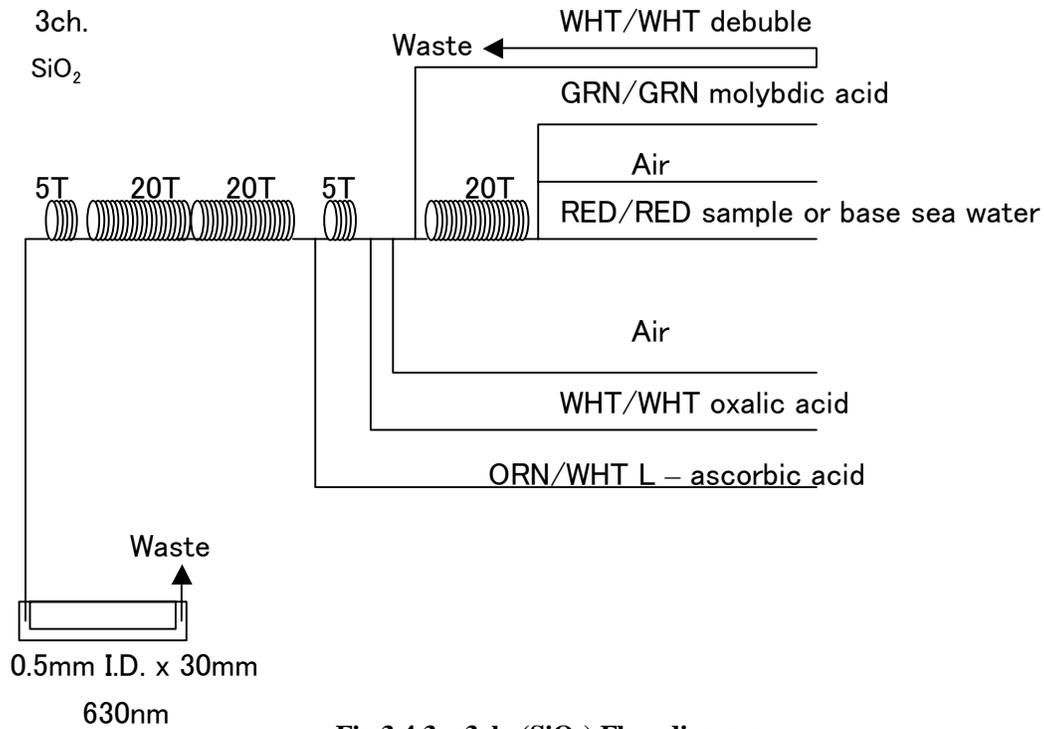


Fig.3.4.3 3ch. (SiO₂) Flow diagram.

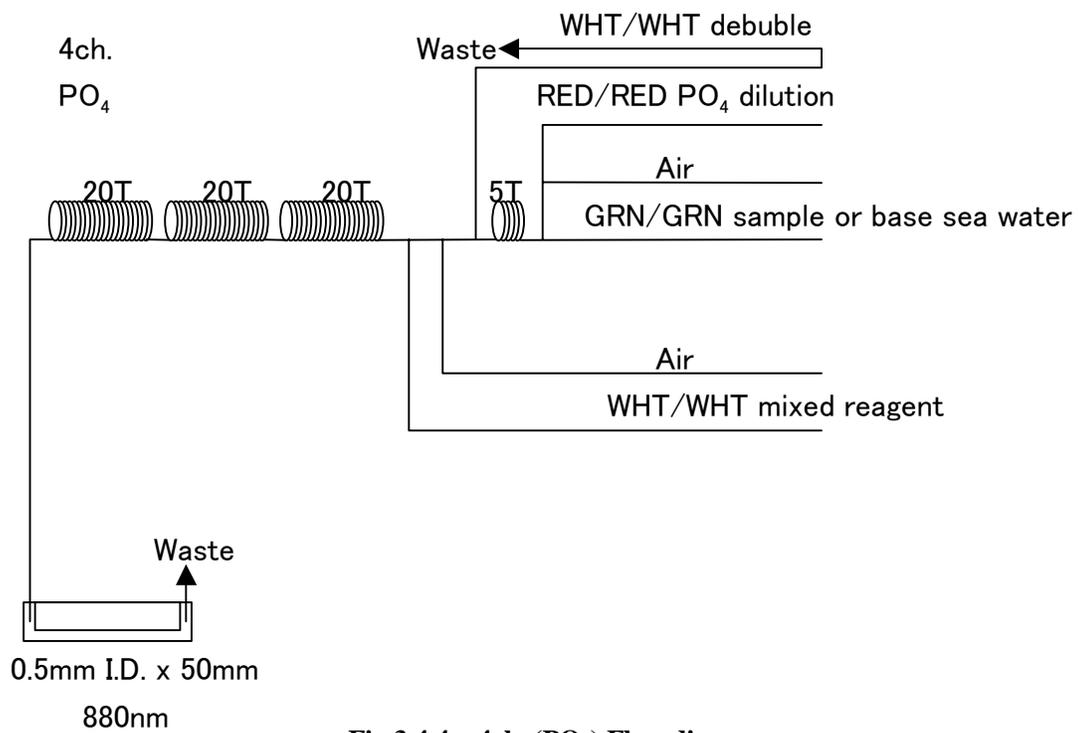


Fig.3.4.4 4ch. (PO₄) Flow diagram.

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 2 K. The weights obtained in the calibration weighings (weightings?) were corrected for the density of water and air buoyancy.

(2) 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

(1) 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 was 98.9%. We use that value to adjust the weights taken.

(2) 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.

(3) Low-Nutrient Seawater (LNSW).

Surface water having low nutrient concentration was taken and filtered using 0.45 μm 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 prior of the cruise.

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 are prepared according recipes as shown in Table 3.4.2. All volumetric laboratory tools were calibrated prior the cruise as stated in chapter 3.4.3.1.1. 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	1350	0.0	13.5	27.0	40.5	54.0
$\text{NO}_2(\mu\text{M})$	4000	40	0.0	0.4	0.8	1.2	1.6
$\text{SiO}_2(\mu\text{M})$	36000	5040	0.0	50	100	150	200
$\text{PO}_4(\mu\text{M})$	4500	90	0.0	0.9	1.8	2.7	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	40 ml
C-2	5 ml	5 ml	30 ml
C-3	10 ml	10 ml	20 ml
C-4	15 ml	15 ml	10 ml
C-5	20 ml	20 ml	0 ml

3.4.3.2 RMNS

To get the more accurate and high quality nutrients data to achieve the objectives stated above, huge number 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 $0.5 \mu\text{mol kg}^{-1}$ for 345 crossovers at world oceans, though the maximum was $1.7 \mu\text{mol kg}^{-1}$ (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).

3.4.3.2.1 RMNS preparation

(1) 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 $5\text{-}50 \mu\text{mol l}^{-1}$) and 0.8% (range $0.5\text{-}5 \mu\text{mol l}^{-1}$), respectively. For phosphate, slight increase by $0.02\text{-}0.07 \mu\text{mol l}^{-1}$ 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.

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 $0.45 \mu\text{m}$ (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 $0.2 \mu\text{m}$ (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.

(2) 180 RMNS packages and 500 bottles of lot AH for this cruise

RMNS lots T, AN, AK, AM and O are prepared to cover the nutrients concentrations in the interested sea area. About 180 sets of 5 RMNS lots are prepared. These packages will be used daily when in-house standard solutions renewed daily. 500 bottles of RMNS lot AH are prepared to use every analysis at every hydrographic stations planned about 500 during the cruise. These RMNS assignment were completely done based on random number.

3.4.3.2.2 The homogeneity of RMNS and consensus values of the lot AH

The homogeneity of lot AH and analytical precision are shown in table 3.4.3. These are for the assessment of the magnitude of homogeneity of the RMNS bottles those are used during the cruise. As shown in table 3.4.3, the homogeneity of RMNS lot AH 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 about factor two. The homogeneity for lot AH is same order of magnitude for previous RMNS of lot K.

Table 3.4.3 Homogeneity of lot AH derived from 30 samples measurements and analytical precision onboard R/V Mirai in May 2003.

	Phosphate	Nitrate	Silicate
	CV%		
RMNS			
AH	0.83%	0.39%	0.13%
(K)	(1.0%)	(0.3%)	(0.2%)
Precision	0.39%	0.36%	13%

note: N=30 x 2

3.4.4 Precision of nutrients analyses during the cruise

Precision of nutrients analyses during the cruise was evaluated based on the replicate analyses of five samples in each run. Summary of precisions are shown in Table 3.4.4. As shown in table 3.4.4 and figures 3.4.5-3.4.7, the precisions for each parameters are generally good considering the analytical precisions estimated from the simultaneous analyses of 60 samples in May 2003. Analytical precisions previously evaluated were 0.39% for phosphate, 0.36% for nitrate and 0.13% for silicate, respectively. Then we can conclude that the analytical precisions for phosphate, nitrate and silicate were maintained throughout leg 1 except a few outliers. We also found that the precisions tend to worse from the beginning to the end of leg 1.

Table 3.4.4 Summary of precision based on the replicate analyses of five samples in each run.

	Phosphate	Nitrate	Silicate
	CV%	CV%	CV%
Mean	0.21	0.20	0.14
Maximum	0.49	0.53	0.33
Minimum	0.0	0.06	0.05
N	75	73	76

The concentrations of replicate samples were 2.2-2.7 $\mu\text{mol kg}^{-1}$ for phosphate, 34-38 $\mu\text{mol kg}^{-1}$ for nitrate and 85-120 $\mu\text{mol kg}^{-1}$ for silicate, respectively.

The time series of precision are shown in figures 3.4.5-3.4.7

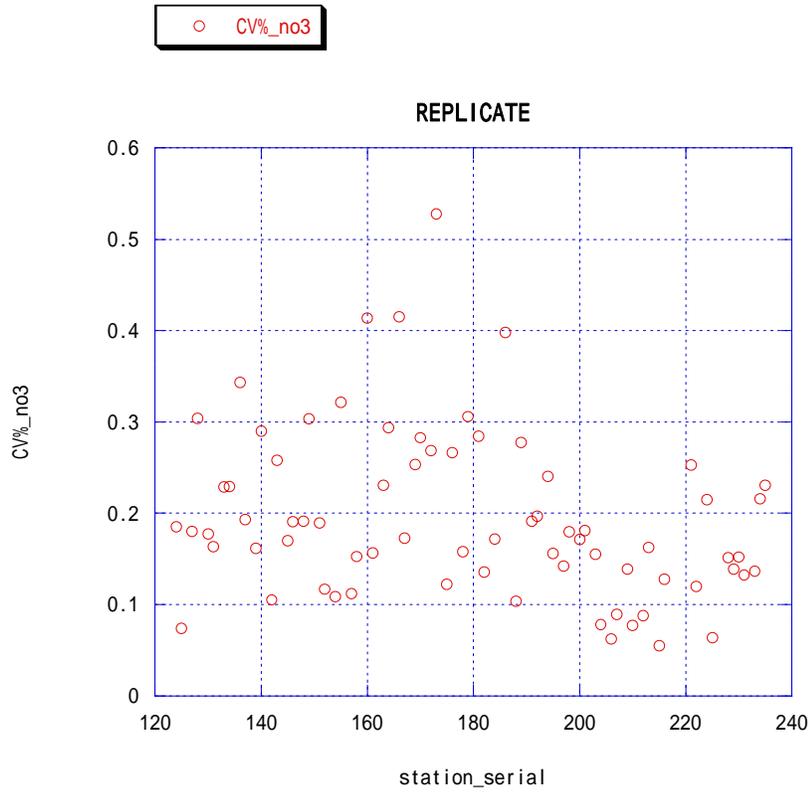


Fig. 3.4.5

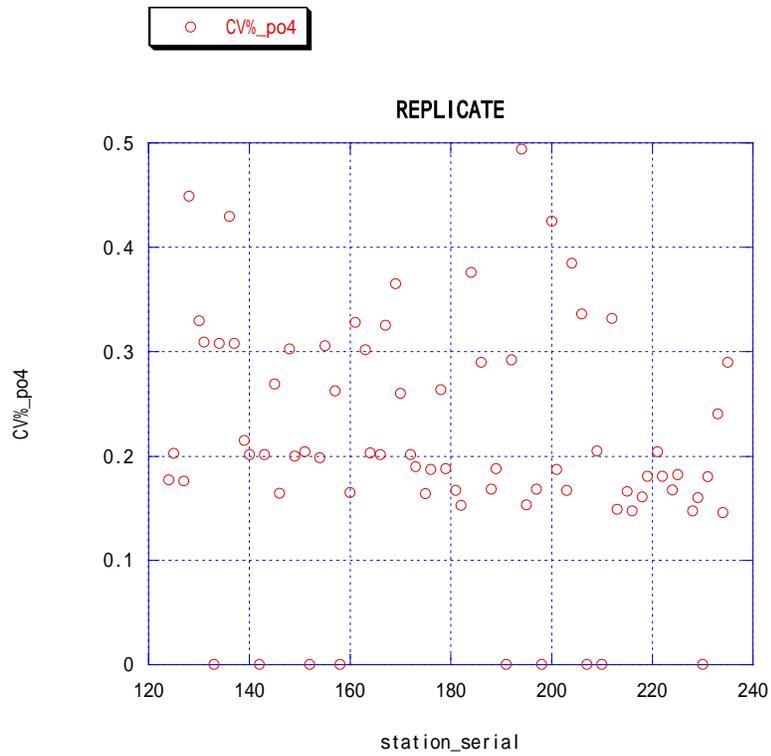


Fig.3.4.6

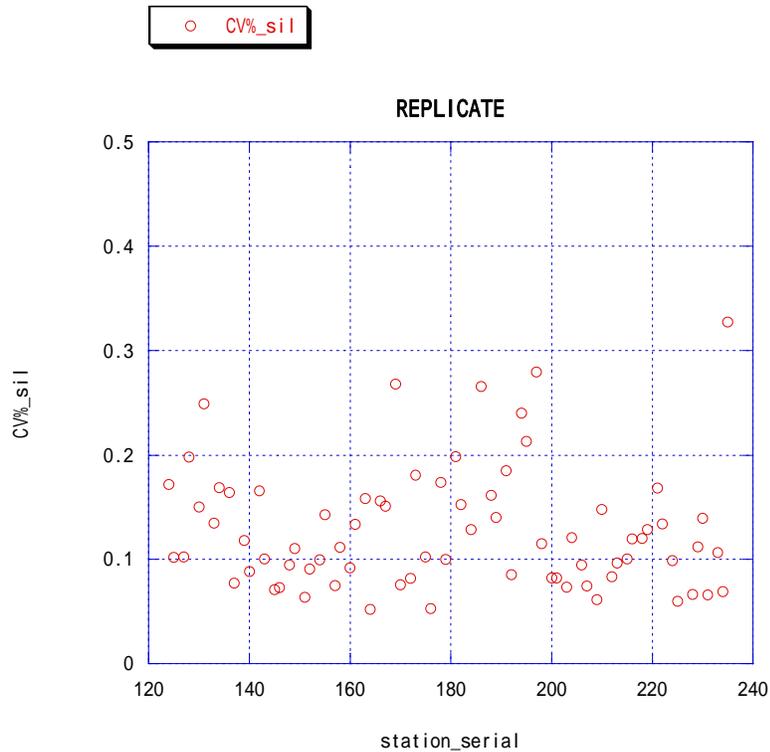


Fig.3.4.7

3.4.5 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 leg 2. The details were discussed post leg meeting at Tsukuba in Nov. 2003. Preliminary results are shown in figures 3.4.8-3.4.10.

During the leg2, nitrate concentrations of RMNS-AH were higher in the first half of the stations and became lower among the second half of the stations. Silicate concentrations of RMNS-AH were going to increase among the first half of the stations, then those were tend to decrease. For the phosphate concentrations, we could not see clear trend, which may be caused due to less resolution of phosphate analyses.

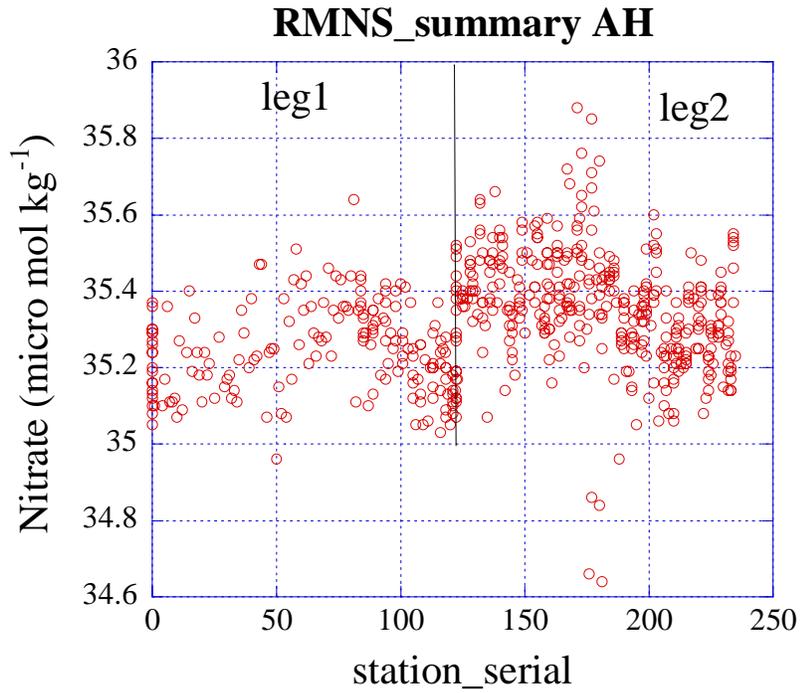


Fig. 3.4.8

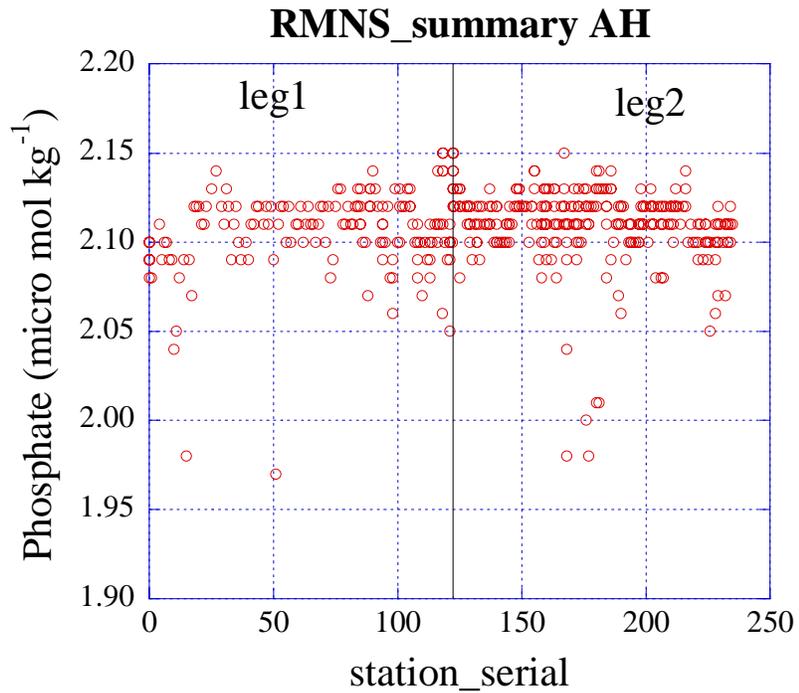


Fig. 3.4.9

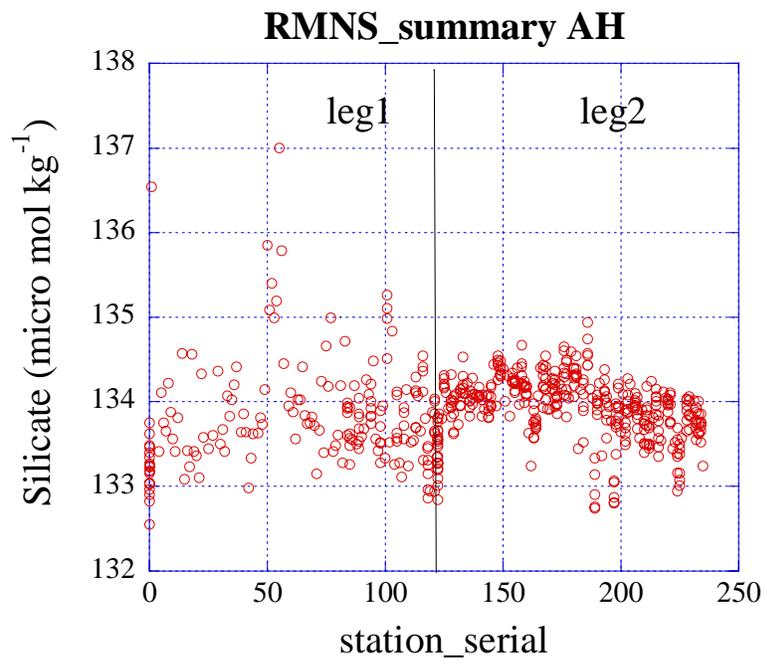


Fig. 3.4.10

3.4.6 Leg-to-leg traceability

Leg-to-leg traceability were examined based on the results of the statistics of RMNS-AH concentrations. As shown in table 3.4.5, the medians and averages of the nutrients concentration of RMNS-AH were in good agreement between leg1 and leg2. The deviation between two legs were less than 0.3% for nitrate, 0.2 % for silicate and 0% for phosphate, respectively.

Table 3.4.5 Results of the statistics of RMNS-AH concentrations

	NO3_Pacific	SiO2_Pacific	PO4_Pacific
Median	35.33	133.95	2.11
Mean	35.32	133.94	2.11
Stdev	0.15	0.45	0.02
CV%	0.42	0.34	1.00
Max	35.88	137	2.15
Min	34.64	132.74	1.97
max-min	1.24	4.26	0.18
Count	537	535	535

	NO3_leg1	SiO2_leg1	PO4_leg1
Median	35.25	133.75	2.11
Mean	35.25	133.88	2.11
Stdev	0.12	0.62	0.02
CV%	0.33	0.46	1.13
Max	35.64	137	2.15
Min	34.96	132.86	1.97
max-min	0.68	4.14	0.18
Count	166	165	165

	NO3_leg2	SiO2_leg2	PO4_leg2
Median	35.37	134	2.11
Mean	35.36	133.96	2.11
Stdev	0.15	0.35	0.02
CV%	0.43	0.26	0.94
Max	35.88	134.94	2.15
Min	34.64	132.74	1.98
max-min	1.24	2.2	0.17
Count	371	370	370

3.4.7 Problems/improvements occurred and solutions.

(1) At Tahiti, a slave unit of #2 machine of TRAACS800 were checked and a board and two cables were replaced because baseline shift were occurred frequently at the end of leg1. During the leg2, baseline shift occurred few at the slave unit of #2 machine of TRAACS800, which were for silicate and phosphate. This might contribute an improvement of reproducibility of silicate analyses during leg2, as shown in Table 3.4.5.

(2) Silicate concentration drift related with the direct flow from an air conditioner in the laboratory
 Silicate concentration drift related with the direct flow from air conditioner in the laboratory were observed during leg1. We changed a nominal laboratory temperature from 20 deg. C to 24 deg. C to avoid rapid temperature change. We also put temporally screen to shut the direct air flow from the air conditioner. We believe that these were also

contributed to get better reproducibility of silicate analyses during leg2.

(3) Decrease a reproducibility of nitrate analyses.

Since the interval of pump tubes was relatively long rather than expected due to the heavy load of analyses, this might decrease the reproducibility of nitrate analyses. We also got a problem that air had invaded into sample lines through a four-way valve at a reduction column.

3.5 Carbon Items : pH, A_T, TCO₂, TOC

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Taeko Ohama (MWJ)
Masaki Moro (MWJ)
Keisuke Matsumoto (MWJ)

3.5.1 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 are aimed at quantifying how much anthropogenic CO₂ absorbed in the Southern Oceans, where intermediate and deep waters are formed, are transported and redistributed in the Pacific, Atlantic and Indian Oceans. For the purpose, we measured CO₂-system parameters such as dissolved inorganic carbon (C_T), total alkalinity (A_T) and pH. For a carbon budget study, we also collected seawater samples for total organic carbon (TOC).

3.5.2 Apparatus

3.5.2.1 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 sea water dispensing system has an auto-sampler (6 ports), which takes sea water in a 300 ml borosilicate glass bottle and dispenses the sea water 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 sea water 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 was 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 sea water sample kept in a pipette is introduced to the stripping chamber by the same method as in adding an acid. The sea water 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, sea water samples (6) was programmed to repeat. The measurement of 2 % CO₂ gas was made to monitor response of coulometer solutions (from UIC, Inc.).

3.5.2.2 A_T

Measurement of A_T was made using a titration systems (Nippon ANS, Inc.). The systems comprise of a water dispensing unit, an auto-burette (Metrohm) and a pH meter (Thermo Orion), which are 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 a 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_T s 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.

3.5.2.3 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 was 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 was kept at 25.00 ± 0.05 °C in a thermostated compartment. First, absorbances of seawater only were measured at three wavelengths (730, 578 and 434 nm). Then the indicator was injected and circulated for about 4 minutes, to mix the indicator and seawater sufficiently. After the pump was stopped, the absorbances of seawater + indicator were 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.

3.5.2.4 TOC

Seawaters for TOC measurement were collected at every 4th to 5th stations. The seawater was collected into a test tube from Niskin bottles (approx. 50 ml) without a drawing tube. The seawater was frozen at approx. -20 °C as soon as possible after the water sampling. TOC will be measured in a laboratory on land.

3.5.3 Performances

3.5.3.1 C_T

The two systems had worked well during the leg without a major malfunction. Replicate analysis was made on every 9th seawater sample. The averages of the differences for systems A and B were 1.1 (n = 98) and 1.9 (n = 84) $\mu\text{mol kg}^{-1}$, respectively. The combined result was 1.5 $\mu\text{mol kg}^{-1}$ (n = 182).

3.5.3.2 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 averages of absolute differences between the replicate samples were 2.6 $\mu\text{mol kg}^{-1}$ (n = 170).

3.5.3.3 pH

The system had worked well with no troubles. The average of absolute differences between replicate samples were 0.0015 pH unit (n = 172).

3.5.4 Results

Cross sections of C_T , A_T and pH are illustrated in Fig. 3.5.1. The maximum of C_T (> 2300) existed in the layers from 1000 to 3000 m. The A_T increased gradually from a depth of about 1000 m to the bottom. The pH showed the minimum (approx. 7.5) in the layers from 1000 to 2000 m.

All the three items showed different distribution patterns in the eastern part of the cross sections.

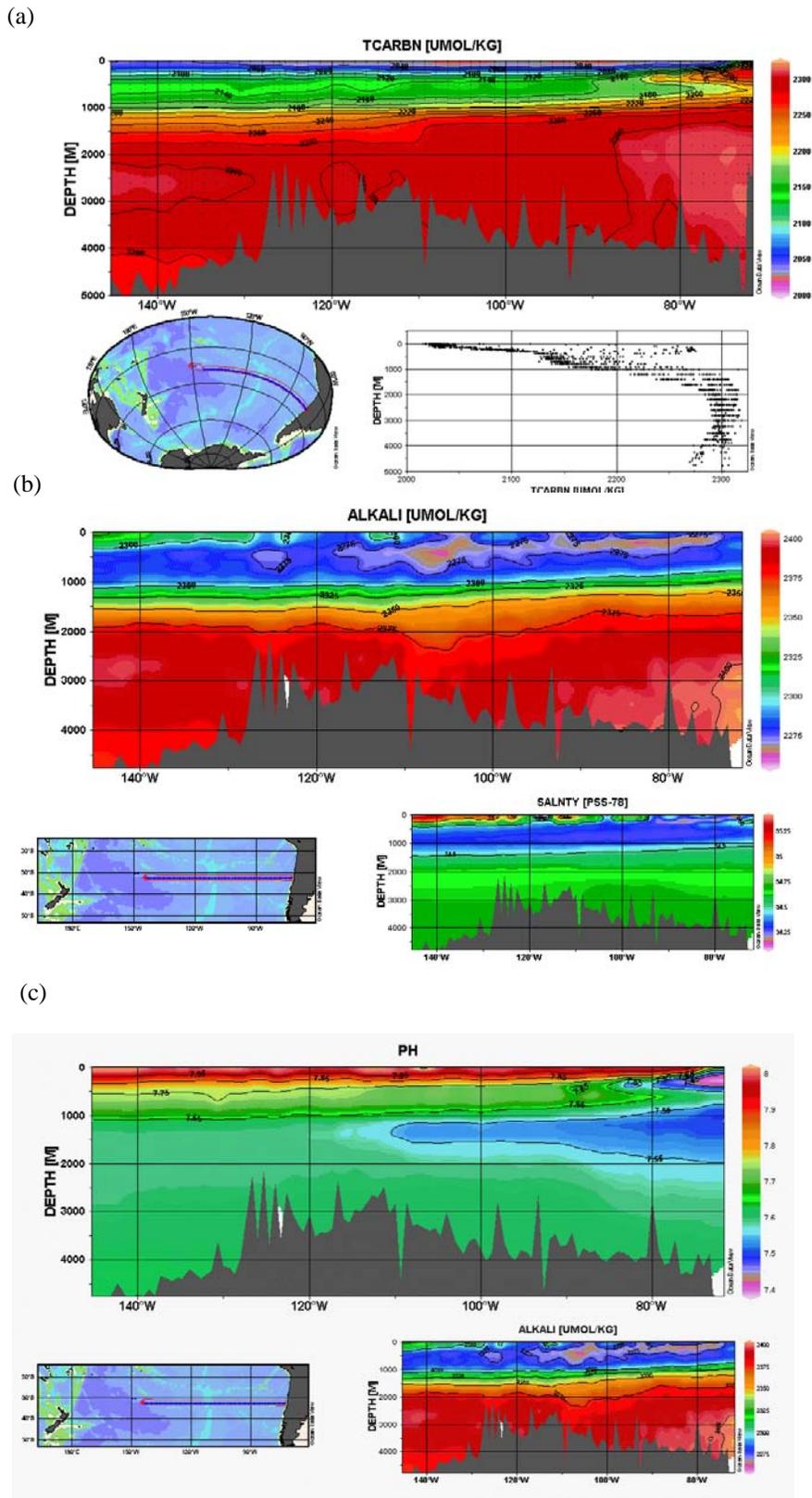


Figure 3.5.1. Cross sections of C_T (a), A_T (b) and pH (c) along the eastern half of WOCE P06 line.

3.6 Carbon-14, carbon-13

Yuichiro Kumamoto (JAMSTEC)

3.6.1 Objective

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

3.6.2 Sample collection

The sampling stations and number of samples are summarized in Table 3.6.1. All samples for carbon isotope ratios were collected at 23 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 0.05 cm³ μ l of saturated HgCl₂ solution. Then the bottle was sealed by a glass stopper with Apiezon M grease and stored in a cool and dark space on board.

3.6.3 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 μ mol), carbon-13 measurement (about 100 μ mol), and archive (about 200 μ mol). The extracted CO₂ gas for radiocarbon will be then converted to graphite catalytically on iron powder with pure hydrogen gas. The carbon-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 3.6.1 The sampling stations and number of samples for carbon isotope ratios.

Station	No. samples	No. replicate samples	Max. sampling pressure /db
P06C-117	31	3	4,762
P06C-113	31	3	4,640
P06C-109	31	3	4,456
P06C-105	29	3	4,306
P06C-101	27	3	3,650
P06C-097	28	3	3,988
P06C-093	20	2	2,183
P06C-089	22	2	2,625
P06C-085	24	3	3,089
P06C-081	26	3	3,352
P06C-077	24	3	2,970
P06E-071	23	2	2,722
P06E-067	30	3	4,496
P06E-063	26	3	3,343
P06E-X18	27	3	3,617
P06E-055	27	3	3,622
P06E-051	28	3	3,847
P06E-047	28	3	4,012
P06E-043	23	2	2,691
P06E-039	27	3	3,741
P06E-X19	27	3	3,774
P06E-031	28	3	4,054
P06E-027	28	3	3,934
P06E-023	23	3	2,811
P06E-019	26	3	3,608
P06E-015	28	3	3,886
P06E-011	36	3	6,054
Total	728	77	

3. 7. Freon

Masahide Wakita (JAMSTEC)
Shuichi Watanabe (JAMSTEC)
Hideki Yamamoto (MWJ)
Yuichi Sonoyama (MWJ)
Shinichi Tanaka (Hokkaido Univ.)

3.7.1 Objectives

Freons (Chlorofluorocarbons, hereafter CFCs) are the artificially formed gas. CFC-11 (CCl₃F), CFC-12 (CCl₂F₂), CFC-113 (C₂Cl₃F₃) are very useful chemical tracers to clarify the water movement. We determined dissolved CFC-11, CFC-12, CFC-113 concentrations in seawater on board.

3.7.2 Apparatus

Dissolved CFCs concentrations in seawater were determined with an electron capture detector - gas chromatograph (ECD-GC) attached the purge and trapping system.

Table 3.7.1 Instruments and analytical conditions

Instruments	
Gas Chromatograph:	GC-14B (Shimadzu Ltd.)
Detector:	ECD-14 (Shimadzu Ltd)
Column:	
Pre column:	Pola PLOT – QHT (i. d.: 0.53mm, length: 2m, tick: 6.0μm)
Main column:	Pola PLOT – QHT (i. d.: 0.53mm, length: 25m, tick: 6.0μm)
Temperature	
Oven:	75 to 130 deg-C
Detector:	270 or 290 deg-C
Trapping & desorbing:	-45 deg-C & 130 deg-C
Gas flow rate	
Carrier gas:	8 ~ 9ml/min
Detector Make UP:	16 ~ 21 ml/min
Column Purge:	4 ~ 7 ml/min
Sample purge:	~ 200ml/min

3.7.3 Procedures

3.7.3.1 Sampling

Seawater samples for CFCs measurement were collected from 12 liter Niskin bottles to N₂ purged 300ml glass bottle with specially ordered Swagelok unions. Two times bottle volumes of seawater sample were overflowed to minimize contamination with atmospheric CFCs.

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

3.7.3.2 Analysis

The CFCs analytical system was modified from the original design of Bullister and Weiss (1988). Sample volume was 150ml. The trap used to hold CFCs consists of a length of 1/8 in. o.d. SS tubing packed with 5 cm of Porapak T (80/100 mesh). Trapping and desorbing temperature were - 45 deg-C and 130 deg -C, respectively. The trapped gas was transformed to GC system directly. Analytical conditions were bellow.

3.7.4 Performance

The precisions of CFC-11, CFC-12 and CFC-113 were ± 0.03 pmol/kg (n = 78), ± 0.02 pmol/kg (n = 78) and ± 0.005 pmol/kg (n = 68), respectively obtained from duplicate determinations. 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.

3.7.5 Results

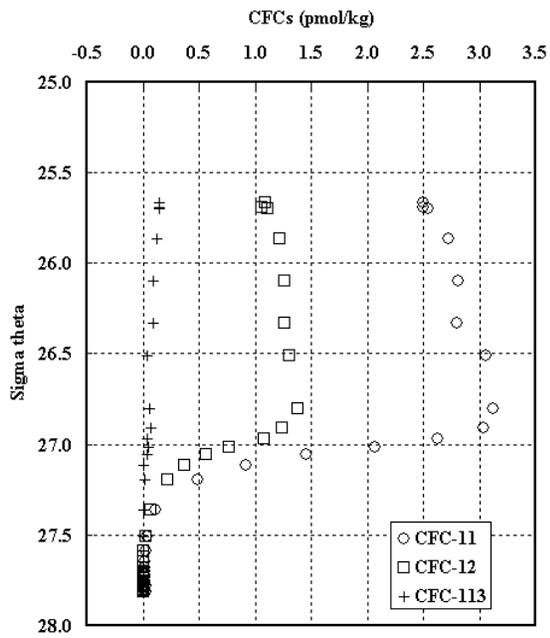
In this region, there had been little CFCs data in water column deeper than 1000 m water depth. We determined the CFC-11, -12 and -113 concentrations from surface to bottom layer, and found that CFC-11 and -12 penetrated up to 1200 m water depth (see figures). Further description and discussions will be done after calibration of standard gases and quality controls of the data.

3.7.6 Data archive

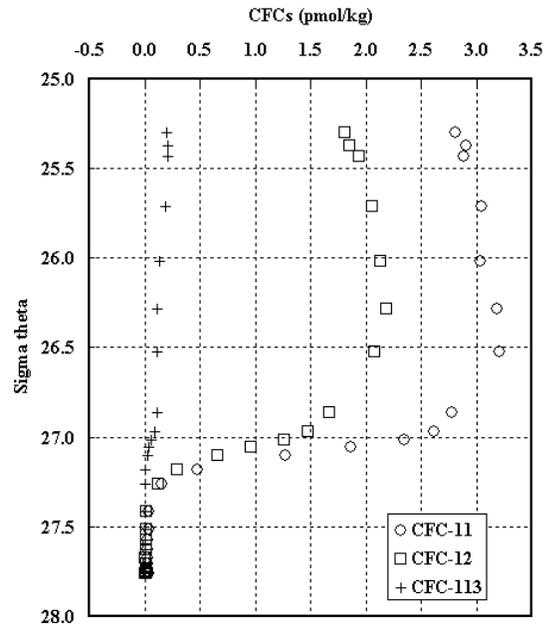
All data will be submitted to JAMSTEC Data Management office (DMO) and under its control.

3.7.7 Reference

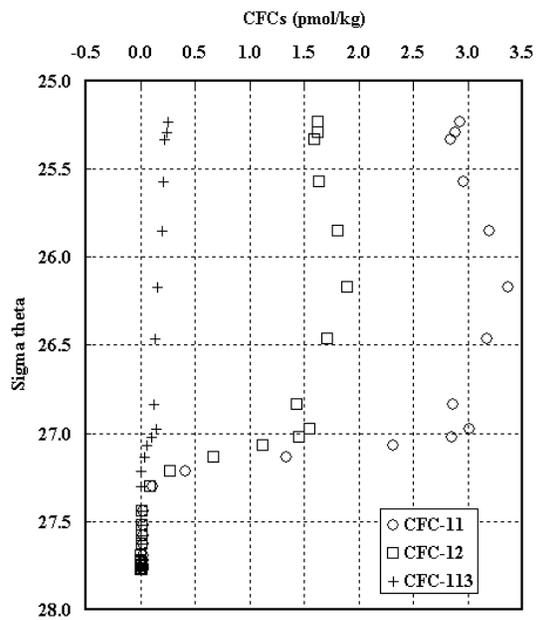
Bullister, J.L and Weiss R.F. 1988. Determination of CCl_3F and CCl_2F_2 in seawater and air. Deep Sea Research, 35, 839-853.



P06C-X17



P06E-X18



P06E-X19

Fig. 3.7.1 The examples of the profiles of dissolved CFCS against sigma theta at P06C-X17, P06E-X18 and P06E-X19. The symbols of circle, square and cross show CFC-11, CFC-12 and CFC-113, respectively.

3. 8. Radionuclides

Michio Aoyama (MRI)
Akira Takeuchi (KANSO)

3.8.1 Objectives

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

3.8.2 Target radionuclides

Main target radionuclides are ^{137}Cs , Pu and tritium.

For some samples, the other parameters such as ^{90}Sr and ^{129}I will be measured.

3.8.3 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 20liter cubitainers from the Niskin bottles. These samples were filtered using 0.45 um pore size filter and filled into appropriate size of tanks, cubitaners and bottle. Filters were also archived. Concentrated Nitric Acid was added to the samples to keep pH1.6 except for tritium samples.

Surface water samples were drawn through intake pump below several meter from the surface. Seawater of 85 liter were collected for ^{137}Cs , Pu and so on. For the tritium, seawater of 1 liter was collected.

3.8.4 Samples accomplished during leg 2

A total of 29 samples were collected for surface sample.

At the 15 stations, a total of 202 samples were collected for water column.

A total amount of the weight of the samples is around 5300kg and stored in a store at temperate temperature.

3.8.5 Problem occurred and solutions.

No problem occurred.

Table 3.8.1

SAMPLING RESULTS

(1/5)

Stn.	LATITUDE	LONGITUDE	SAMPLES		FILTER		REMARKS
			DEPTH	VOL	PORE SIZE	QUANTITY	
P06C-127	32°30' S	149°50' W	0db	86L	0.45 μ m	1	Cs137,Pu,H3,Sr
			100db	7L	0.45 μ m	1	Cs137,Pu,H3
			200db	8L	0.45 μ m	1	Cs137,Pu,H3
			400db	7L	0.45 μ m	1	Cs137,Pu,H3
			600db	21L	0.45 μ m	1	Cs137,Pu,H3
			800db	8L	0.45 μ m	1	Cs137,Pu,H3
			1000db	21L	0.45 μ m	1	Cs137,Pu,H3
			1200db	8L	0.45 μ m	1	Cs137,Pu,H3
			1400db	6L	0.45 μ m	1	Cs137,Pu,H3
			2000db	9L	0.45 μ m	1	Cs137,Pu,H3
			2400db	9L	0.45 μ m	1	Cs137,Pu
			3000db	9L	0.45 μ m	1	Cs137,Pu,H3
			3500db	9L	0.45 μ m	1	Cs137,Pu
			4000db	9L	0.45 μ m	1	Cs137,Pu,H3
			4500db	9L	0.45 μ m	1	Cs137,Pu
5000db	8L	0.45 μ m	1	Cs137,Pu,H3			
5151db	21L	0.45 μ m	1	Cs137,Pu,H3			
P06C-120	32°30' S	144°00' W	0db	86L	0.45 μ m	1	Cs137,Pu,H3,Sr
			100db	7L	0.45 μ m	1	Cs137,Pu,H3
			200db	8L	0.45 μ m	1	Cs137,Pu,H3
			400db	7L	0.45 μ m	1	Cs137,Pu,H3
			600db	21L	0.45 μ m	1	Cs137,Pu,H3
			800db	9L	0.45 μ m	1	Cs137,Pu,H3
			1000db	21L	0.45 μ m	1	Cs137,Pu,H3
			1200db	8L	0.45 μ m	1	Cs137,Pu,H3
			1400db	9L	0.45 μ m	1	Cs137,Pu,H3
			2000db	9L	0.45 μ m	1	Cs137,Pu,H3
			2400db	9L	0.45 μ m	1	Cs137,Pu
			3000db	8L	0.45 μ m	1	Cs137,Pu,H3
			3500db	7L	0.45 μ m	1	Cs137,Pu
			4000db	8L	0.45 μ m	1	Cs137,Pu,H3
			4500db	9L	0.45 μ m	1	Cs137,Pu
5000db	8L	0.45 μ m	1	Cs137,Pu,H3			
5153db	21L	0.45 μ m	1	Cs137,Pu,H3			
P06C-117	32°30' S	141°30' W	0db	86L	0.45 μ m	1	Cs137,Pu,H3,Sr
P06C-114	32°30' S	139°20' W	0db	86L	0.45 μ m	1	Cs137,Pu,H3,Sr
			100db	9L	0.45 μ m	1	Cs137,Pu,H3
			200db	21L	0.45 μ m	1	Cs137,Pu,H3
			400db	8L	0.45 μ m	1	Cs137,Pu,H3
			600db	21L	0.45 μ m	1	Cs137,Pu,H3
			800db	8L	0.45 μ m	1	Cs137,Pu,H3
			1000db	21L	0.45 μ m	1	Cs137,Pu,H3
			1200db	9L	0.45 μ m	1	Cs137,Pu,H3
			1400db	8L	0.45 μ m	1	Cs137,Pu,H3
			2000db	9L	0.45 μ m	1	Cs137,Pu,H3
			2400db	8L	0.45 μ m	1	Cs137,Pu
			3000db	9L	0.45 μ m	1	Cs137,Pu,H3
			3500db	9L	0.45 μ m	1	Cs137,Pu
			4000db	9L	0.45 μ m	1	Cs137,Pu,H3
			4500db	9L	0.45 μ m	1	Cs137,Pu
5054db	21L	0.45 μ m	1	Cs137,Pu,H3			

3.9 Bio Optical

Gadiel Alarcon (Univ. of Concepcion)
Alexander Galan (Univ. of Concepcion)
Dante Matellini (Peruvian Marine Research Institute)
Serkan Sancack (Middle East Technical University)

3.9.1 Introduction

The **Blue EArth GLobal Expedition 2003, 'BEAGLE 2003'**, is an oceanographic research program developed by Japan Marine Science and Technology Centre (JAMSTEC). The principal objective of this project is to enhance oceanographic research activities in the Southern Hemisphere, in accordance with the Sao Paulo Declaration (POGO, 2000). These are pointed out as follows: 1) To detect and quantify temporal changes in the Antarctic Overturn System corresponding to the global ocean and the southern Ocean warming during this century through high quality and spatially dense observation along old WHP (World Ocean Circulation Experiment Hydrographic Program 1991-2002) lines. 2.) To estimate the amount of anthropogenic carbon uptaken by the Antarctic Ocean. 3.) To provide a training environment in which trainees could get a hand-on experience in collecting biological, optical samples and optical data.

3.9.2 The Ship

The Oceanographic Research Vessel (R/V) "MIRAI" belongs to JAMSTEC and was completed in August 1997. As one of the largest research vessels in the world, it has equipment that is designed to reduce vibrations of the hull, so that it can make possible observation under stormy weather, and has a capacity of about 8.672 tons. Moreover, many buoys equipped with sensors for oceanographic and meteorological observation can be carried on board for efficient deployment and work. R/V Mirai's length, cruising speed and range are 128,58 meters, 16 knots and 12.000 nautical miles (about 22.000 km), respectively. This vessel can be extensively used year around in the Pacific Ocean and in high latitude sea areas where weather is harsh.

3.9.3 Bio-optical Objectives

The general objectives of the biological optical experiments of the cruise were:

- To know the Pacific Ocean primary productivity and bio-physical relationship in order to provide an important data base of bio-optical measurements in the Southern Ocean.

To reach this objective, light measurements will be made and data will be collected to obtain concentrations and kinds of photosynthetic pigments, and primary production rates. These observations will provide an important database for the Southern Oceans. Besides, bio-optical measurements will contribute to develop and validate algorithms of satellite-derived chlorophyll and primary production rates by sensors such as SeaWiFS, MODIS, and MERIS.

- To provide a training environment in which trainees could get a hands-on experience in collecting biological-optical and optical data. In addition, to obtain a feeling with the magnitudes, analysing and processing of bio-optical data.

3.9.4 Sampling Strategy

In order to attain the bio-optics objectives, experiments, water sampling and optics instruments were used according to standard protocols (taken from URL), therefore no specification about these will be provided here. The former were carried out onboard, some of the second will be analysed in different research laboratories (see below), and computing of the later will be developed onboard as preliminary process. Most of the water samples were collected around 8-10 a.m. and 2-4 p.m. (local time) and the light measurement were done close to the sampling times and when possible at midday. All measurements done are listed below:

I. BIOLOGICAL

Photosynthesis v/s Irradiance (PI) Experiments

Everyday 2 experiments were carried out onboard. The seawater was collected from surface using a bucket or the 12 litre Niskin bottles of the rosette (5-10 m.), depending on weather conditions. 42 bottles (+ 3 dark) were incubated with ¹³C in a Larsen box for 3 hours, then filtered and dried in an oven.

Storing: filters were labelled and stored in sets of 15 envelopes.

CDOM

The Coloured Dissolved Organic Matter analysing was immediately scanned with 0.2 µm filtered seawater in a 10 cm quartz cuvette into a CARY spectrophotometer.

Storing: no samples were stored. Results are in folder JAMSTEC/CDOM/Leg2/dailyfolder

Photosynthetic Pigments

A profile for Chlorophyll-a and Phaeopigments concentration were done in every PI experiment. Six standard depths were selected: Surface, 10, 50, 100, 150 and 200 meters. The pigments estimates were done onboard using a digital Turner Designs fluorometer.

Storing: no samples were stored. Results are in folder JAMSTEC/Leg2/Chl/daily files

Particulate Absorption

Two samples were collected from same depth of PI experiment. One sample was scanned into CARY spectrophotometer and the other was stored to be analysed in Bedford Institute of Oceanography (Att: Dr. Venetia Stuart). Besides, a blank was scanned everyday and one blank was stored as same as particulate absorption sample.

Storing: First sample results are in folder JAMSTEC/Absorption/Leg2/dailyfolder. Second, were frozen in liquid nitrogen into a labelled cryogenic vial and then stored in a deep freezer (-80°C).

High Performance Liquid Chromatography

Two samples were collected from same depth of PI experiment. These samples will be analysed using High Performance Liquid Chromatography in 2 different laboratories: Cape Town and Hobart.

Storing: Both samples were frozen in liquid nitrogen and then stored in 2-separated labelled aluminium foil envelopes into a deep freezer (-80°C).

II. OPTICS

The weather conditions were not good for collecting optics data due to high cloud cover most of the time. However, when there was no rain or drizzle to interfere with data collection, 2 rounds of measurements were carried out.

SIMBAD

The hand-held battery operated radiometer collects data in five spectral bands which are centred at 443, 490, 560, 670, 870 nm. This instrument has an external GPS antenna and measures direct sunlight intensity and water leaving radiance. The GPS must first find the instruments position before readings can be made. The sequence of measurements are 1 Dark, 3 Sun, 6 Sea, 3 Sun, and 1 Dark.

Storing: The files are in the folder JAMSTEC/Leg2/simbada/dailyfolder.

SIMBADA

This instrument is an above-water radiometer and it measures water-leaving radiance and aerosol optical thickness in 11 spectral bands. The bands are centred at 350, 380, 412, 443, 490, 510, 565, 620, 670, 750 and 870 nm. The instrument has an internal GPS antenna that must home in on 3 or more satellites before readings can be taken. The sequence of measurements are 1 Dark, 3 Sun, 6 Sea, 3 Sun, and 1 Dark. Under rough sea conditions it is not easy to maintain the instrument at the right angle.

Storing: The files are in the folder JAMSTEC/Leg2/simbada/dailyfolder.

Hyperspectral radiometer

This instrument has a large wavelength range. It measures the irradiance from 350 to 1000 nm at 0.5 nm intervals and has a special fibre optic that collects the irradiance from the sky and the sea surface. The downwelling irradiance is measured using a spectralon that diffuses the incident irradiance.

Storing: Files are in folder JAMSTEC/Leg2/HyperSp/dailyfolder.

Photosynthetic Active Radiation (PAR)

The PAR sensor was mounted outside, above the Atmospheric Observation laboratory. The Licor 1400 data logger connected to the sensor reads measurements every 60 seconds and records hourly average on the hour.

3.9.5 Pogo Students Activities

The general activities involved the participation in activities of water sampling from the rosette and the gaining of experience in biological experiments and optical instruments handling.

Students Remarks

Alex

I would like to thank POGO for this great training opportunity and to all the JAMSTEC people for their collaboration.

The knowledge of the techniques used to validate the remote sensing information has an incalculable value for me and is the bases for the development of my thesis project, the likes of which is part of the compromise with the entity that I represent.

Likewise, the recording and management of information has allowed me to improve the applications of these tools and the viability to be able to develop them in different types of research in the eastern coastal boundaries, as is the Chilean upwelling system.

The handling of this information that has permitted some bio-optical characterizations (mainly absorption of photosynthetic pigments and reflectance data) in an oligotrophic system, as is the South Pacific Gyre and the highly productive coastal system, has generated questions which lead to the placement of my working hypothesis, which I hope to prove during the development of my thesis.

Dante

About $\frac{3}{4}$ of the way through, we experienced some problems with the SIMBAD 7 and the SIMBAD 1.1 software. Both malfunctioned at the same time. When turning on the SIMBAD 7 a continuous beep would be heard and all the lights would light up. When initialising the SIMBAD 1.1 software it would crash every time so we had to use the 1.0 version. However when using the latter version to download the data all at once, some of the files would be corrupt, so we had to download them one at a time.

Simbada worked well and was easy to use. It was a shame we could not process the data. It is more practical to use on a rocking ship than Simbad although the sun is harder to find.

The hyperspectral radiometer worked well although we couldn't work out why the instrument took longer to stabilize during some measurements. The data was processed as indicated in the protocol and we obtained remote sensing reflectance. 5 wavelengths were chosen that approximate to the SeaWiFS bands. We compared the ratios of 4 bands with the highest band and plotted this against chlorophyll. This information could be used to calculate a new algorithm for primary production.

When making a note of some meteorological parameters such as cloud cover and sea condition, there was a difference in the interpretation depending on the observer. It would be useful to have some guide or visual scale to make these observations more precise.

All the lab experiments went well although we made some small mistakes at the beginning. It will be interesting to see how our results compare with those to be obtained from the duplicate samples.

The rosette sampling with the people from JAMSTEC was a good experience and taught me the necessity for strict control. I am happy to know that I have participated in this project.

In general I was able to learn and experience what it is to work in a laboratory on a ship for such a long time and simultaneously process the data. The light measurements were also new to me and I will transmit this experience to the people at my home institute in Peru in the hope that we can begin recording this kind of data when at sea.

Serkan

The SIMBAD data is processed using *calc_marref_v16PC.exe* for the first 20 measurements. The output file (simbad.leg2) can be found under Leg2 data in SIMBAD section. The files processed with *calc_marref_v16PC* as follows: For the first sea measurement of a cast first sun measurement is used, for the seconds the second sun measurements are used and so on up to sixth measurement. And first dark file is used for first three sea measurements and the second dark measurement used for last three sea measurements.

The absorption measurements were made with two different sessions with the software. Only for the last seven days of the sampling the same session was used for both measurement in a day. So the one blank measurement made in the morning has done with the same zero setting for two absorption measurements. In the beginning the second sampling of the day used a different zero setting than the zero setting for blank, due to exiting and opening of the program again.

The colour observations for sea also made by naked eye. It is observed that the colour changes dramatically near Tahiti and as getting far from Tahiti green colour changes to deep blue within tens of meters. During the cruise the

colour of the sea remained same (deep blue) and changed to green again at the station one before the one where the land (Chilean cost) can be seen with naked eye.

It was really interesting for me to have the chance to compare the bio-optical data collected in this cruise from the Pacific Ocean and the data we had in my institute cruises from Black Sea and Mediterranean. I think it will be very interesting to compare Pacific data with Mediterranean data that looks to have both similarities and dissimilarities. If it will be possible for me to use the bio-optical data of Beagle 2003 I would like to collaborate with other scientists from this cruise and work on the comparison of two oligotrophic seas (Pacific and Mediterranean). This also would be a great topic for my PhD thesis, which I have to start to write in the next semester in my institute.

3.9.6 Preliminary Results

This preliminary analysis of the results consists of data taken during 38 days of navigation on board the R/V Mirai, but needs to be reviewed later as no quality control has been carried out. Temperature, oxygen and salinity distributions were computed from CTD data, and correspond to downcast only. The photosynthetic pigments were analysed onboard, but they still have to be review too. The optical data for the hyperspectral radiometer and simbad have been processed but not the simbada data as this is an experimental instrument. The PI stations are shown in figure 3.9.1.

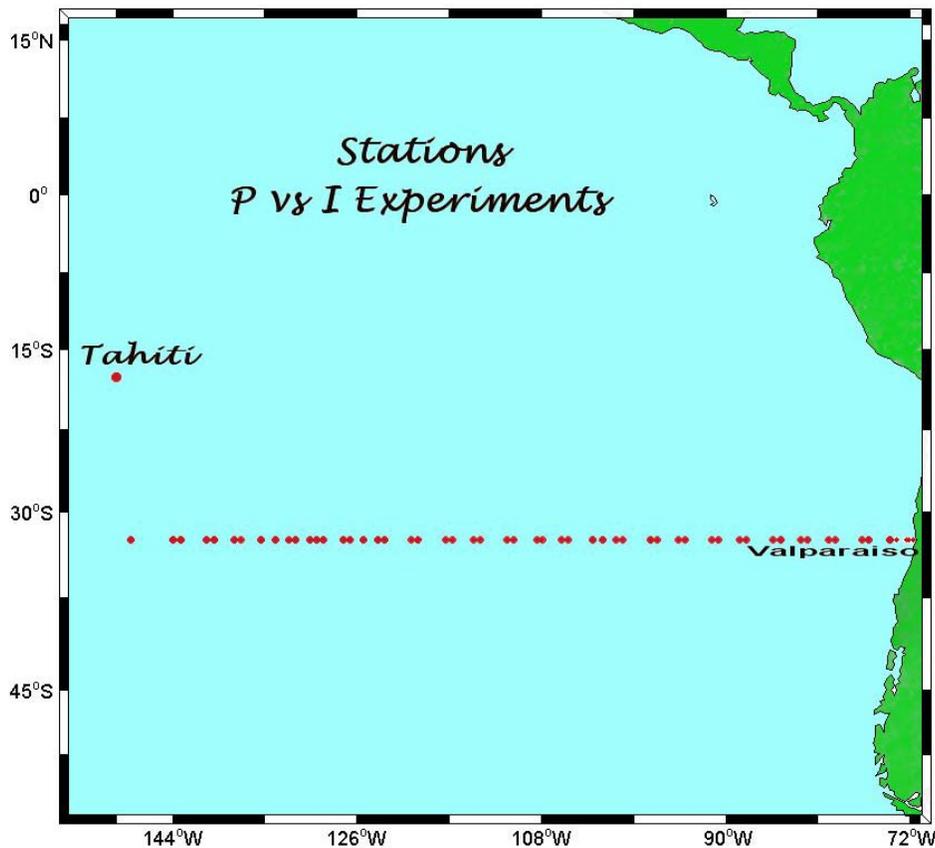


Figure 3.9.1. PI stations during Leg2 CTD data

Figure 3.9.2 shows the vertical structure of Temperature, Oxygen and Salinity between approximately 149°W and 71°W taken between the 12th September and 12th of October. The data corresponds to 114 CTD downcasts. Although in most stations the rosette reached the bottom of the ocean, we are only showing the top 500m that are to be used in the analysis of the bio-optical data. The temperature section seems to have a fairly even horizontal distribution with the thermocline appearing to be at a depth of around 150 to 200m between 149°W and 95°W.

Approximately at 95°W it begins to rise and upwells near the coast proving to be a typical distribution for the South Eastern Pacific. Meanwhile the oxygen and salinity sections show decreases in values around 130°W and 124°W respectively possibly indicating the meeting of two different water masses. However further analysis possibly involving water currents are required. Finally near the coast we can observe the oxygen minimum at a depth of about 150m. Note: to convert μM to ml/L divide by 44.6.

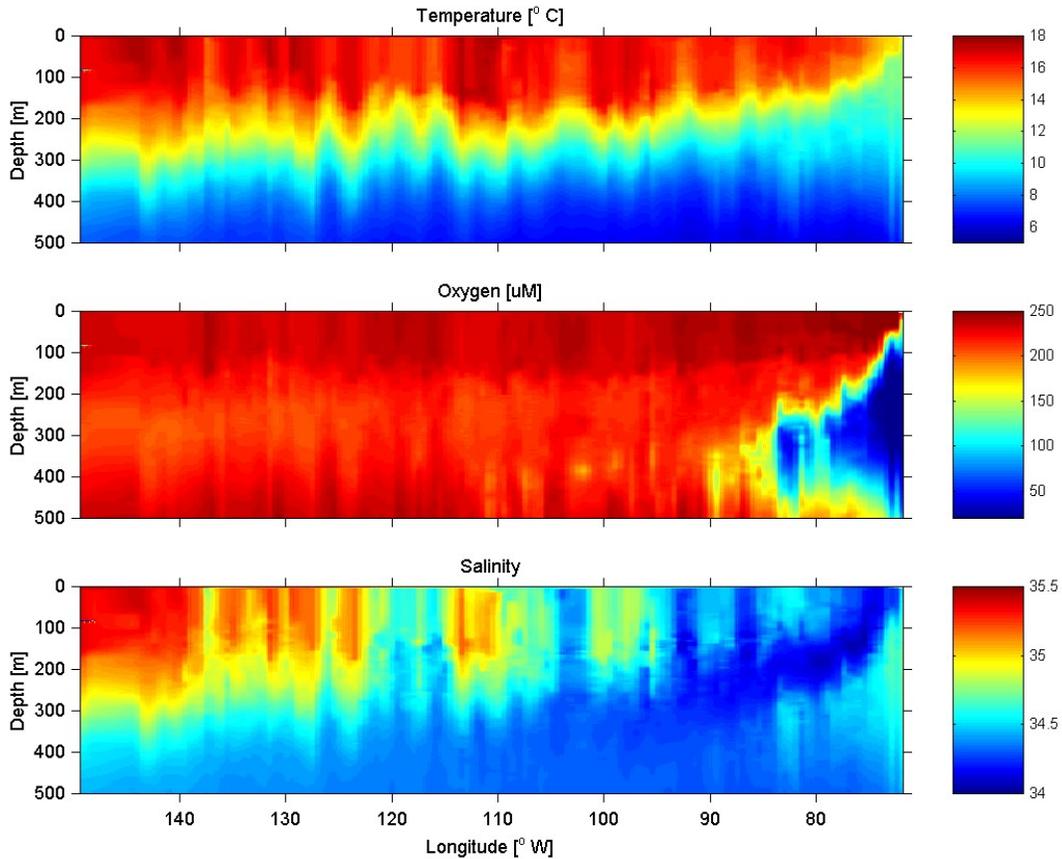


Figure 3.9.2 Temperature, oxygen, and salinity profiles.

Photosynthetic pigments

The chlorophyll-*a* and phaeopigments distribution from the surface to 200 meters depth of 56 profiles is shown in Figure 3.9.3. The highest concentrations were found near the coast and the maximum value was ca. $1.86 \text{ mg of Chl-}a \text{ m}^{-3}$ around 72°W. The lowest concentrations were located at 200m depth and several stations along the transect presented similar minimum values. At higher longitudes a daily shifting of chlorophyll-*a* between 100 and 150m was observed. The preliminary results suggest an important effect of the light penetration, depending on the sampling time (AM/PM). Between 120°W and 100°W the values became closer because of higher mixing of the water column mainly due to the high wind speed on those days. The phaeopigments were higher near to the coast too. The higher concentrations at 150 m along the transect probably are due to other kind of pigments (e.g. chlorophyll-*b*) and not as a degradation product. The HPLC analyses will give more details about what kind and how much pigments are presented in the water column.

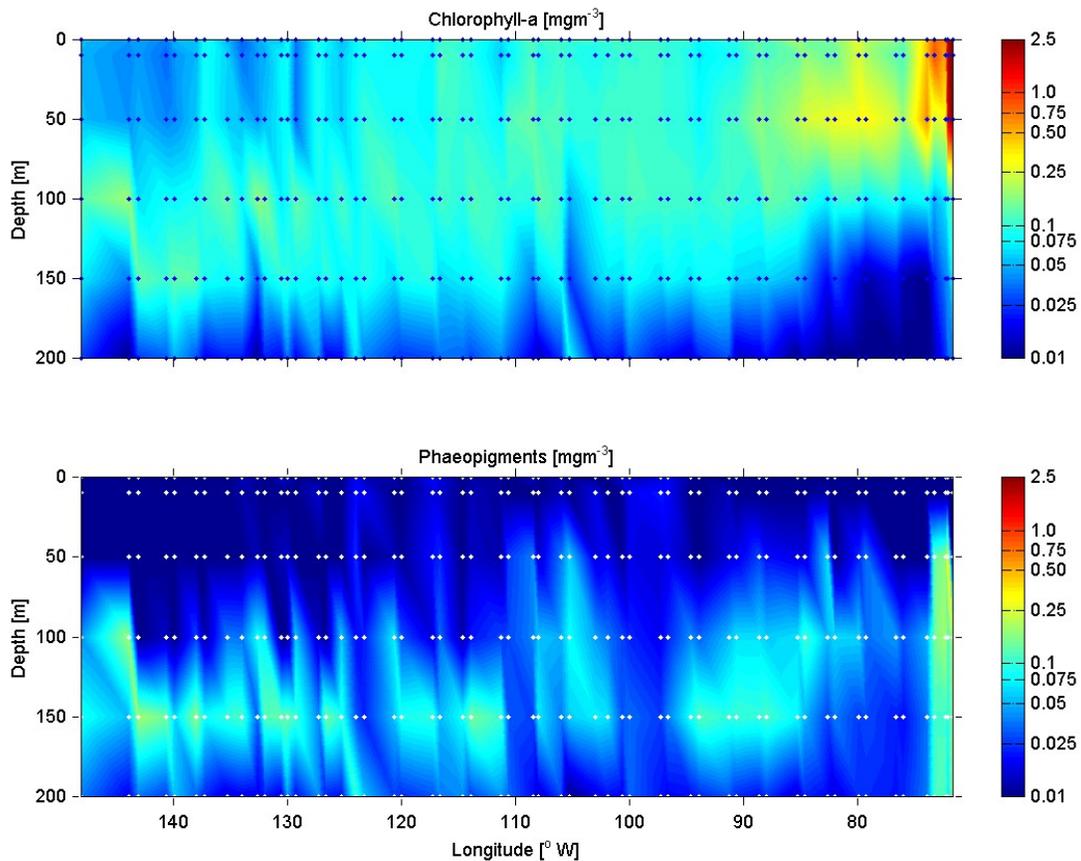


Figure 3.9.3 Chlorophyll and Phaeopigments section

Absorption

53 particulate and dissolved (CDOM) absorption scans were done onboard. The same amount of samples will be sent to Bedford Institute of Oceanography to be scanned by Dr. Venetia Stuart. A matlab routine was developed to analyse data, as follows:

```
% Routine for absorption averages of Particulate Sample (PS)
% Detritus Sample (DS); Particulate Blank (PB); Detritus Blank (DB)
% -----
% Condition 1: files should be belonging to the same scan
% Condition 2: files should have “ ; “ - “ and two lines of header
% Step 1: Make a list of kind of selected files
% Step 2: Make a change of signs by empty space and delete header
% Step 3: Store wavelength and average 10 scans of each one
% output: data of averaged values of absorption, data of spectral
%         absorption coefficients of phytoplankton and data of specific
%         absorption coefficient of phytoplanktonic pigments.
% Obs 1: Fluorometer Chl-a concentration must be download for
%        each scan
% Obs 2: A plot of specific absorption coefficient of phytoplanktonic
%        pigments for each analysis will be provide
% -----
```

% Thanks to Victor Villagran for supporting in function and script
% development
% Gadiel Alarcon
% Bio-optics group
% JAMSTEC Oceanographic cruise 'BEAGLE 2003'. R/V Mirai.
% Leg 2. Papeete - Valparaiso
% September 9th to October 16th. 2003

The data outputs will be provide in: JAMSTEC/Leg2/PreliminaryResult/Absorption.

Figure 3.9.4a and 4b, show the absorption averages spectrum for particulate (blue) and detritus (green) sample. The first scans should be checked.

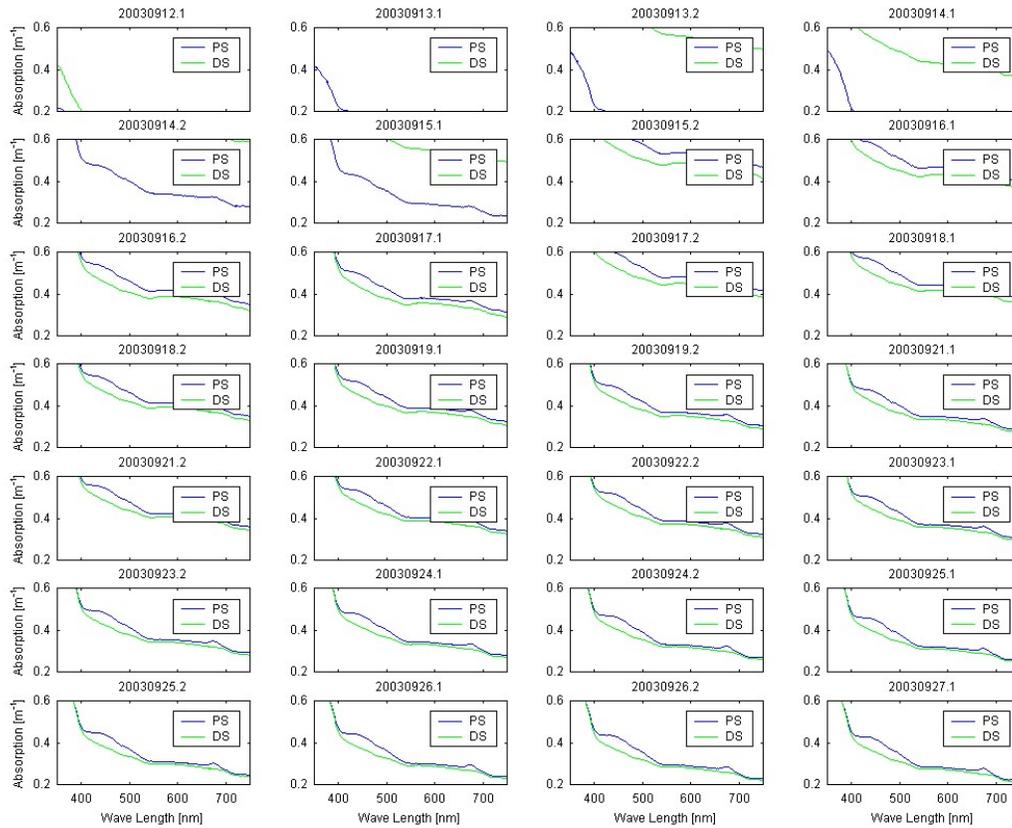


Figure 3.9.4a. Absorption averages spectrum particulate (blue) sample and detritus (green) sample

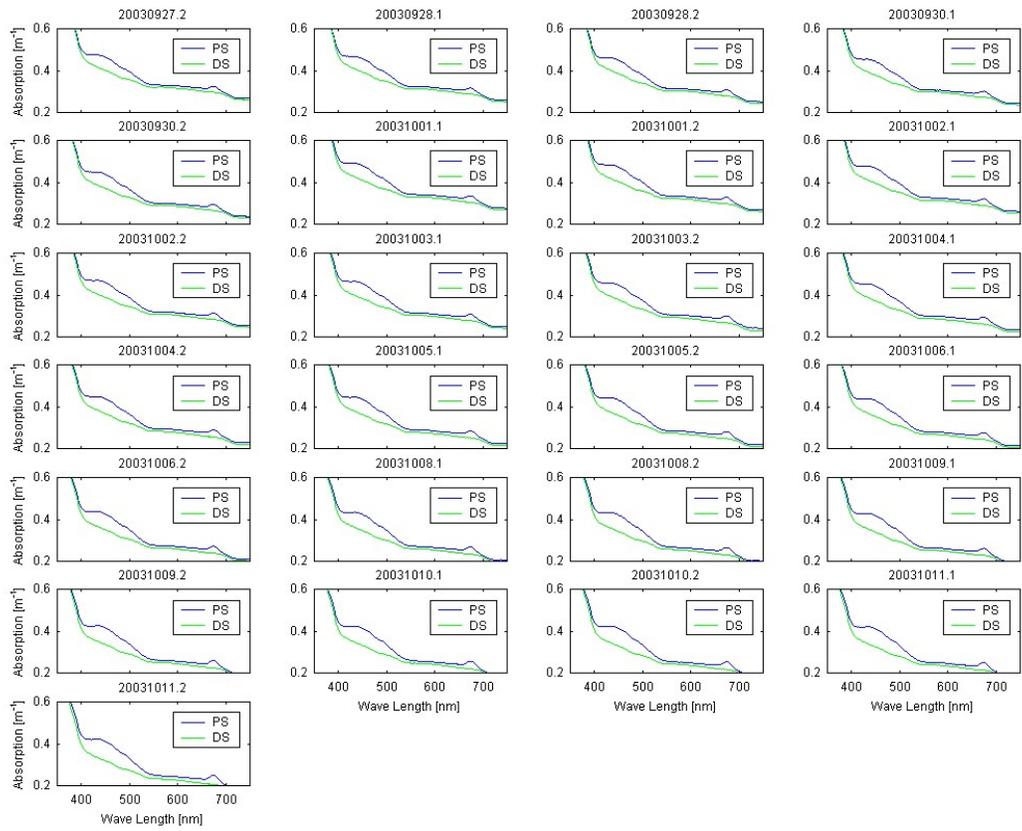


Figure 3.9.4b. Absorption averages spectrum particulate (blue) sample and detritus (green) sample

Figure 3.9.5a and 5b, show the absorption coefficient particles in suspension using two **Beta** values to correct for pathlength increase due to multiple scattering in the filter, according to Hoepffner and Sathyendranath (1992) (Beta 1)

$$\text{Beta 1} = 0.31[\text{OD}_{\text{pf}}(\lambda)] + 0.57[\text{OD}_{\text{pf}}(\lambda)]^2$$

This **Beta** is used for most kind of phytoplankton cells. Moore *et al.* (1995)

$$\text{Beta 2} = 0.291[\text{OD}_{\text{pf}}(\lambda)] + 0.051[\text{OD}_{\text{pf}}(\lambda)]^2$$

This **Beta** is used when high numbers of small cells are presented.

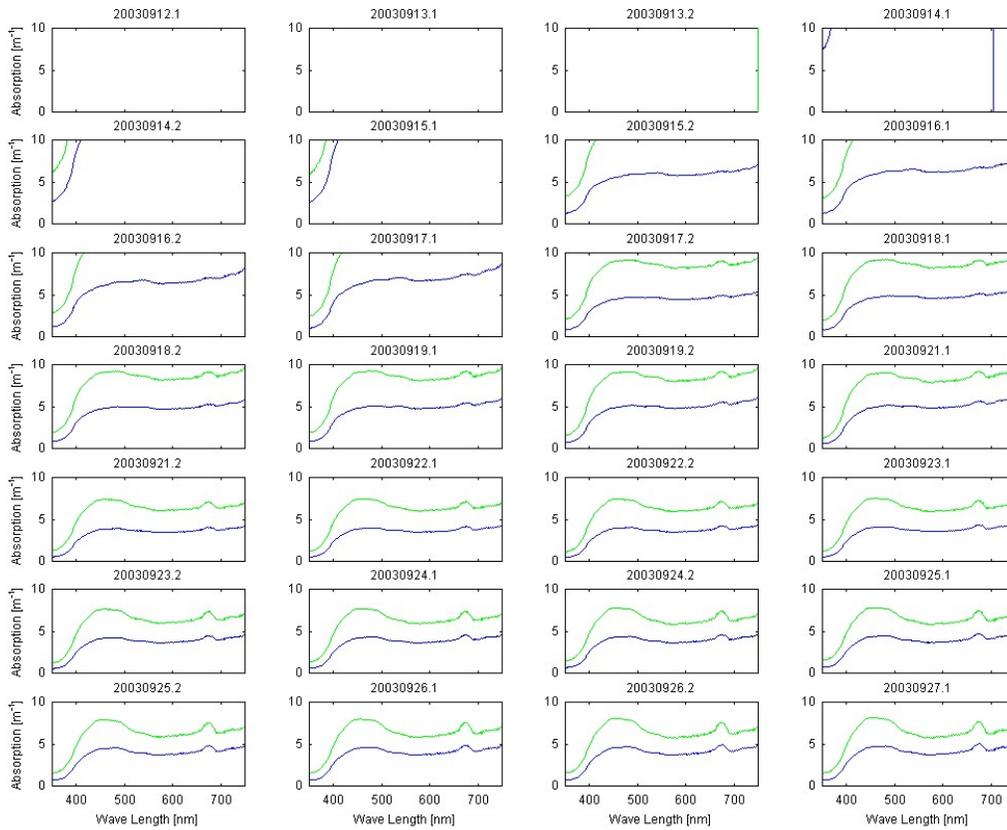


Figure 3.9.5a. Absorption coefficient particles in suspension (blue: using Beta 1; green using Beta 2)

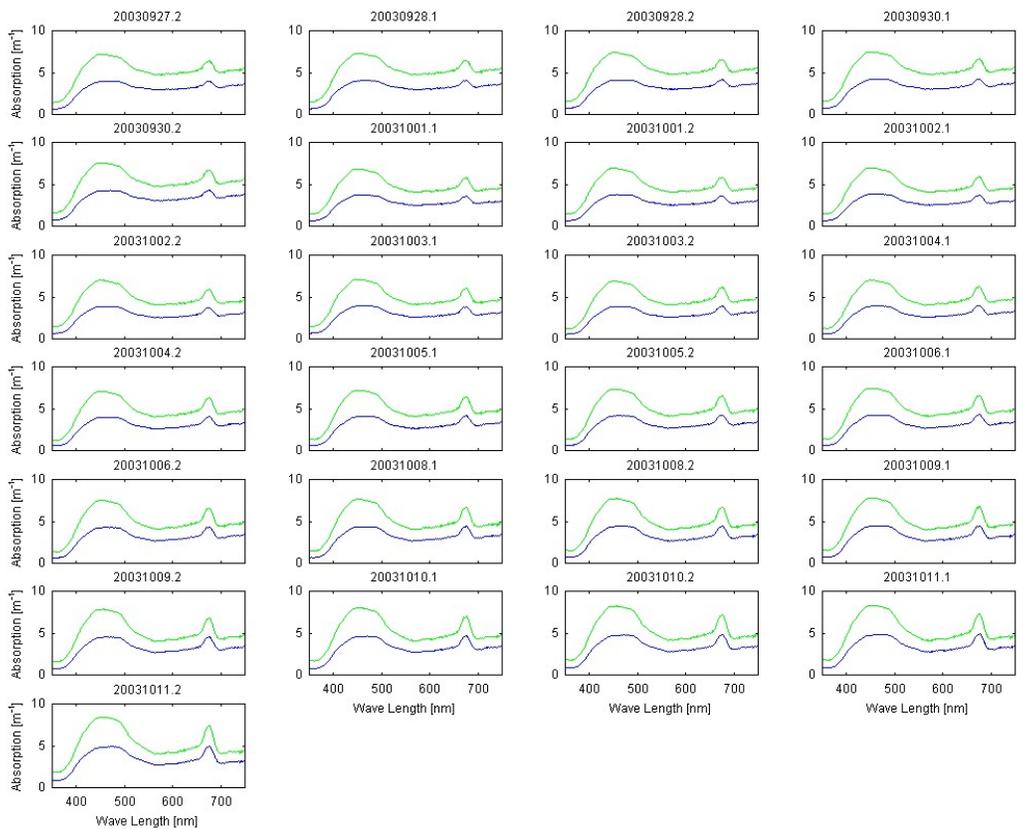


Figure 3.9.5b. Absorption coefficient particles in suspension (blue: using Beta 1; green using Beta 2)

Figure 3.9.6a and 6b, show the pigment specific absorption coefficient of phytoplankton (SAC), normalized by his corresponding chlorophyll-a concentration (fluorometry). SAC is computed using the *Beta 1* and SAC₂ using *Beta 2*.

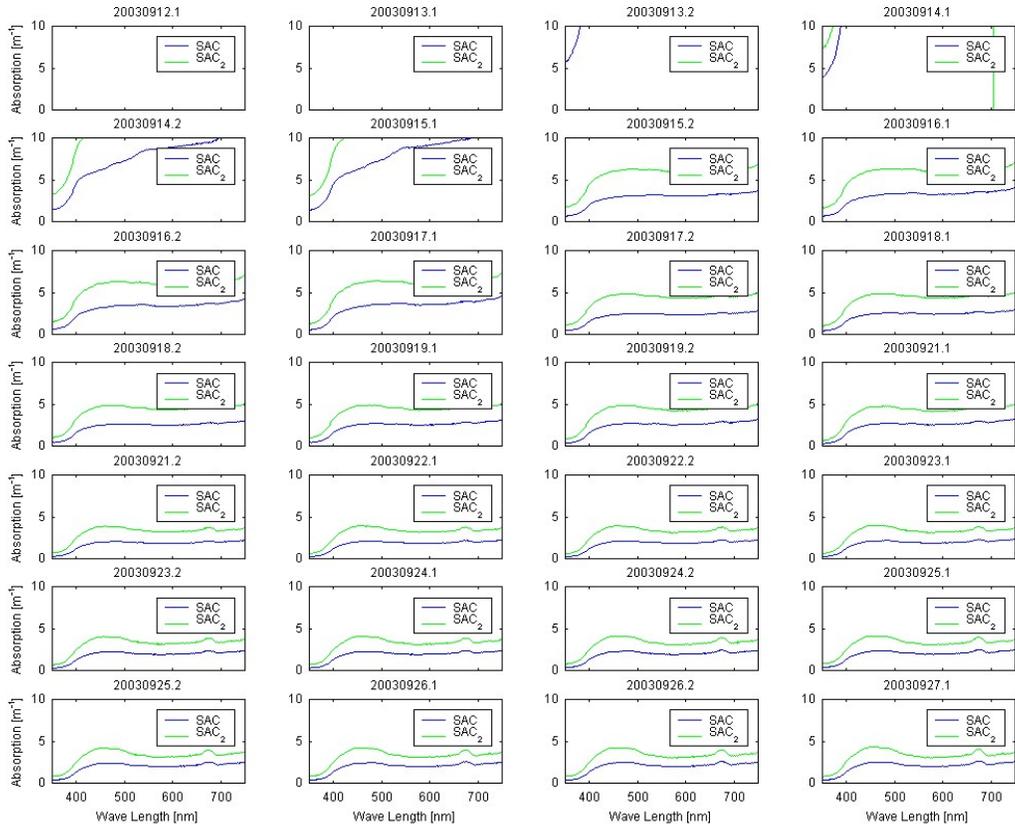


Figure 3.9.6a. Pigment specific absorption coefficient of phytoplankton

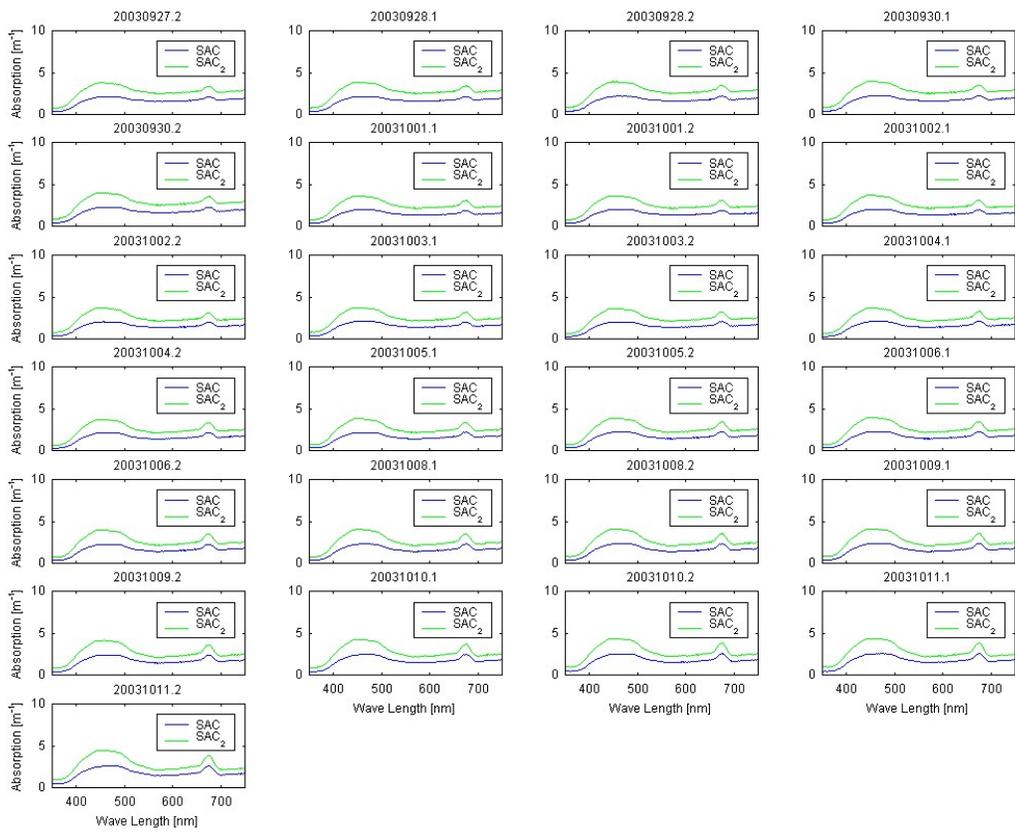


Figure 3.9.6b. Pigment specific absorption coefficient of phytoplankton

Figure 3.9.7a and 7b, show the CDOM absorption for the whole cruise. A routine similar to the absorption one was applied to process this data.

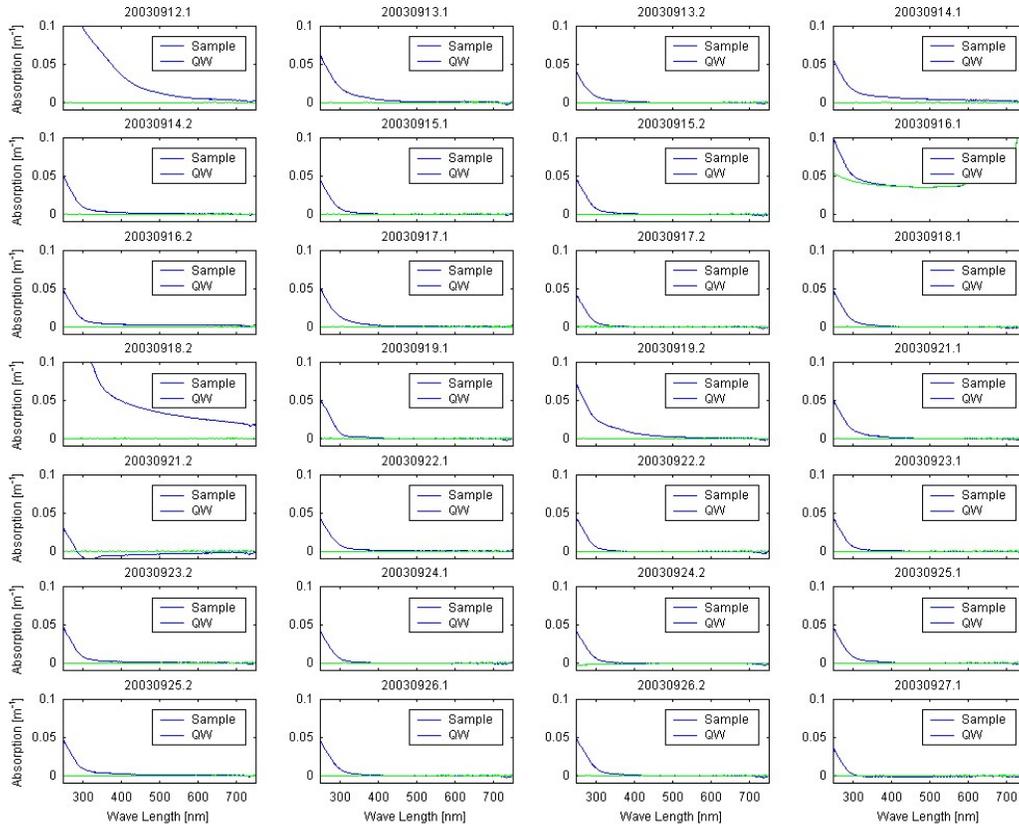


Figure 3.9.7a. CDOM absorption

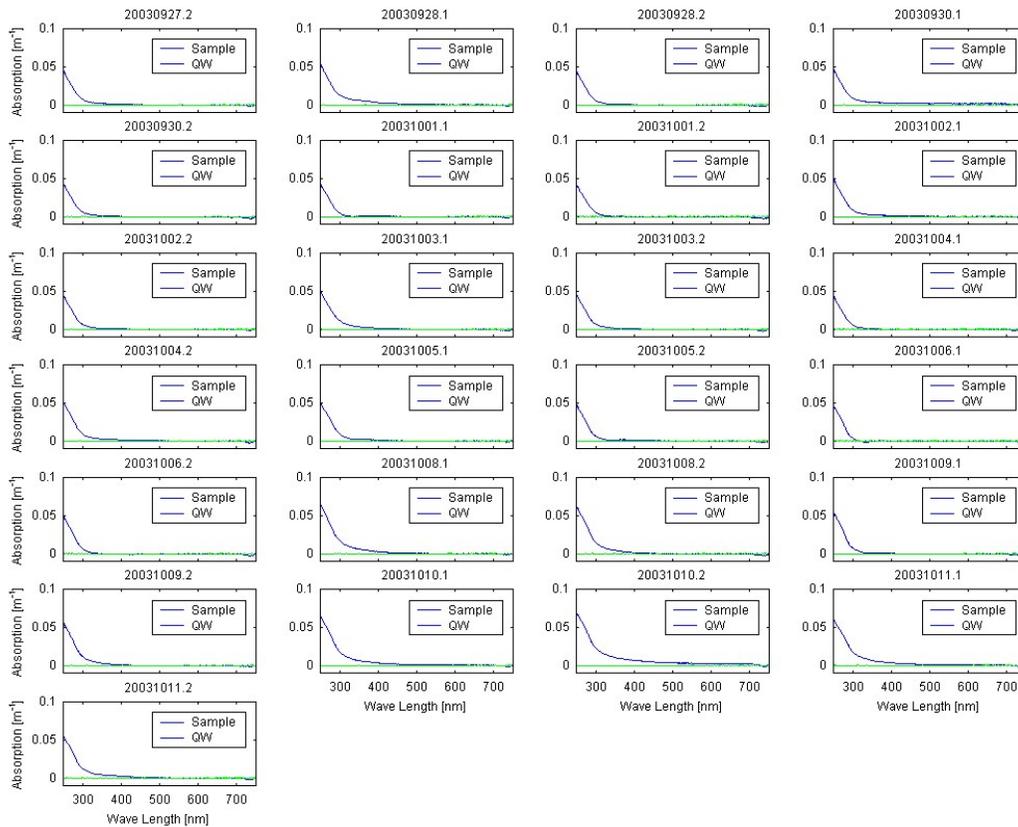


Figure 3.9.7b. CDOM absorption (cont.)

Bio-optics

A total of 33 hyperspectral radiometer measurements were taken. The data was computed using a matlab routine, as follows:

```
% Routine for hyperspectral radiometer data average, which include
% spectralon, sky and sea measurements. Besides, Rrs computing
% -----
% Condition 1: files should be belonging to the same observation
% Condition 2: files should have header and footprint
% Step 1: Make a list of kind of selected files
% Step 2: Erase header and footprint and download data
% Step 3: Store wavelength and average each observation.
% Step 4: Store integration time for each measure
% output: Data of averaged values of espectralon, sky and sea
%         measurements. Besides, Remote Sensing Reflectance (Rrs) and
%         corrected Rrs are computed.
% Obs 1 : A spectralon calibration file should be download to
%         correct all computing.
% Obs 2 : 2 graphics are provided. The former include averages values
%         of espectralon, sky ans sea plots. The last include Rrs
%         and corrected Rrs plots.
% -----
```

% Thanks to Victor Villagran for supporting in function and script
 % development
 % Gadiel Alarcon
 % Bio-optics group
 % JAMSTEC Oceanographic cruise 'BEAGLE 2003'. R/V Mirai.
 % Leg 2. Papeete - Valparaiso
 % September 9th to October 16th. 2003

Figure 3.9.8 shows the averaged spectrums of spectralon, sky and sea observations.

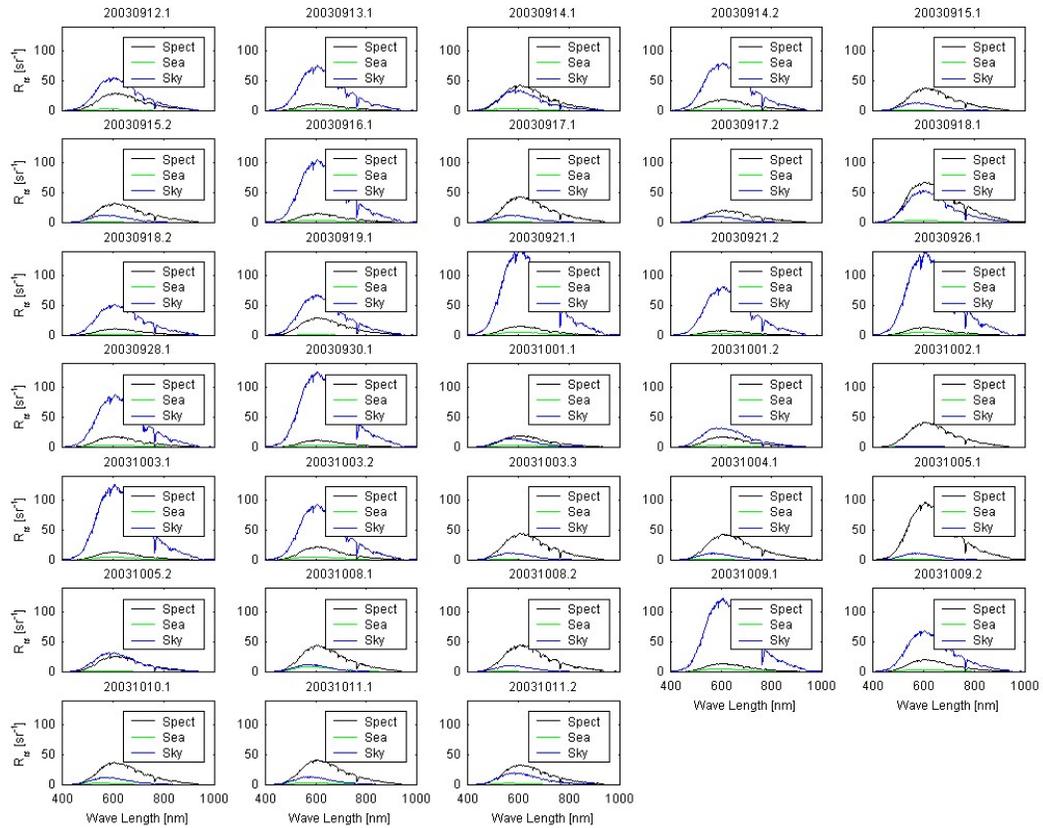


Figure 3.9.8 Averaged spectrums of spectralon, sky and sea observations

Figure 3.9.9 shows the computed remote sensing reflectance and corrected reflectance. This data was obtained from the hyperspectral radiometer.

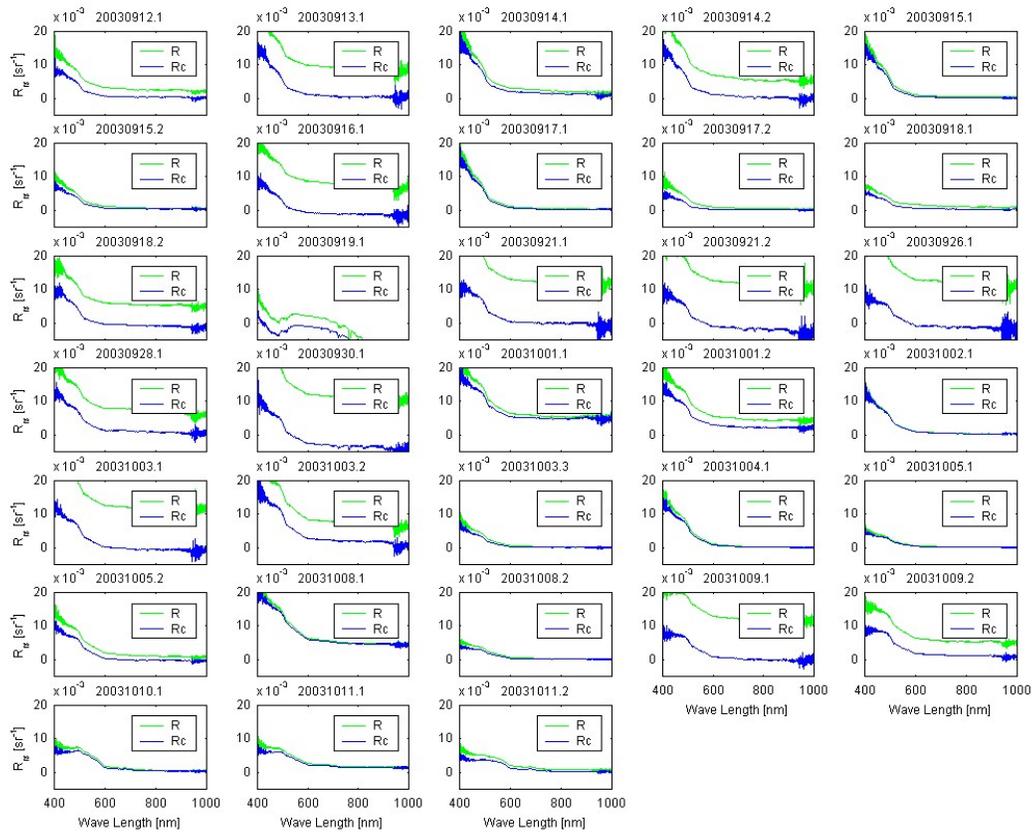


Figure 3.9.9 Remote sensing reflectance

The corrected reflectance (sr⁻¹) was obtained between 350 and 1009.5 nm. 4 wavelengths ratio with 550 nm were chosen in order to see which ratio correlates better with the surface pigments variation. The ratios were 412/550, 440/550, 490/550, and 510/550. Pigments to ratios plots are shown in figures 3.9.10a, 10b, 10c, and 10d with the last 3 stations taken out as the pigment values shot up. In figures 3.9.10a and 3.9.10b there is more scatter in the points but in figures 3.9.10c and 3.9.10d the range of the ratios are lower.

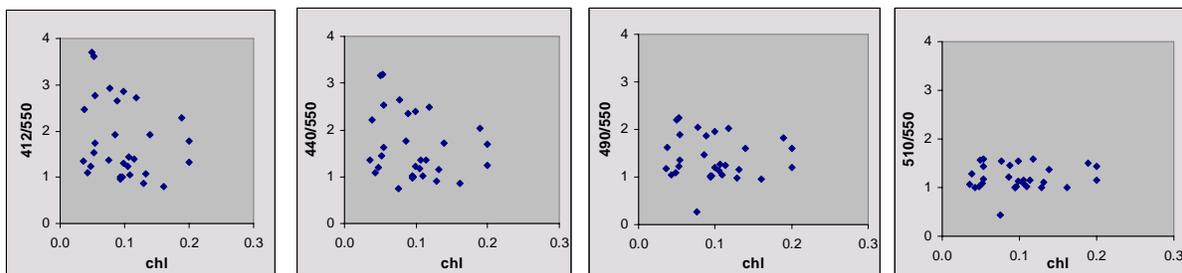


Figure 3.9.10a-d. Rrs ratios versus surface pigments

The ratios were then plotted together for each of the 33 measurements using a bar chart and the pigment concentration was plotted as a line on the same graph (figure 3.9.11). It is clearly visible that the lowest

wavelength ratio (412/550) has the highest value most of the time. The white circles indicate regions where the 412/550 ratio is no longer dominant and coincides with variations of pigment concentration, hence to understand this graph we need to use other parameters that have been collected during the cruise. Only then can we explain why the ratio are changing with respect to each other at some parts of the Pacific.

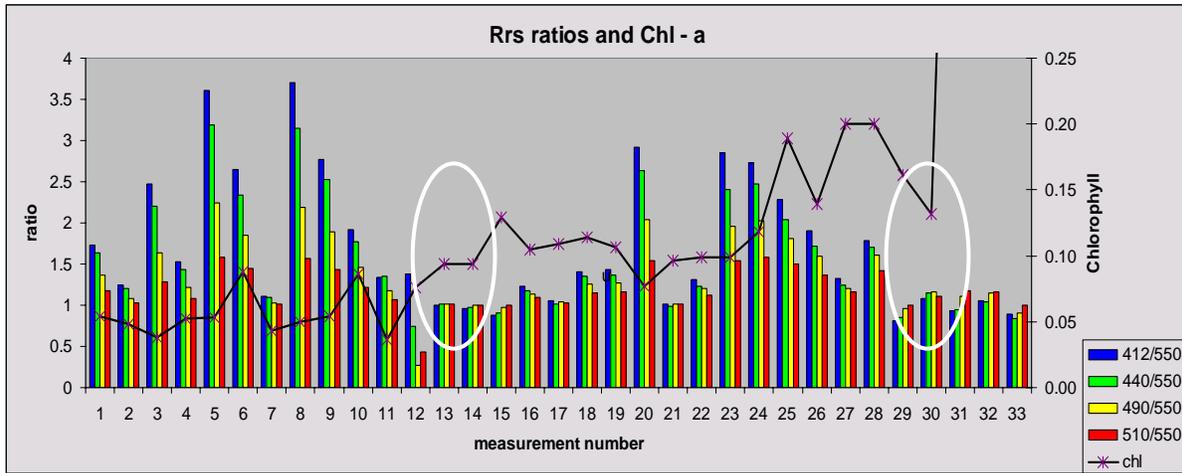


Figure 3.9.11 Rrs ratios variation and surface pigment

3.9.7 Acknowledgement

Thanks to the people of POGO and JAMSTEC for giving us the opportunity of being able to participate in BEAGLE 2003. The experience will be very useful to us in our future work. Thanks to Shubbha, Venetia, and others for their long distance help. Also thanks to Shuichi Watanabe chief scientist, Masao Fukasawa, Yuichiro Kumamoto, Hideki Yamamoto and team, as well as the captain with all the ship crew for all their support and safety on board.

Appendix A

Readme file
Jamstec Cruise Leg 2

Participants:

Gadiel Alarcon [bio-optics specialist]
Alexander Galan [trainee]
Dante Matellini [trainee]
Serkan Sancak [trainee]

This is a guide to find the data collected into directories and files, as follows:

Absorption : C:/Jamstec/Leg2/Absorption
CDOM : C:/Jamstec/Leg2/CDOM
Chlorophyll : C:/Jamstec/Leg2/Chlorophyll
CTD : C:/Jamstec/Leg2/CTD
Ocean Optics : C:/Jamstec/Leg2/HyperSp
Meteorology : C:/Jamstec/Leg2/Meteorology
PAR : C:/Jamstec/Leg2/PAR_sensor_data
Simbad : C:/Jamstec/Leg2/Simbad
Simbada : C:/Jamstec/Leg2/Simbada

Preliminary results : C:/Jamstec/Leg2/PreliminaryResults
Report : C:/Jamstec/Leg2/Report

Besides, in the main folder there is a summary_leg2.xls file where you can have a quick look to the biological collected data.

Absorption:

The same directory system is used with CDOM. (Check for CDOM section).

For each station there is 80 files in the directory. In each directory generally there is 160 files for two stations visited in the morning and in the afternoon. The file names contains six digit sample label number. If there is two sampling files in a directory (120 in total, not 160 because one blank for a day; however for the first two days we made two blanks for a day and had 160 files), please check the Log Book, for which one is sampled in the morning and which one is sampled in the afternoon.

CDOM:

The directory names are given as 8 digit numbers. First four digit represent the year; 5th and 6th represent month and the last two represent the day of the sampling time.

eg.

20030912 : 12th September 2003

In each directory the data taken on that day can be found. Generally two different sampling was made at two different times of the day. The two different sampling can be separated by their file names.

Files for air, q-water, q-water after setting the q-water as the baseline, and sample are named as follow:

xxxxxxair.csv

xxxxxxair.DSW

These two files are for air measurements. xxxxxx represent the number on the label used for the sample taken at the station. eg. 264214. The same number is used also for HPLC, absorption and flow cytometry (picoplankton) samples.

xxxxxxqw.csv

xxxxxxqw.DSW

These two files are for q-water measurements.

xxxxxxqw1.csv

xxxxxxqw1.DSW

These two files are for q-water measurements after setting the q-water as the baseline.

xxxxxx.csv

xxxxxx.DSW

These two files are for sample measurements.

In total 8 files for each sampling.

If there is two different set of files with two different label number (eg. 264213 and 264214; in total 16 files), that means two sampling made in that day. One in the morning and one in the afternoon. (Check the Log Book for which one is which).

Chlorophyll:

Here you can find each day photosynthetic pigments readings. They are named as xxxyyz.xls (e.g. oct04a.xls).

xxx = month

yy = day

z = a or b. (a morning extraction; b evening extraction)

The flow system pigments are found in these files too. Besides, there is a compilation for profile measurements (chl_leg2.xls).

CTD::

Here you can find down cast information of the CTD data.

HyperSp:

The data is organized in directories by day, as follows:

yyyymmdd.n

yyyy = year

mm = month

dd = dd

n = 1 or 2 (1, morning round; 2, evening round)

Inside of each directory, three kind of files can be found:

- For spectralon measurements: e.g.

sept122003spect.time.00000.Master.scope

- For sky measurements: e.g.

sept122003sky.time.00000.Master.scope

- For sea measurements: e.g.

sept122003sea.time.00000.Master.scope

Meteorology:

Here you can find daily meteorology information. A 'SOJ_readme.txt' and 'SOJ_format' files are provided in order to understand the information.

PAR sensor data:

Here you can find the PAR data collected during Leg 2.

SIMBAD and SIMBADA:

The data is organized in directories, as follows:

yyyymmdd, where

yyyy = year

mm = month

dd = day

Inside you'll find sub-directories, named as am or pm.

am = morning rounds

pm = evening rounds

Preliminary Results:

Here you can find preliminary processed data, organized in directories, as follows:

Absorption. Each file has a header with the scan day (e.g. 20030913.1 for morning and 20030913.2 for evening).

ps.dat : averaged data for particulate sample

ds.dat : averaged data for detritus sample

pb.dat : averaged data for particulate blank

ds.dat : averaged data for detritus blank

wavelength.dat : averaged wavelength
 aphi_1.dat : phytoplankton absorption using Beta 1
 aphi_2.dat : phytoplankton absorption using Beta 2
 csp.dat : specific abs coefficient using Beta 1
 csp2.dat : specific abs coefficient using Beta 2
 chl_abs.dat : chl-a concentration for each scan
 xx.jpg : output figures for each analysis

CDOM. Each file has a header with the scan day (e.g. 20030913.1 for morning and 20030913.2 for evening).

s_cdom.dat : sample data of each scan
 qw_cdom.dat : Q water of each scan
 wavelength_q.dat : wavelengths for Q water
 wavelength_s.dat : wavelengths for sample
 xx.jpg : output figures for each analysis

Chl. Contains a file with photosynthetic file for leg 2 (chl_leg2.xls) and plot contour of pigments distribution.

ctd_leg2. Contains a plot contour for temperature, oxygen and salinity distribution.

HyperSRad. Each file has a header with the scan day (e.g. 20030913.1 for morning and 20030913.2 for evening).

espectralon.dat : averaged data for espectralon observations
 Cal_espect.dat : calibration file for espectralon
 sea.dat : averaged data for sea observations
 sky.dat : averaged data for sky observations
 Reflectance.dat : computed Reflectance data
 Reflectance_c.dat: computed corrected Reflectance data
 integ_espect.dat : integration times of espectralon for each measure
 integ_sea.dat : integration times of sea for each measure
 integ_sky.dat : integration times of sky for each measure
 w_length.dat : wavelengths
 surface_chl.txt : surface pigments values (Chl+Phaeopigments)
 comparison.xls : comparison for Rrs vs surface chl
 xx.jpg : output figures for each analysis

Simbad/Simabada. both directories have ancillary information for each observation.

Simbad07_03_report.xls
 simbad_leg2 : analyzed files for all leg 2

Simbada21_report.xls

Bio-optic Group
 Leg 2

Appendix B

We also participated in the sampling of the rosette. The parameters sampled were:

- Salinity
- Oxygen
- SiO₄
- NO₃
- NO₂
- PO₄

- CFC11
- CFC12
- H-3
- He-3/He-4
- C14
- C13
- Ar
- Cs-137
- DIC
- Alkalinity
- pH
- CFC113
- Nitrous Oxide
- Chlorophyll a

- Phaeophytin

- Nitrogen(gas)
- Total Organic Carbon (TOC)
- Pu(238,239,240,241)
- Primary Production
- Total Inorganic Carbon (TIC)

Continuous recordings were made of meteorological data, sea current and bathymetry.

3.10 Nitrogen/Argon

Shinichi Tanaka (MAG, Hokkaido Univ.)
Yutaka Watanabe (MAG, Hokkaido Univ.)

3.10.1 Objective

(a) Detect to climate change evidence

Recently, It is estimated that Climate will be changing by human activity. To detect for Climate change signals in the ocean, we use air sea gases exchange. Middle and Deep seawater is almost made by vertical convection at the winter surface. If clear to time series gases concentrations change of each water mass, we can detect to climate change evidence apply to air sea gases exchange process. Therefore, we choice dissolved N₂, Ar concentration because there is main gasses and non reactive, it is appropriate for this study.

(b) Estimate to more accurate oxygen utility's in the middle and deep sea

Dissolved oxygen is regarded to estimate bio activity in middle and deep sea. Usually, its calculation method used apparent oxygen utility (AOU), but this calculation method has uncertainty, because this method defined that DO was saturated when water mass stayed surface. If we can estimate that's saturation ratio, it is possible to calculate more accurate oxygen utility.

To estimate more accurate oxygen utility, we use dissolved N₂,Ar. N₂, Ar and O₂ is main component gases of atmosphere and has same solubility and non reactive gases in the seawater. Middle and deep sea almost made vertical mixing and convection at winter, and if DO and N₂,Ar concentrations determined air sea gases exchange in the winter surface (starting point of water masses), it is possible to estimate more accurate oxygen utility used by N₂ and Ar concentrations in the middle and deep water masses. Also, more accurate oxygen utility's will reconstruct preformed-Nutrients used by Redfield Ratio.

3.10.2 Sea area

MR03-K04,Leg.2 was researched East South Pacific Ocean. This area has variant sea water masses and it is very important through way of southward – northward thermohaline circulations. It is expected that dissolved N₂ and Ar concentration in the water masses have evidence of climate variance and change.

3.10.3 Method

(a) Sampling

Water samples were collected at 15 stations,

Station P06C-117,109,99,89,85,75,P06E-67,59,51,42,X19,29,21,15,11.

Seawater samples were collected with Niskin Bottle. Each sample was collected in a 50ml-glass bottle.

At the sampling, seawater was allowed to overflow more than four times the bottle volume. A 50 μ L aliquot of saturated HgCl₂ solution was added to each sample to avoid biological change after sampling and it was stored in refrigerator.

(b)Analysis

Analysis will be determined onshore laboratory use by TCD-GC system. (Fig.3.10.1). Each gases analytical precision has below 0.1%.

3.10.4 Result

After finish this cruise, Sample analysis and data adjustment.

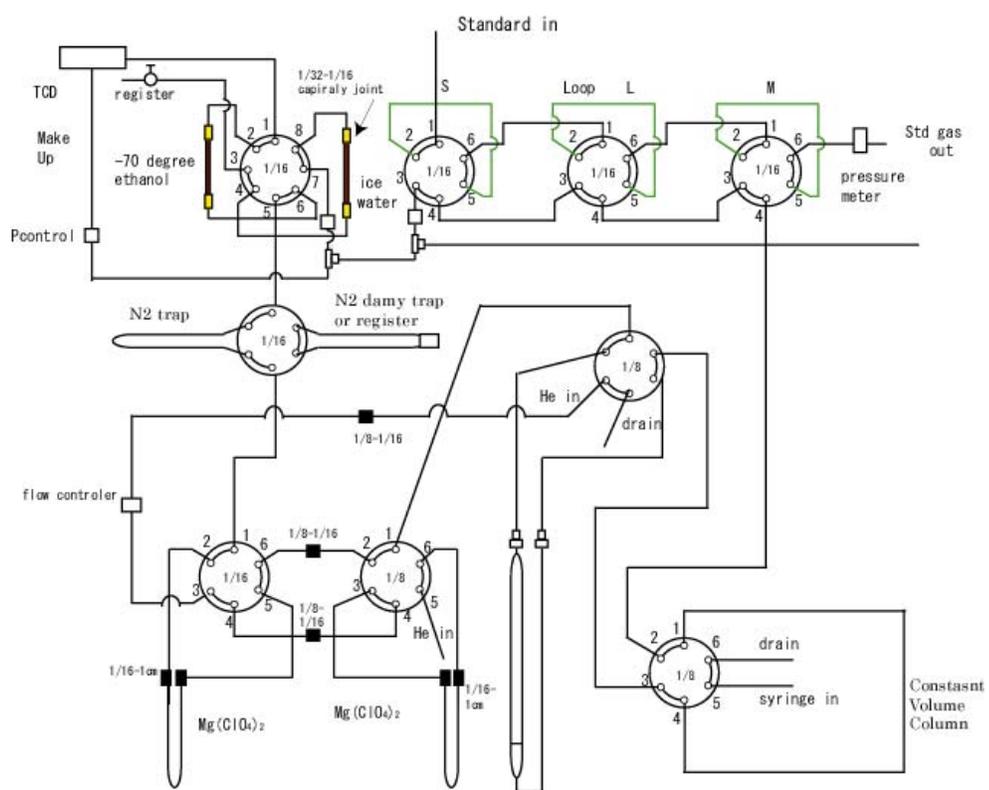


Fig.3.10.1 TCD-GC system

3.11 Helium Isotopes in seawater

Shuichi Watanabe (JAMSTEC)
Akihiko Murata (JAMSTEC)
Yuichiro Kumamoto (JAMSTEC)

3.11.1 Objective

Helium isotope ratio is one of important chemical tracers for discussion of water movement. Helium-3 is mainly diffused from earth interior and produced by decay of tritium (Clark, Beg and Craig, 1969). In southern hemisphere, former helium-3 is important. Distribution of helium-3 in mid-depth ocean indicates the source of helium-3 is hydrothermal activity in mid-ocean ridge and is spreading in the deep ocean waters (for example, Craig and Lupton, 1981, Lupton, 1998). Its distribution in the shallow ocean is related with tritium distribution. This helium is important to discuss mixing and transport to deeper ocean (for example, Jenkins, 1998).

During this leg, water samples for helium isotope analysis were collected at P06-118, -106, -68, and -40 to discuss the lateral transport of deep ocean water in the South Pacific.

3.11.2 Sampling method

Water sampling method is according to the WOCE Hydrographic Operation manual. Seawater samples were transferred from the Niskin bottle to the annealed copper tubing (o.d.: 3/8 inches, thickness: 1.5 mm, length: about 1 m) through plastic tubing. The seawater volume flushed through the copper tubing was about 6 times sample volume. During flushing, copper tubing was hit with wooden hammer and air babbles were removed completely. Plastic tubing both side of copper tubing was clipped with stopper. The copper tubing was clamped both side with special clamps inside of laboratory on board and these samples were kept inside room.

3.11.3 Analysis

Helium isotopes are analyzed with static mass spectrometer after dissolved helium is degassed from seawater and purified. The determination of helium isotopes will be ordered to specialist.

References

- Clark, W., M. A. Beg and H. Craig (1969) Excess ^3He in the sea: evidence for terrestrial primordial helium. *Earth Planet. Sci. Lett.*, **6**, 213-220.
- Craig, H. and J. E. Lupton (1981) Helium-3 and mantle volatiles in the ocean and the oceanic crust. *The Sea, 7: The Oceanic Lithosphere*. Ed. C. Emiliani, Wiley and Son, New York, 391-428.
- Jenkins W. J.(1998) Studying subtropical thermocline ventilation and circulation using tritium and ^3He . *J. Geophys. Res.*, **103**, 15817-15831.
- Jenkins W. J., D. E. Lott, M. W. Davis, S. P. Birdwhistell and M. O. Matthewson (1991) Measuring Helium Isotopes and Tritium in Seawater Samples. In: *WOCE hydrographic Operations and Methods, WOCE Operations Manual*, 3, Section 3.1, Part 3.1.3, WHP Office Report WHPO 91-1, WOCE Report No. 68/91, 21pp.
- Lupton, J. E. (1998) Hydrothermal Helium Plumes in the Pacific Ocean. *J. Geophys. Res.*, **103**, 15853-15863.

3.12 N₂O: Automatic System for measuring Nitrous Oxide, SIMON

Mauricio Gallegos (Univ. of Concepcion)

Victor Villagran (Univ. of Concepcion)

3.12.1 Introduction

The study of nitrous oxide (N₂O) has drawn special attention because of its importance on the stratospheric ozone layer (Crutzen, 1970) and also because it contributes significantly to global warming. Atmospheric N₂O has both natural and antropogenical sources; however, significant information about their budgets still remains uncertain. World oceans are contributing up to about 20% of this total annual input to the atmosphere. However, the estimations of the ocean to atmosphere exchange depend primarily on the degree of saturation in the surface water and the transfer velocity of the gas under study across the air water interface. The concern is that human activity could be responsible of significant changes in the magnitude of source and sink strengths for N₂O. It is therefore important to quantify sources and sinks for atmospheric N₂O in both soil and sea water.

Due to the magnitude of natural variations in the samples is often small at sea, it is essential to select an equipment as precise as possible. Unfortunately, it does not exist companies focus on this kind of specific applications so that We decided developing our own automatic measurement system that we called “SIMON”. The valuable experience of colleagues was the more reliable and fast way to get starting. We have to thank the collaboration of Professor Ray Weiss from Scripps, Institution of Oceanography.

Our system, actually, is based on Weiss scheme and of course, on its equilibrator.

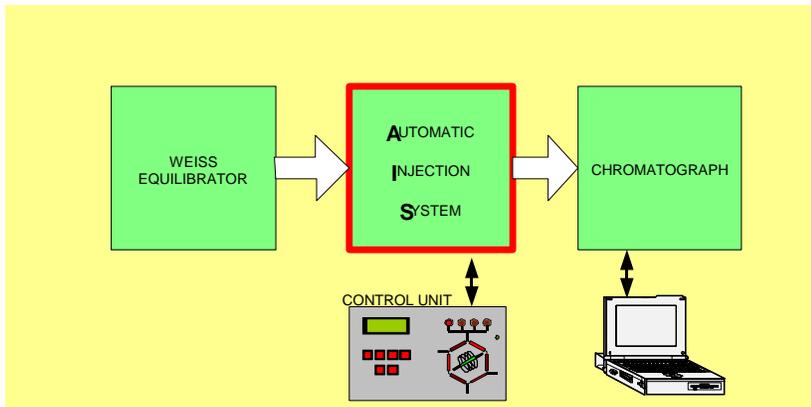
However, the control and acquisition architecture of SIMON represents, by itself, a new approach and it was designed and developed at PROFC Lab in University of Concepcion.

The next report includes some information of our measurement system as well as a preliminary evaluation about how the system worked on the cruise. Further information should be asked to Dr. Laura Farías after this cruise.

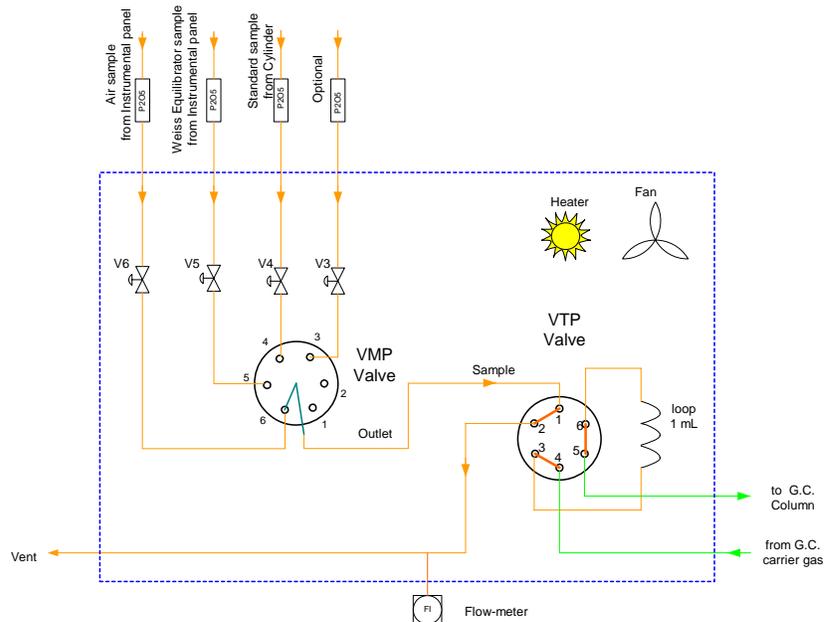
3.12.2 Brief description of SIMON

The measurement of nitrous oxide is done by electron capture chromatography using a chromatograph shimadzu GC-17.

The chromatograms obtained in each sample are saved in the laptop computer which also provides to the user an interface platform for configuring and setting tasks.



The scheme shows the core of AIS which permits injecting the sample into the G.C. column. This operation takes place in two states, first the sample loop connected in the two position valve, VTP, must be filled with the gas sample. For this purpose, the valve VTP is set to “position A” and the valve VMP is previously set for selecting the input port desired. In the second state the VTP is changed to “position B” which means the contained of the sample loop is displaced by the mobile phase and is carried into the column.



As the amount of gas in the sampling loop depends on the temperature and on barometric pressure, the control of these variables is necessary to get high performance in the measurements. Changes in barometric pressure can normally be neglected, but temperature control has to be made. This task is performed by the Control Unit which has a temperature sensor inside the Valve Module

Engineering developing started running in March 2003 after visiting Scripps. Later, in 08 August fig.3.12.1 shows the first prototype of the Automatic Injection System. In fig. 3.12.2 is shown Control Unit, Valve Module and the GC when the system was under test on Mirai.

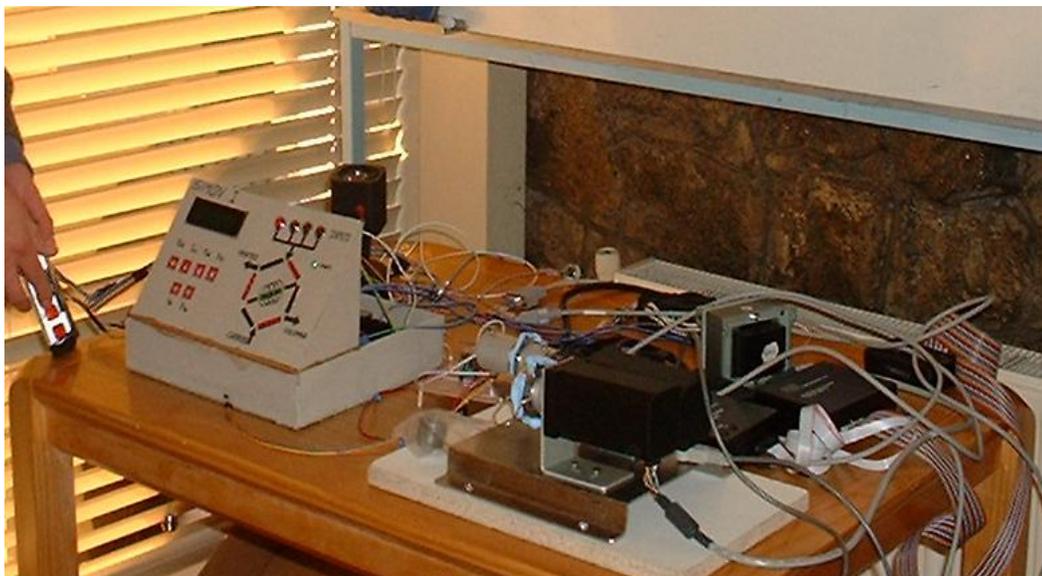


Figure 3.12.1 After the formal presentation in PROFC gathering room (08 August)



Figure 3.12.2 Mirai lab room, Jamstec Cruise (14 Sept 2003)

3.12.3 Main Purposes on this cruise

- (1) Test how SIMON works for first time and according to that, proposes necessary changes in order to improve its performance.
- (2) Obtain something N₂O profiles taking samples in water column through out the WHP/P6 transect.
- (3) Get data from SIMON so that they can be carefully analyzed at Lab of the Program Regional of Physical Oceanographic and Climate in Concepcion

3.12.4 Methods

Measurements were made from September 9th to October 16th on board the R/V Mirai in the cruise BEAGLE 2003 (*Blue Earth Global Expedition 2003*) over the Pacific Ocean.

The measurements of nitrous oxide were performed with chromatographic gas GC Shimadzu 17A equipped with one electron capture detector (ECD ⁶³Ni) and with column Porapack Q of length of 30 meters and 0.25 mm. The volume of the sample was one aliquot of the 1 ml.

The carrier gas used for the ECD detector was Nitrogen, supplied at a rate of 20 ml/min, and the concentration of the standard gas used were 300 ppb and 1500 ppb.

The selection of an absorbent for drying columns was one trap with Sieve molecular and Dierite.

Seven stations including oceanic and cost stations were chosen to take N₂O samples in the water column as it shown in Table 3.12.1.

Table 3.12.1 Station sampling nitrous oxide MR03-K04 Leg 2

Station	Date	Latitude	Longitude	Depth
PO6E-047 C	01 / 10 / 2003	32 30.00' S	96 00.09' W	3946
PO6E-042 C	03 / 10 / 2003	32 30.04' S	92 40.09' W	4702
PO6E-033 C	05 / 10 / 2003	32 30.02' S	86 40.00' W	3766
PO6E-025 C	07 / 10 / 2003	32 29.89' S	81 19.91' W	3891
PO6E-021 C	08 / 10 / 2003	32 30.32' S	78 39.63' W	4037
PO6E-017 C	09 / 10 / 2003	32 29.99' S	76 00.14' W	4181
PO6E-013 C	10 / 10 / 2003	32 29.95' S	73 20.18' W	3825
PO6E-006 C	11 / 10 / 2003	32 30.01' S	71 49.97' W	2000

PO6E-005 C	11 / 10 / 1003	32 30.08' S	71 40.06' W	500
PO6E-004 C	12 / 0 / 2003	32 29.96' S	71 30.11' W	200

In addition, one Air sample and one standard gas sample were taken in a pressured canister so that they can be analyzed on Land (Figure 3.12.4 (A)). The air sample was taken on the highest part of ship, far from any contaminants effect. Is preferred this canister, especially for the detectors such as el ECD because are prone to interference effects. These samples will be send to Scripps Lab.

Table 3.12.2 Take the sampling for calibration standar gas.

Canister	Date	Latitude (S)	Longitude (W)	Wind (m/s)	T air	TSM	P atm (hPa)	P sample
1 oceanic	01/10/2003	32 30.5595'	96 15.8531'	10.4	16.3	16.2	1021.2	20 psi
2 Standard	10/10/2003							



A



B



C



D



E

Figure 3.12.3 Different components of SIMON; A) Canister for sample air, B) Valve Valco, C) Pump, D) Flujometer and E) Regulator pressure.

3.12.5 Results

The start up of SIMON took place from September 9th to September 16th. This included the installation of electronic parts, instrumentation, equilibrator and Chromatograph.

N₂O peak detection at Chromatograph

Previously to operate the system the Chromatograph's parameters had to be adjusted in order to get a good separation and definition of the N₂O peak. The parameters obtained in this test processes are shown below. Therefore, the separation of the N₂O peak was carried out at approximately 45 celsius degrees .

1. Temperature Parameters

Column Temperature:	45 °C
Detector Temperature:	235 °C
Injector Temperature:	150 °C

2. Flow Parameters

Column Pressure:	2,5 psi
Control mode:	Split
Column Flow:	3.5
Linear velocity (cm·s ⁻¹):	25
Total Flow (ml·m ⁻¹):	5
Split rate (1/x):	8
Purge Flow :	5 ml·m ⁻¹

3. Detector parameters

Detection Range:	0
Current of detection :	0.5 mV

Typical chromatograms for a 1 ml standard, equilibrator gas and air sample measured under shipboard conditions, is shown in figure 3.12.4 and 3.12.5.

It was found that death volume, CO₂ and N₂O time retention were 2.23, 3.04 and 3.25 seconds respectively. The area reached for the N₂O peak was for atmospheric sample about 600 count, for the equilibrator sample was about 500 count and the 300 ppbv standard gas was about 450 count. The N₂O peaks showed a good resolution,

furthermore they were correctly separated from CO₂ peaks. The whole analysis takes 5 minutes.

Drying columns

The original traps used by the AIS had to be changed because they seemed to remove every gas including N₂O. Magnesium Perchlorate into a teflon tubes was the absorbent used as trap. It is also relevant the fact that absorbents had to be removed and changed periodically by other dry absorbent. Usually, after three days the absorbents in equilibrator and air drying columns were quite wet.

Observations

The SIMON were operated more than 500 hr (20 days) of continuous analyses under conditions of shipboard. SIMON showed to be a reliable automatic control system.

The experimental conditions for detection of N₂O (eg. Column temperature, rate flow etc) were not critical during this cruise.

A preliminary results shows the system reached a good repeatability in standard measurement both the 300ppbv cylinder and 1500ppbv cylinder. Detailed analysis of chromatograms will be done after cruise.

One point important is the election gas carrier, in the case was N₂, but it is possible to have systematic errors for N₂O, because the oxidation state of the detector walls is affected by the varying amounts of O₂ or other oxidants in the samples (Weiss, pers. com). The ion chemistry of N₂O detection is complicated. When do use P5 carrier (Ar/CH₄), the CH₄ in the carrier assures that the detector remains in a reducing chemical state.

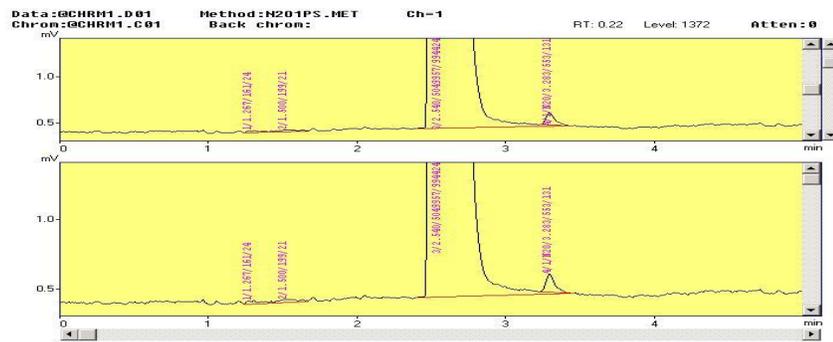
The precision of the ECD technique makes this method ideal for the measurements of spatial variations such as those made from a moving platform.

A simple view the method described here proved to be convenient for shipboard operation and performed as well as sea in the laboratory. The high sensitivity of the ECD for N₂O make it possible to carry out the analysis with one high signal attenuations which minimize the effects of the ship motion on detector response.

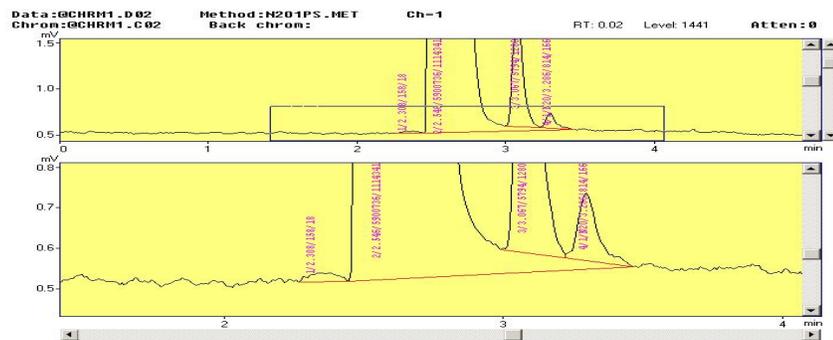
Acknowledgment

We thank to Dr. Suichi Watanabe and Yuichiro Kumamoto for their support during this cruise. We also want to thank the assistance of the captain, crew and scientific group aboard R/V Mirai.

a)



b)



c)

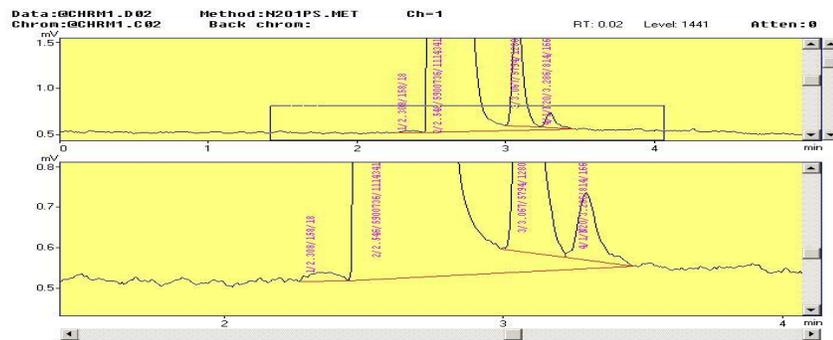
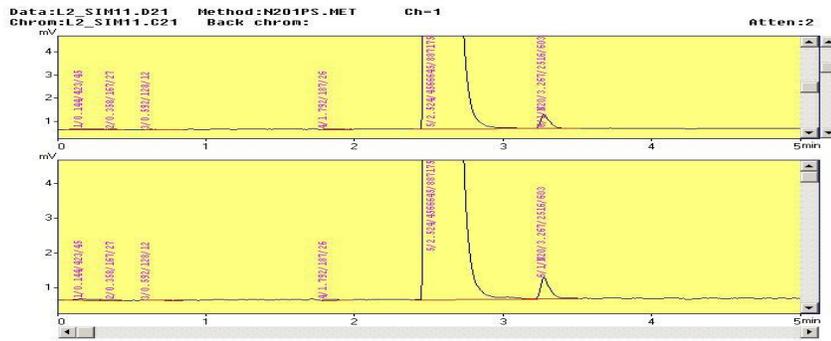


Figure 3.12.4 Chromatographer typical, a) Standar gas (300 ppbv), b) sample equilibrator, c)sample air.

a)



b)

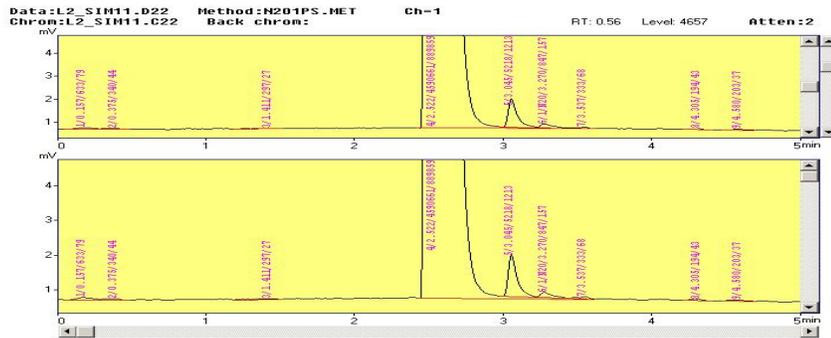


Figure 3.12.5 Chromatographer typical, a) Standar gas (1500 ppbv), b) sample equilibrator, c)sample air.

3.13 Lowered Acoustic Doppler Current Profiler

Y. Yoshikawa (JAMSTEC)

Direct flow measurement from sea surface to bottom was carried out by using an lowered acoustic Doppler current profiler (LADCP). The instrument used was an RDI Monitor 307.2 kHz unit (S/N 2553). The instrument was attached on CTD/RMS frame, and oriented downward. CPU firmware version was 16.20. The data will be analyzed by using the method of Visbeck (2002) with CTD and navigation data.

4. Argo float

Nobie Shikama (JAMSTEC)

Eitarou Oka (JAMSTEC)

Miki Yoshiike (MWJ)

Ken-ichi Katayama (MWJ)

4.1 Objectives

The objective of deployment is to clarify the structure and temporal/spatial variability of water masses in the subtropical South Pacific such as the South Pacific Eastern Subtropical Mode Water. The profiling floats launched in this cruise obtain vertical profiles of temperature and salinity automatically every ten days. The data from the floats will enable us to understand the phenomenon mentioned above with time/spatial scales much smaller than those in the previous studies.

4.2 Parameters

Water temperature, salinity, and pressure

4.3 Methods

We launched 9 APEX floats of FORSGC and 9 SOLO floats of Scripps Institution of Oceanography (SIO). These floats equip an SBE41 CTD sensor manufactured by Sea-Bird Electronics Inc. The floats usually drift at a depth of 2000 dbar (called the parking depth), rising up to the sea surface every ten days by increasing their volume and thus changing the buoyancy. During the ascent, they measure temperature, salinity, and pressure. They stay at the sea surface for approximately nine hours, transmitting their positions and the CTD data to the land via the ARGOS system, and then return to the parking depth by decreasing volume. The status of floats and their launches are shown in Table 4.1.

4.4 Data archive

All data acquired by the FORSGC floats through the ARGOS system is stored at FORSGC. The real-time data are provided to meteorological organizations via Global Telecommunication System (GTS) and utilized for analysis and forecasts of sea conditions.

Table 4.1 Status of floats and their launches

Float (FORSGC)

Float Type	APEX floats manufactured by Webb Research Ltd.
CTD sensor	SBE41 manufactured by Sea-Bird Electronics Inc.
Cycle	10 days (approximately 9 hours at the sea surface)
ARGOS transmit interval	30 sec
Target Parking Pressure	2000 dbar
Sampling layers	71 (2000, 1900, 1800, 1700, 1600, 1500, 1400, 1300, 1250, 1200, 1150, 1100, 1050, 1000, 975, 950, 925, 900, 875, 850, 825, 800, 780, 760, 740, 720, 700, 680, 660, 640, 620, 600, 580, 560, 540, 520, 500, 480, 460, 440, 420, 400, 380, 360, 340, 320, 300, 280, 260, 240, 220, 200, 190, 180, 170, 160, 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10 [dbar])

Float (SIO)

Float Type	SOLO floats manufactured by Scripps Institution of Oceanography
CTD sensor	SBE41 manufactured by Sea-Bird Electronics Inc.
Cycle	10 days
Target Parking Pressure	2000 dbar

Launches

Owner	Type	S/N	ARGOS PTT ID	Date and Time of Reset (UTC)	Date and Time of Launch (UTC)	Location of Launch
FORSGC	APEX	933	25284	06:45, Sep. 14	08:05, Sep. 14	32-28.94 S, 142-20.93 W
SIO	SOLO	2204	unknown	22:52, Jul. 30	09:18, Sep. 15	32-30.46 S, 139-17.46 W
FORSGC	APEX	934	25287	12:11, Sep. 16	13:25, Sep. 16	32-28.94 S, 136-00.61 W
SIO	SOLO	2205	unknown	22:55, Jul. 30	15:43, Sep. 17	32-29.30 S, 133-19.78 W
FORSGC	APEX	935	25288	19:40, Sep. 18	20:41, Sep. 18	32-29.19 S, 129-59.26 W
SIO	SOLO	2206	unknown	22:57, Jul. 30	18:32, Sep. 19	32-28.75 S, 127-19.00 W
FORSGC	APEX	936	25293	13:41, Sep. 21	14:53, Sep. 21	32-29.58 S, 124-00.23 W
SIO	SOLO	2207	unknown	22:59, Jul. 30	11:53, Sep. 22	32-29.87 S, 121-18.95 W
FORSGC	APEX	660	11478	14:10, Sep. 23	15:27, Sep. 23	32-30.42 S, 117-59.04 W
SIO	SOLO	2208	unknown	23:00, Jul. 30	13:18, Sep. 24	32-29.33 S, 115-19.56 W
FORSGC	APEX	938	25594	12:40, Sep. 25	14:00, Sep. 25	32-29.97 S, 111-59.55 W
SIO	SOLO	2209	unknown	23:02, Jul. 30	11:03, Sep. 26	32-28.79 S, 109-20.87 W
FORSGC	APEX	940	25596	16:57, Sep. 27	17:30, Sep. 27	32-29.46 S, 106-01.87 W
SIO	SOLO	2210	unknown	23:59, Jul. 30	16:20, Sep. 28	32-30.13 S, 103-00.53 W
FORSGC	APEX	939	25595	18:20, Sep. 30	20:06, Sep. 30	32-30.80 S, 100-00.49 W
SIO	SOLO	2211	unknown	00:02, Jul. 31	17:08, Oct. 01	32-30.67 S, 097-20.23 W
FORSGC	APEX	941	25597	18:27, Oct. 02	19:50, Oct. 02	32-30.93 S, 093-59.28 W
SIO	SOLO	2212	unknown	00:04, Jul. 31	16:50, Oct. 03	32-31.49 S, 091-18.75 W