CRUISE REPORT: P09
(Updated MAR 2021)
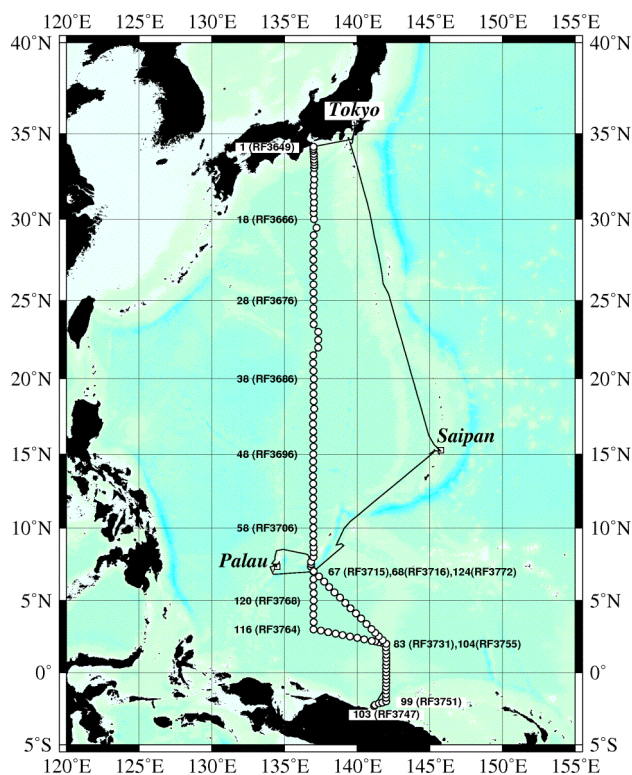
HIGHLIGHTS

CRUISE SUMMARY INFORMATION

WOCE Section Designation	**P09 (RF10-05)**
Expedition designation (ExpoCodes)	**49UP20100706**
Chief Scientists	**Toshiya Nakano**
Dates	2010 JUL 06 - 2010 AUG 22
Ship	*R/V Ryofu Maru*
Ports of call	Tokyo - Palau - Saipan
Geographic Boundaries	34° 14.92' N 136° 47.11' E 142° 0.12' E 2° 19.81' S
Stations	124
Floats and drifters deployed	One drifting ocean data buoy
Moorings deployed or recovered	0

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Final report assembly by Jerry Kappa, SIO/UCSD

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Data History (CCHDO)

A. Cruise narrative

1. Highlights

Cruise designation: RF10-05（WHP-P09 revisit）

a. EXPOCODE: 49UP20100706

b. Chief scientist: Toshiya NAKANO (nakano_t@met.kishou.go.jp)

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c. Ship name: R/V Ryofu Maru

d. Ports of call: Leg 1: Tokyo - Palau, Leg 2: Palau - Saipan

e. Cruise dates: Leg 1: 6 July 2010 - 28 July 2010

　　　　　　　　Leg 2: 1 August 2010 - 22 August 2010

f. Floats and drifters deployed: one drifting ocean data buoy

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2. Cruise Summary Information

RF10-05 cruise was carried out during the period from July 6 to September 1, 2010. The cruise started from the south of Honshu, Japan, and sailed towards south along approximately 137°E meridian. This line was observed by JMA in 1994 as 'WHP-P9', which is a part of WOCE (World Ocean Circulation Experiment) Hydrographic Programme.

A total of 124 stations was occupied using a Sea-Bird Electronics (SBE) 36 position carousel equipped with 10-liter Niskin water sample bottles, a CTD system (SBE911plus) equipped with SBE35 deep ocean standards thermometer, JFE Advantech oxygen sensor (RINKO III), Teledyne Benthos altimeter, and Teledyne RD Instruments Lowered Acoustic Doppler Current Profiler (L-ADCP). To examine consistency of data, we carried out the observation three times at 7°N, 137°E (Stn.67, 68 and 124) and twice at 2°N, 142°E (Stn.83 and 104). Cruise track and station location are shown in Figure 1.

At each station, full-depth $CTDO_2$ (temperature, conductivity (salinity) and dissolved oxygen) profile and up to 36 water samples were taken and analyzed. Water samples were obtained from 10 dbar to approximately 10 m above the bottom. In addition, surface water was sampled by a stainless steel bucket at each station. Sampling layer is designed as so-called staggered mesh as shown in Table 1 (*Swift*, 2010). The bottle depth diagram is shown in Figure 2.

Water samples were analyzed for salinity, dissolved oxygen, nutrients, dissolved inorganic carbon (DIC), total alkalinity (TA), pH, CFC-11, CFC-12 and phytopigment (chlorophyll-a and phaeopigmens). Samples for dissolved organic carbon (DOC) and ^{13}C were also collected at the selected stations. Underway measurements of partial pressure of carbon dioxide (pCO$_2$), temperature, salinity, chlorophyll-a, subsurface current, bathymetry and meteorological parameters were conducted along the cruise track.

R/V Ryofu Maru departed Tokyo (Japan) on July 6, 2010. Before the observation at the first station, all watch standers were drilled in the method of sample drawing and CTD operations

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near Izu-Oshima (34°40'N, 139°37'E). In order to estimate the misalignment of the ship-mounted Acoustic Doppler Current Profiler (ADCP), we collected the bottom tracking data for about an hour off Omaezaki (around 34°22'N, 137°55'E). The hydrographic cast of $CTDO_2$ was started at the first station (Stn.1 (34°15'N, 137°E; RF3649)) on July 7. Leg 1 consisted of 67 stations from Stn.1 to Stn.67 (7°N, 137°E; RF3715). She called for Palau (Republic of Palau) on July 28, 2010 (Leg 1). She left Palau on August 1, 2010 for Saipan (Commonwealth of the Northern Mariana Islands) and arrived on August 22, 2010 (Leg 2). Leg 2 consisted of 57 stations from Stn.68 (7°N, 137°E; RF3716) to Stn.124 (7°N, 137°E; RF3772).

To wait the issue of a clearance letter for the EEZ of Papua New Guinea, we carried out from Stn.105 (2°03'N, 141°45'E; RF3732) to Stn.107 (2°09'N, 141°15'E; RF3734) after observation at Stn.83 (2°N, 142°E; RF3731) on August 5. After the issue of the clearance letter, we resumed from Stn.84 (1°45'N, 142°E; RF3735) on August 6. To carry out four stations from Stn.100 (2°05'S, 141°45'E; RF3750) to Stn.103 (2°22'S, 141°08'E; RF3747) near the coast of Papua New Guinea during the daytime, we sailed to Stn.103 (2°22'S, 141°08'E; RF3747) after at Stn.95 (1°S, 142°E; RF3746), and resumed on August 9.

One drifting ocean data buoy (WMO number : 21595) was deployed at 32°01.988'N, 137°00.620'E on July 8, 2010.
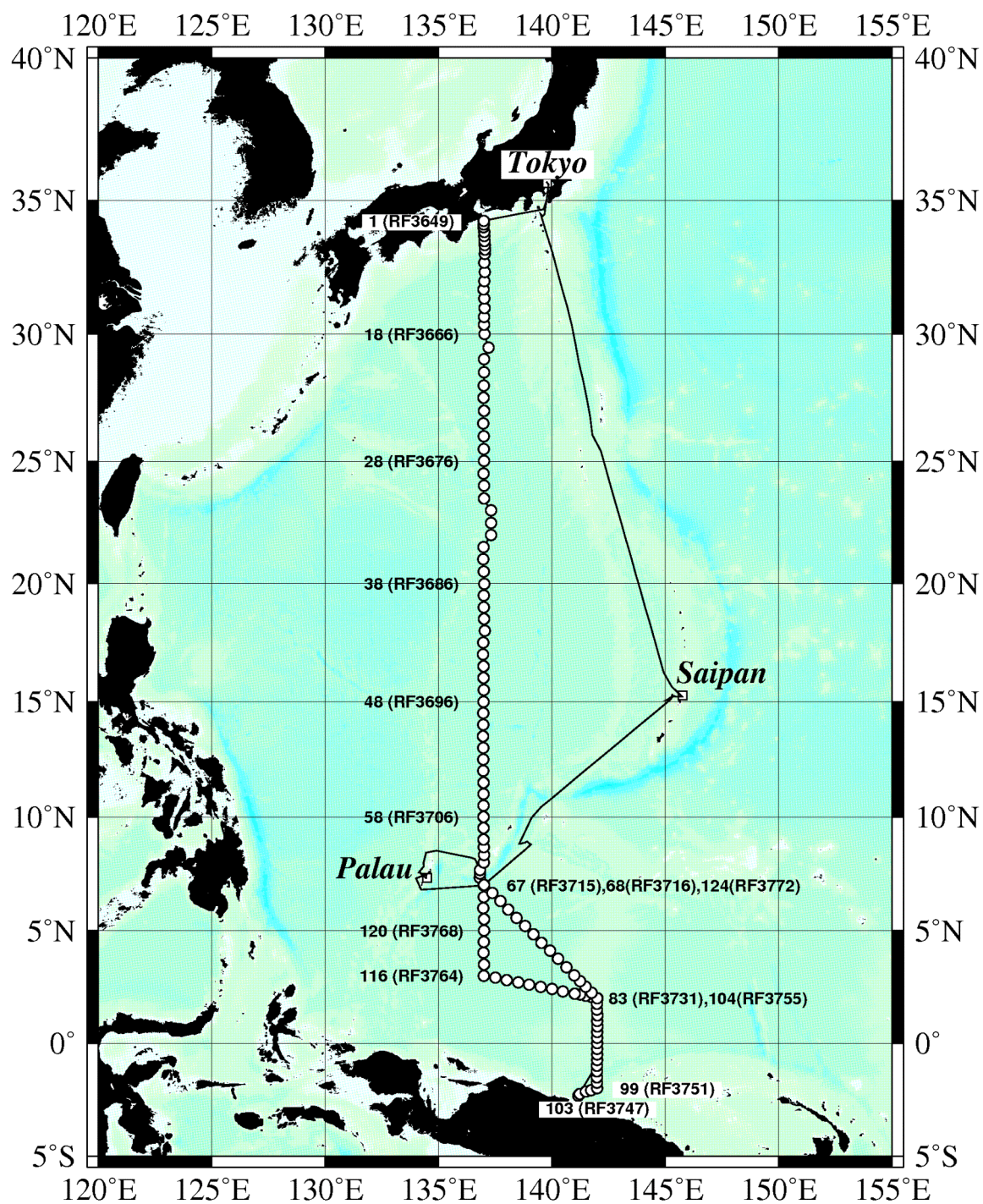
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Figure 1. Cruise track of RF10-05.
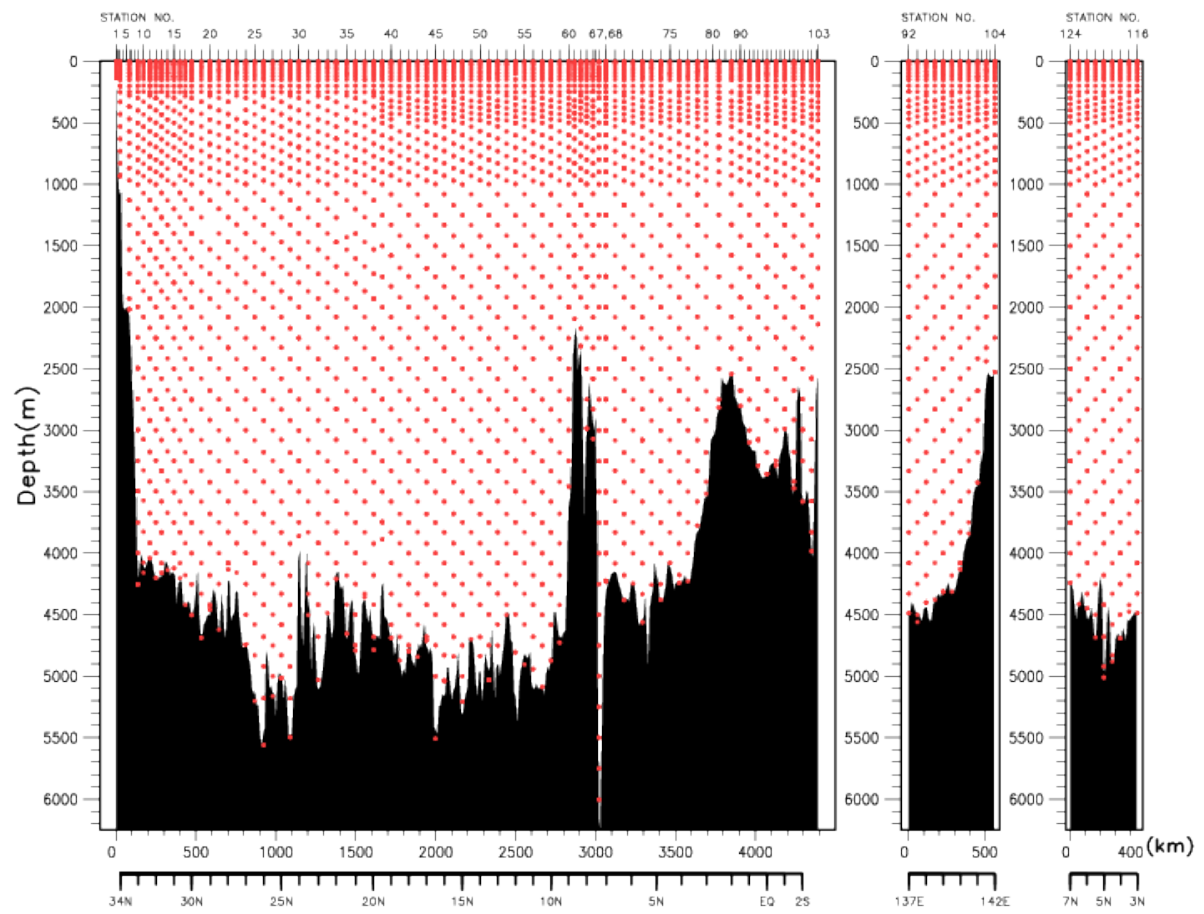
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Figure 2. The bottle depth diagram for WHP-P9 revisit.

Table 1. The scheme of sampling layer in meters.

Bottle count	North of 20°N (Stn.1 - Stn.38)			South of 20°N (Stn-38 - Stn.124)			Yap Trench (Stn.66)
	scheme1	scheme2	scheme3	scheme4	scheme5	scheme6	scheme7
1	10	10	10	10	10	10	10
2	25	25	25	25	25	25	50
3	50	50	50	50	50	50	75
4	75	75	75	75	75	75	100
5	100	100	100	100	100	100	125
6	125	125	125	125	125	125	150
7	150	150	150	150	150	150	200
8	200	200	200	200	200	200	250
9	250	250	250	250	250	250	300
10	300	330	280	300	320	280	400
11	400	430	370	350	370	330	500
12	500	530	470	400	420	380	600
13	600	630	570	450	470	430	700
14	700	730	670	500	530	480	800
15	800	830	770	600	630	570	900
16	900	930	870	700	730	670	1000
17	1000	1070	970	800	830	770	1250
18	1200	1270	1130	900	930	870	1500
19	1400	1470	1330	1000	1080	970	1750
20	1600	1670	1530	1250	1330	1170	2000
21	1800	1870	1730	1500	1580	1420	2250
22	2000	2080	1930	1750	1830	1680	2500
23	2250	2330	2170	2000	2080	1920	2750
24	2500	2580	2420	2250	2330	2170	3000
25	2750	2830	2680	2500	2580	2420	3250
26	3000	3080	2920	2750	2830	2680	3500
27	3250	3330	3180	3000	3080	2920	3750
28	3500	3580	3420	3250	3330	3180	4000
29	3750	3830	3680	3500	3580	3420	4250
30	4000	4080	3920	3750	3830	3680	4500
31	4250	4330	4180	4000	4080	3920	4750
32	4500	4580	4420	4250	4330	4180	5000
33	4750	4830	4680	4500	4580	4420	5250
34	5000	5080	4920	4750	4830	4680	5500
35	5250	5330	5180	5000	5080	4920	5750
36	5500	5580	5420	5250	5330	5180	6000

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Table 2. Station data of RF10-05 cruise. The 'RF' column indicates the JMA station identification number.

Leg	Station		Position		Leg	Station		Position	
	Stn.	RF	Latitude	Longitude		Stn.	RF	Latitude	Longitude
1	1	3649	34-14.85 N	136-59.47 E	1	36	3684	20-59.83 N	136-58.21 E
1	2	3650	34-06.71 N	136-59.24 E	1	37	3685	20-29.06 N	136-59.41 E
1	3	3651	34-00.94 N	136-58.40 E	1	38	3686	19-58.25 N	137-00.39 E
1	4	3652	33-50.14 N	137-00.82 E	1	39	3687	19-29.39 N	136-59.28 E
1	5	3653	33-41.22 N	137-00.79 E	1	40	3688	18-59.74 N	136-59.04 E
1	6	3654	33-30.31 N	137-01.55 E	1	41	3689	18-30.52 N	136-59.94 E
1	7	3655	33-21.12 N	137-02.20 E	1	42	3690	18-00.58 N	137-01.81 E
1	8	3656	33-11.27 N	137-02.34 E	1	43	3691	17-30.53 N	136-57.81 E
1	9	3657	33-01.56 N	137-02.01 E	1	44	3692	17-00.27 N	136-57.57 E
1	10	3658	32-42.25 N	137-00.65 E	1	45	3693	16-30.38 N	136-58.83 E
1	11	3659	32-20.90 N	137-01.94 E	1	46	3694	16-00.61 N	136-58.58 E
1	12	3660	32-00.61 N	137-00.75 E	1	47	3695	15-29.31 N	136-59.09 E
1	13	3661	31-41.64 N	136-58.71 E	1	48	3696	14-58.91 N	136-58.90 E
1	14	3662	31-21.19 N	137-00.50 E	1	49	3697	14-29.66 N	136-58.10 E
1	15	3663	30-59.46 N	137-01.14 E	1	50	3698	14-00.03 N	136-58.18 E
1	16	3664	30-39.21 N	136-59.69 E	1	51	3699	13-29.87 N	136-57.56 E
1	17	3665	30-21.57 N	136-59.92 E	1	52	3700	12-59.96 N	136-58.26 E
1	18	3666	30-00.10 N	137-01.43 E	1	53	3701	12-30.05 N	136-58.33 E
1	19	3667	29-28.67 N	137-11.93 E	1	54	3702	12-00.31 N	136-58.25 E
1	20	3668	29-01.75 N	136-59.89 E	1	55	3703	11-29.76 N	136-58.70 E
1	21	3669	28-31.08 N	137-00.02 E	1	56	3704	11-00.26 N	136-58.61 E
1	22	3670	27-59.90 N	136-59.33 E	1	57	3705	10-29.85 N	136-58.61 E
1	23	3671	27-31.45 N	136-58.97 E	1	58	3706	10-00.08 N	136-58.83 E
1	24	3672	27-00.52 N	136-59.86 E	1	59	3707	9-30.74 N	136-58.65 E
1	25	3673	26-30.40 N	136-57.70 E	1	60	3708	9-00.24 N	136-58.45 E
1	26	3674	25-59.83 N	136-59.19 E	1	61	3709	8-40.27 N	136-59.58 E
1	27	3675	25-29.17 N	136-59.31 E	1	62	3710	8-20.10 N	136-59.98 E
1	28	3676	25-00.65 N	137-00.21 E	1	63	3711	7-59.77 N	136-59.20 E
1	29	3677	24-30.44 N	136-58.66 E	1	64	3712	7-40.05 N	136-49.64 E
1	30	3678	24-00.94 N	136-59.92 E	1	65	3713	7-30.48 N	136-49.37 E
1	31	3679	23-29.77 N	136-59.67 E	1	66	3714	7-20.26 N	136-48.74 E
1	32	3680	23-00.92 N	137-18.82 E	1	67	3715	7-00.04 N	136-58.93 E
1	33	3681	22-29.37 N	137-18.40 E	2	68	3716	7-00.88 N	136-59.76 E
1	34	3682	21-59.97 N	137-18.57 E	2	69	3717	6-39.49 N	137-21.88 E
1	35	3683	21-29.80 N	136-58.52 E	2	70	3718	6-17.74 N	137-43.07 E

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Table 2. Continue.

Leg	Station		Position		Leg	Station		Position	
	Stn.	RF	Latitude	Longitude		Stn.	RF	Latitude	Longitude
2	71	3719	5-55.67 N	138-03.99 E	2	101	3749	2-08.67 S	141-29.57 E
2	72	3720	5-33.31 N	138-25.79 E	2	102	3748	2-15.11 S	141-13.64 E
2	73	3721	5-11.89 N	138-48.44 E	2	103	3747	2-19.60 S	141-09.45 E
2	74	3722	4-50.02 N	139-10.52 E	2	104	3755	1-59.43 N	142-00.12 E
2	75	3723	4-27.07 N	139-31.75 E	2	105	3732	2-03.14 N	141-44.45 E
2	76	3724	4-06.04 N	139-54.57 E	2	106	3733	2-06.16 N	141-29.56 E
2	77	3725	3-44.95 N	140-15.73 E	2	107	3734	2-09.49 N	141-13.84 E
2	78	3726	3-21.94 N	140-37.71 E	2	108	3756	2-11.70 N	140-59.67 E
2	79	3727	3-00.77 N	140-58.68 E	2	109	3757	2-17.51 N	140-28.74 E
2	80	3728	2-45.45 N	141-14.11 E	2	110	3758	2-24.22 N	139-59.72 E
2	81	3729	2-30.34 N	141-28.92 E	2	111	3759	2-30.02 N	139-30.12 E
2	82	3730	2-14.41 N	141-44.74 E	2	112	3760	2-35.75 N	138-59.52 E
2	83	3731	1-59.46 N	141-59.05 E	2	113	3761	2-41.87 N	138-30.87 E
2	84	3735	1-44.79 N	141-58.73 E	2	114	3762	2-47.99 N	138-00.11 E
2	85	3736	1-29.52 N	141-58.56 E	2	115	3763	2-54.55 N	137-29.93 E
2	86	3737	1-14.31 N	141-59.87 E	2	116	3764	2-59.58 N	136-59.63 E
2	87	3738	0-59.52 N	141-59.07 E	2	117	3765	3-29.59 N	136-59.81 E
2	88	3739	0-44.71 N	141-59.89 E	2	118	3766	4-01.31 N	136-58.47 E
2	89	3740	0-29.62 N	141-59.51 E	2	119	3767	4-29.55 N	136-59.55 E
2	90	3741	0-14.50 N	141-59.26 E	2	120	3768	4-59.94 N	136-59.75 E
2	91	3742	0-00.24 N	141-59.11 E	2	121	3769	5-30.16 N	137-00.06 E
2	92	3743	0-15.42 S	141-59.21 E	2	122	3770	5-59.22 N	136-58.21 E
2	93	3744	0-29.95 S	141-59.54 E	2	123	3771	6-29.06 N	136-59.06 E
2	94	3745	0-44.90 S	141-59.39 E	2	124	3772	7-00.20 N	136-59.16 E
2	95	3746	1-00.14 S	141-58.81 E					
2	96	3754	1-15.01 S	141-58.48 E					
2	97	3753	1-31.09 S	141-58.78 E					
2	98	3752	1-45.22 S	141-58.92 E					
2	99	3751	2-00.11 S	141-59.09 E					
2	100	3750	2-05.25 S	141-43.59 E					

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3. List of Principal Investigators for all Measurements

The principal investigator (PI) and the person in charge responsible for major parameters measured on the cruise are listed in Table 3.

Table 3. List of principal investigator and the person in charge on the ship for RF10-05.

Item	Principal Investigator（PI）	Person in charge on the ship
Hydrography		
CTDO$_2$ / LADCP	Hitomi KAMIYA	Tetsuya NAKAMURA
Salinity	Hitomi KAMIYA	Keizo SHUTTA
Dissolve oxygen	Hitomi KAMIYA	Yusuke TAKATANI
Nutrients	Hitomi KAMIYA	Takahiro KITAGAWA
Phytopigment	Hitomi KAMIYA	Yusuke TAKATANI
DIC	Hitomi KAMIYA	Shinji MASUDA
Total Alkalinity	Hitomi KAMIYA	Shinji MASUDA
pH	Hitomi KAMIYA	Shinji MASUDA
CFCs	Hitomi KAMIYA	Kazuki ISHIMARU
DOC	Masao ISHII	Shinji MASUDA
^{13}C	Masao ISHII	Shinji MASUDA
Underway		
Meteorology	Hitomi KAMIYA	Keizo SHUTTA
Thermo-Salinograph	Hitomi KAMIYA	Shinji MASUDA
_p_CO$_2$	Hitomi KAMIYA	Shinji MASUDA
Chlorophyll-a	Hitomi KAMIYA	Yusuke TAKATANI
ADCP	Hitomi KAMIYA	Tetsuya NAKAMURA
Bathymetry	Hitomi KAMIYA	Takahiro SEGAWA

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4. Scientific Program and Methods

In recent years, the global environmental issues such as global warming and climate change have become one of the major socio-economic concerns, and it has become apparent that the ocean plays a key role in the climate system. For the better understanding and assessment of global environmental conditions, continuous monitoring of climate variables, concentrations of greenhouse gases both in the ocean and in the atmosphere. To meet those requirements, JMA has been conducting operational oceanographic observations by research vessels in the western North Pacific on a seasonal basis. RF10-05 cruise is one of these activities. The purposes of this cruise are as follows:

(1) To observe profiles of seawater temperature, salinity, dissolved oxygen, nutrients and carbon parameters, as well as upper ocean current;

(2) To observe concentrations of greenhouse gases both in the ocean and in the atmosphere;

(3) To observe bio-geochemical parameters to study carbon cycle in the ocean.

These activities are expected to contribute to international projects related to global environmental issues such as the World Climate Research Programme (WCRP), IOCCP (International Ocean Carbon Coordination Project) and the Global Atmosphere Watch (GAW).

5. Major Problems and Goals not Achieved

Owing to kink in the wire, we reconnected the CTD cable at Stn.19 (29°30'N, 137E; RF3667). After the observation at Stn.104 (2° N, 142°E; RF3755), owing to damage in the wire, we cut the wire about 700 m in length, and reconnected the CTD cable.

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6. List of Cruise Participants

The cruise participants of the cruise is listed in Table 4.

Table 4. List of cruise participants for RF10-05.

Name	Responsibility	Affiliation
Yasuaki BUNGI	Salinity	GEMD / JMA
Kazutaka ENYO	Carbon Items	GEMD / JMA
Hiroyuki FUJIWARA	Nutrients	GEMD / JMA
Sho HIBINO	Dissolved Oxygen	GEMD / JMA
Yoshikazu HIGASHI	CTDO / ADCP / LADCP	GEMD / JMA
Kazuki ISHIMARU	CFCs	GEMD / JMA
Takahiro KITAGAWA	Nutrients	GEMD / JMA
Tomoyuki KITAMURA	CTDO / ADCP / LADCP	GEMD / JMA
Naohiro KOSUGI	Carbon Items	MRI / JMA
Shinji MASUDA	Carbon Items / Thermo-Salinograph	GEMD / JMA
Tetsuya NAKAMURA	CTDO / ADCP / LADCP	GEMD / JMA
Toshiya NAKANO	Chief Scientist	GEMD / JMA
Etsuro ONO	CFCs	GEMD / JMA
Takahiro SEGAWA	Salinity / Bathymetry	GEMD / JMA
Kazuhiro SAITO	Nutrients	GEMD / JMA
Keizo SHUTTA	Salinity / Meteorology	GEMD / JMA
Yusuke TAKATANI	Dissolved Oxygen / Phytopigment	GEMD / JMA
Shinichiro UMEDA	Dissolved Oxygen / Phytopigment	GEMD / JMA

GEMD / JMA: Marine Division, Global Environment and Marine Department, JMA

MRI / JMA: Geochemical Research Department, Meteorological Research Institute, JMA

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Reference

Swift, J. H. (2010): Reference-quality water sample data: Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.14, ICPO Pub. 134, 2010 ver.1*.

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B. Underway measurements

1. *Navigation and Bathymetry*

(1) Personnel

Takahiro SEGAWA (GEMD/JMA)

Tetsuya NAKAMURA (GEMD/JMA)

Keizo SHUTTA (GEMD/JMA)

Yoshikazu HIGASHI (GEMD/JMA)

Tomoyuki KITAMURA (GEMD/JMA)

Yasuaki BUNGI (GEMD/JMA)

(2) Navigation

(2.1) Overview of the equipment

The ship's position was measured by navigation system made by FURUNO ELECTRIC CO., LTD. JAPAN. The system has two 3-channels GPS receivers (GP-80, GP-150). GPS antennas was installed at Compass deck. We switched the receivers to choose better receiving state if the number of GPS satellites decreased or HDOP increased. GPS data, gyro heading and log speed were integrated and delivered to two workstations. One workstation works as primary NTP (Network Time Protocol) server and the other works secondary server.

The navigation data were obtained approximately every one second and one minute data were extract from one second data. These one minute data were recorded as "LOG data".

(2.2) Data Period

05:00, 06 Jul. 2010 to 00:00, 1 Sep. 2010(UTC)

(3) Bathymetry

(3.1) Overview of the equipment

R/V Ryofu Maru equipped a single beam echo sounder, Kongsberg EA 600 (SIMRAD Fisheries Research, Norway). The main objective of the survey is collecting continuous bathymetry data along ship's track. At first we set up system choosing 1500 m/s for sound speed. During the cruise, we used averaged sound velocity data obtained from the nearest CTD cast to get accurate depth data. Data interval was about 8 seconds at 6000m.

(3.2) System Configuration and Performance

System:	Kongsberg EA 600
Frequency:	12kHz
Transmit power:	2kW
Transmit pulse interval:	Within 20seconds
Depth range:	5 to 15,000m
Depth resolution:	1cm
Depth accuracy:	Within 20cm

(3.3) Data Period

The collecting bathymetry data was carried out during the cruise except for port of Palau and Saipan.
05:00, 06 Jul. 2010 to 00:00, 1 Sep. 2010(UTC)

(3.4) Data Processing

The bathymetry data are obtained using a mean sound velocity calculated from the data of nearest CTD cast. The formula of the sound velocity calculated in SEASAVE, CTD data acquisition software, is *Chen and Millero* (1977). The system combines bathymetry data with navigation data, so the data file consists of date, time, location, depth and flag of bathymetry data.

If the erroneous data were obtained, the bathymetry data flag was set to '9' and the data was

set to '0' automatically.

Reference

Chen, C.-T. and F. J. Millero (1977): Speed of sound in seawater at high pressures. *J. Acoust. Soc. Am. **62(5)***, 1129-1135.

2. *Maritime Meteorological Observations*

(1) Personnel

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Tomoyuki KITAMURA (GEMD/JMA)

(2) Data Period

09:00, 6 Jul. 2010 to 23:00, 31 Aug. 2010(UTC)

(3) Methods

The maritime meteorological observation system on R/V Ryofu Maru is Ryofu Maru maritime meteorological measurement station (RMET). Instruments of RMET are listed in Table B.2.1. All RMET data were collected and processed by KOAC-7800 weather data processor made by Koshin Denki Kogyo CO., Ltd. Japan.

Figure B.2.1 and B.2.2 show maritime meteorological observation data.

Table B.2.1. Instruments and locations of RMET.

Sensor	Parameter	Manufacture (Type)	Location (Height from maximum load line)
Thermometer	Air Temperature	Koshin Denki Kogyo (Electric type)	Compass deck (13.3m)
Hygrometer	Relative humidity	Koshin Denki Kogyo (Electrostatic type)	Compass deck (13.3 m)
Thermometer	Sea Temperature	Koshin Denki Kogyo (Electric type)	Engine Room (–4.7 m)
Aerovane	Wind Speed Wind Direction	Koshin Denki Kogyo (Propellar type)	Mast top (19.8 m)
Wave gauge	Wave Height Wave period	Tsurumi-Seiki (Micro wave type)	Ship front (6.5 m)
Barometer	Pressure	Koshin Denki Kogyo (Electrostatic type)	Observation room (2.8 m)

Note that there are two set of thermometer and hygrometer at starboard and port sides.
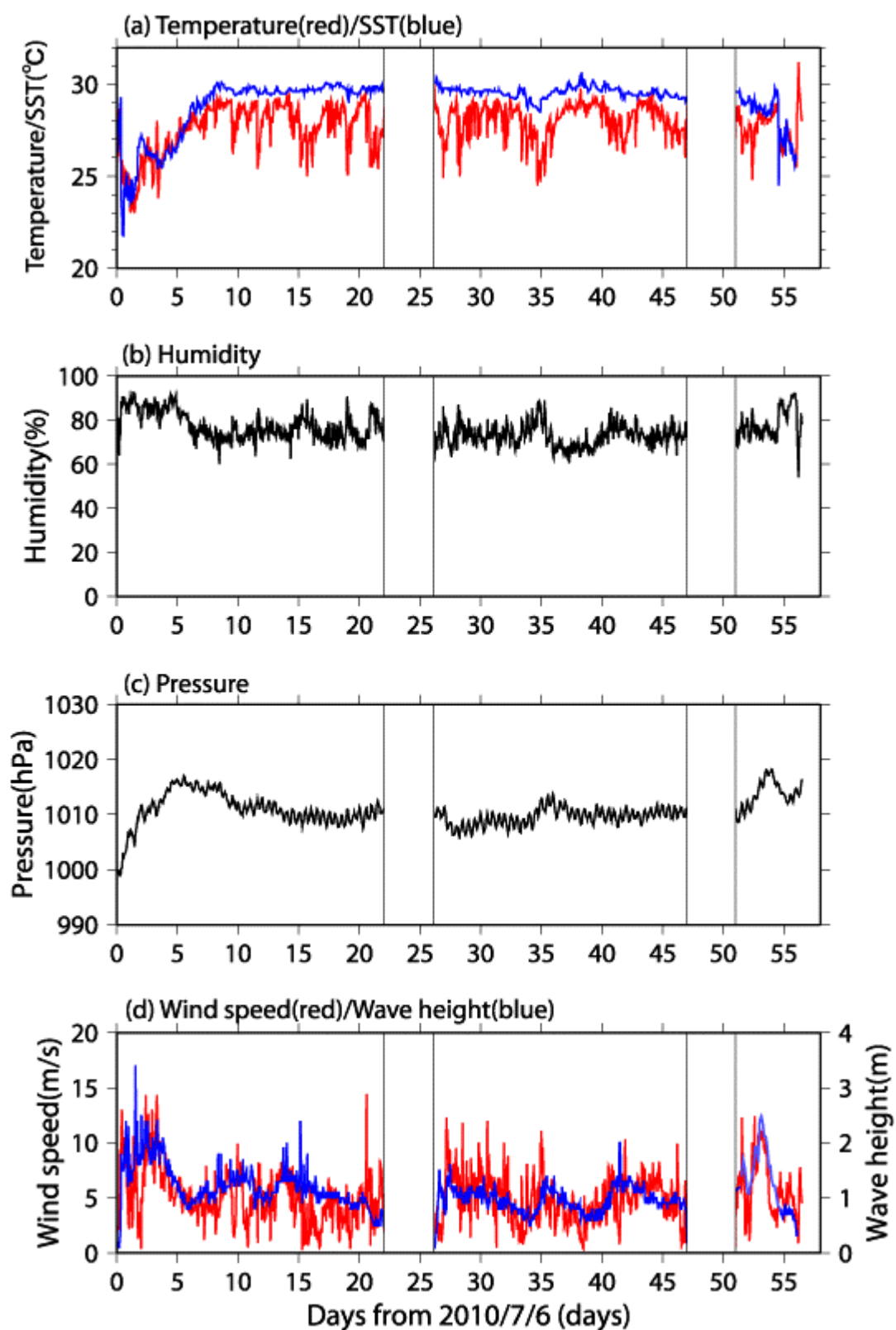
Figure B.2.1. Time series of (a) air and sea surface temperature, (b) relative humidity, (c) pressure, (d) wind speed and wave height. The light blue in (d) panel, light blue line shows the non-instrumental observation of wave height. Day 0 correspond to July 6 (JST), 2010.
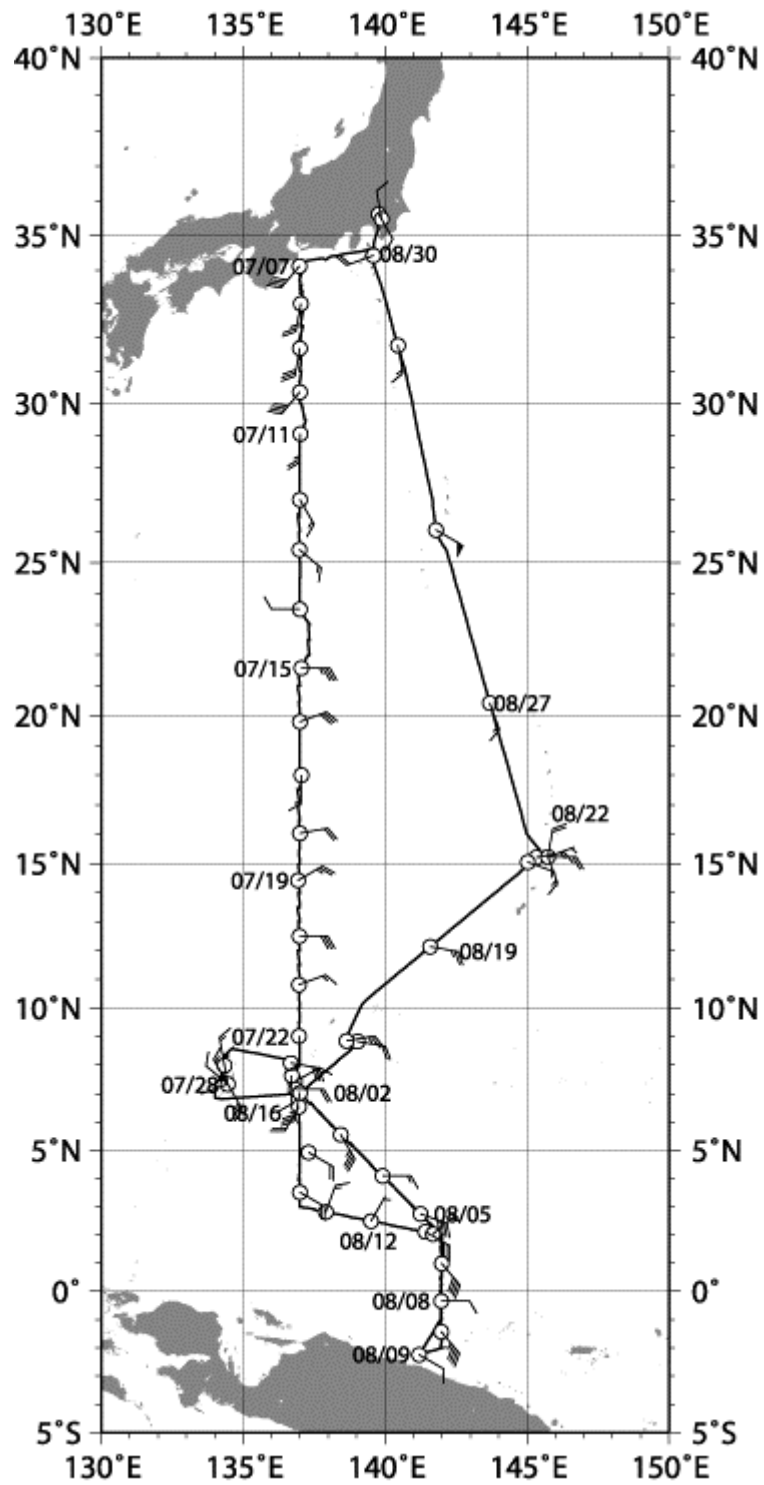
Figure B.2.2. Wind verb along Ryofu Maru at every noon position. Black flag corresponds to 10m/s, long line corresponds to 2m/s and short line corresponds to 1m/s.

(4) Data processing and Data format

All raw data were recorded every 6-seconds. 1-minute and 10-minute values are averaged from 6-seconds values. 10-minute value of every three hours is available at JMA web site (http://www.data.kishou.go.jp/kaiyou/db/vessel_obs/data-report/html/ship/cruisedata_e.php?id=RF1005).

Since the thermometers and hygrometers are equipped on both starboard/port sides on the Compass deck, we used air temperature/relative humidity data taken at upwind side. Dew point temperature was calculated from relative humidity and air temperature data.

No adjustment to sea level values is applied except for pressure data. During the cruise, fixed value +0.5hPa is used for sea level correction. Data are stored in ASCII format and representative parameters are as follows. Time in UTC, longitude (E), latitude (N), ship speed (knot), ship direction (degrees), sea surface pressure (hPa), air temperature (degrees Celsius), dew point temperature (degrees Celsius), relative humidity (%), sea surface temperature (degrees Celsius), wind direction (degree) and wind speed (m/sec).

Wave height and period are observed twice an hour. The sampling duration is 20 minutes and each sampling starts at 5 minutes and 35 minutes after the hour. In addition to those data, ship's position and observation time are recorded in ASCII format.

(5) Data quality

To ensure the data quality, each sensor was checked as follows.

Temperature/Relative humidity sensor:

Temperature and relative humidity (T/RH) sensors were checked by manufacturer and, they were also checked by using calibrated Asman psychrometer before the cruise and arrival at the port. The discrepancy between T/RH sensors and Asman psychrometer were within ±0.4 degrees Celsius and ±4 % respectively at both sides.

Thermometer (Sea Temperature):

Sea temperature sensor was calibrated once per year by the manufacturer. Certificated accuracy of sea temperature sensor is better than ±0.4 degrees Celsius. The values are also compared with bucket samples after the departure.

Pressure sensor:

Using calibrated portable barometer (Vaisala 765-16B, certificated accuracy is better than ± 0.1 hPa), pressure sensor was checked before the cruise. Mean difference of RMET pressure sensor and portable sensor is less than 0.7 hPa.

Aerovane:

Aerovane was checked once per year by the manufacturer and, once per five years by the Meteorological Instrument Center, JMA.

(6) Ship's weather observation

Non-instrumental observations such as weather, cloud, visibility, wave direction and wave height were made by the ship crews every three hours. We sent those data together with RMET data to the Global Collecting Centre for Marine Climatological Data in IMMT (International Maritime Meteorological Tape) -III format. The RMET data is available at JMA web site.

(http://www.data.kishou.go.jp/kaiyou/db/vessel_obs/data-report/html/ship/cruisedata_e.php?id=RF1005).

5. *Chlorophyll-a*

(1) Personnel

Yusuke TAKATANI (GEMD/JMA)

Shinichiro UMEDA (GEMD/JMA)

(2) Method

The Continuous Sea Surface Water Monitoring System of fluorescence (Nippon Kaiyo Co. Ltd.) automatically had been continuously measured seawater which is pumped from a depth of about 4.5 m below the maximum load line to the laboratory. The flow rate of the surface seawater was controlled by several valves and adjusted to about 0.6 L/min. The sensor in this system is a fluorometer (10-AU, S/N:7063) manufactured by Turner Designs. The system measured every one minute.

(3) Measurement

Periods of measurement and problems are listed in Table B.5.1.

(4) Calibration

In order to calibrate the fluorescence sensor, we collected 200 ml of surface seawater from outlet of water line of the system for measuring chlorophyll-*a*. The seawater samples were collected at nominally 60 N. miles intervals. The seawater sample was gently filtrated by low vacuum pressure through Whatman GF/F filter (diameter 25mm). The filter was immediately transferred into 9 ml of N, N-dimethylformamide (DMF) and then stored at -30°C to extract chlorophyll-*a* for more than 24 hours. Concentrations of chlorophyll-*a* were measured by a fluorometer (10-AU, S/N: 6718, TURNER DESIGNS) that was previously calibrated against a pure chlorophyll-*a* (Lot.:BCBB4166, Sigma chemical Co.) by the method described in UNESCO (1994). In order to calibrate the fluorometer, fluorometric measurement of chlorophyll-*a* was performed by the method of *Holm-Hansen et al*. (1965) and *Holm-Hansen and Riemann* (1978). The results of the measurements are shown in Table B.5.2. The fluorescence sensor may be contaminated while measuring. Therefore, we calibrated the

fluorescence value of the sensor to 0 (deionized water) and 10 (0.1 ppm Rhodamine solution) at the start of a leg, and measured a solution of the same concentration at the end of a leg. The results are shown in Table B.5.3.

The data is calculated by the following procedure;

- The fluorescence value of the sensor is calibrated by deionized water and a Rhodamine solution at the starting and the ending.
- The ratio between a calibrated fluorescence value and a chlorophyll-*a* concentration of a seawater sample is interpolated by distance.
- The chlorophyll-*a* concentration is calculated by multiplying a calibrated fluorescence value by an interpolated ratio.

(5) Data and Result

Quality controlled data, those file name is "20120202_p09_in-vivo.txt", is distributed by JMA format. The record structure of JMA format is shown below.

Column1: observed date [UTC]

Column2: observed time [UTC]

Column3: observed latitude

Column4: observed longitude

Column5: fluorescence value

Column6: fluorescence value calibrated by deionized water and a Rhodamine solution

Column7: ratio between a calibrated fluorescence value and a chlorophyll-*a* concentration of a seawater sample interpolated by distance

Column8: calculated chlorophyll-*a* concentration (μg/L)

Result of chlorophyll-*a* concentration of underway measurement in shown in Figure B.4.1. Chlorophyll-*a* data on Figure B.4.1 is averaged over 2-hours.
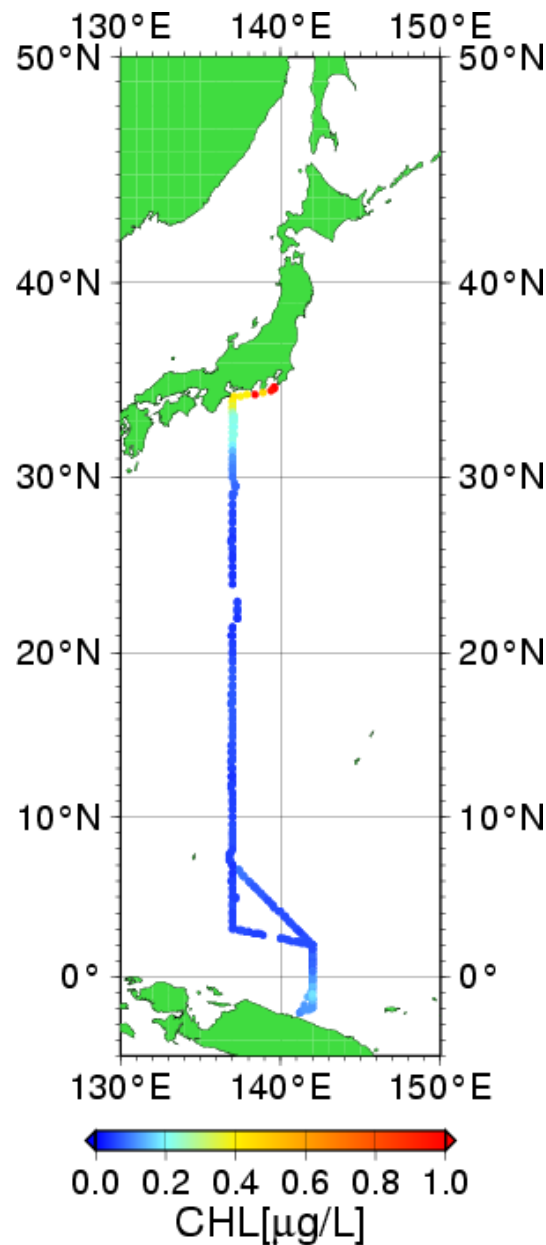
Figure B.4.1. Result of chlorophyll-*a* concentration of underway measurement.

References

Holm-Hansen, O., and B. Riemann (1978): chlorophyll *a* determination: improvements in methodology. *Oikos, 30*, 438-447.

Holm-Hansen, O., C. J. Lorenzen, R. W. Holmes and J. D. H. Strickland (1965): Fluorometric determination of chlorophyll. *J. Cons. Perm. Int. Explor. Mer., 30*, 3-15.

UNESCO (1994), Protocols for the joint global ocean flux study (JGOFS) core measurements: Measurement of chlorophyll *a* and phaeopigments by fluorometric analysis, *IOC manuals and guides 29, Chapter 14.*

Table B.5.1. Events list of the fluorescence sensor.

Date [UTC]	Time [UTC]	Event
6-Jul-10	08:51	The measurement started. (Leg 1 start)
6-Jul-10	12:19	Error data due to the flow line
6-Jul-10	22:13	Error data due to the flow line
7-Jul-10	00:21	Error data due to the flow line
8-Jul-10	07:26	Error data due to the flow line
8-Jul-10	12:14	Error data due to the flow line
9-Jul-10	12:46	Error data due to the flow line
13-Jul-10 -14-Jul-10	21:54-09:48	Error data due to the flow line.
15-Jul-10	01:43-02:56	Failure of data storage due to the PC trouble.
19-Jul-10	21:33	Error data due to the flow line
23-Jul-10	14:29	The measurement stopped. (Leg 1 end)
2-Aug-10	02:38	The measurement started. (Leg 2 start)
2-Aug-10	05:16-05:25	GPS data error.
4-Aug-10	21:03	Error data due to the flow line
4-Aug-10	22:18	Error data due to the flow line
6-Aug-10	09:41-10:26	Failure of data storage due to the PC trouble.
6-Aug-10	21:10	Error data due to the flow line
7-Aug-10	02:56-03:03	Failure of data storage due to the PC trouble.
7-Aug-10	14:38	Error data due to the flow line
8-Aug-10	05:49-08:00	Failure of data storage due to the PC trouble.
9-Aug-10	04:32	Error data due to the flow line
9-Aug-10	18:50	Error data due to the flow line
10-Aug-10	08:57	Error data due to the flow line
10-Aug-10	13:52	Error data due to the flow line
11-Aug-10	12:35-13:16	Failure of data storage due to the PC trouble.
11-Aug-10 -12-Aug-10	22:09-11:09	Error data due to the flow line.

16-Aug-10	08:51	The measurement stopped. (Leg 2 end)

Table B.5.2. Comparison of sensor fluorescence and bottle chlorophyll-*a* collected from the pump in each sampling point.

Date [UTC]	Time [UTC]	Latitude	Longitude	Sensor Fluorescence	Chlorophyll-*a* (µg/L)
6-Jul-10	08:51	35˚02.06'N	139˚41.04'E	1.242	0.76
7-Jul-10	00:23	34˚14.80'N	136˚59.37'E	0.632	0.48
7-Jul-10	04:48	34˚00.97'N	136˚58.39'E	0.719	0.40
7-Jul-10	15:03	33˚30.36'N	137˚01.73'E	0.507	0.27
8-Jul-10	04:05	33˚03.12'N	137˚03.42'E	0.240	0.21
8-Jul-10	17:38	32˚21.66'N	137˚04.83'E	0.261	0.18
9-Jul-10	05:14	31˚43.51'N	136˚58.28'E	0.453	0.27
9-Jul-10	17:49	30˚58.89'N	137˚02.15'E	0.157	0.09
10-Jul-10	10:38	30˚00.04'N	137˚02.44'E	0.098	0.08
11-Jul-10	03:01	29˚03.78'N	137˚00.31'E	0.056	0.08
11-Jul-10	16:00	27˚59.81'N	136˚58.89'E	0.050	0.04
12-Jul-10	04:43	27˚00.72'N	136˚59.28'E	0.070	0.04
12-Jul-10	19:01	25˚59.15'N	136˚58.26'E	0.049	0.04
13-Jul-10	08:27	25˚01.70'N	137˚00.67'E	0.038	0.04
13-Jul-10	21:52	24˚01.35'N	136˚59.80'E	0.043	0.05
14-Jul-10	12:37	23˚01.36'N	137˚17.09'E	0.009	0.04
15-Jul-10	00:14	21˚59.46'N	137˚16.84'E	-0.004	0.05
15-Jul-10	13:39	21˚00.03'N	136˚55.59'E	0.025	0.03
16-Jul-10	01:15	19˚57.38'N	136˚59.99'E	0.029	0.05
16-Jul-10	13:25	18˚59.38'N	136˚58.47'E	0.086	0.07
17-Jul-10	03:10	18˚00.68'N	137˚02.40'E	0.050	0.07
17-Jul-10	17:16	17˚00.64'N	136˚55.61'E	0.127	0.07
18-Jul-10	06:56	16˚00.56'N	136˚57.81'E	0.129	0.08

18-Jul-10	18:48	14˚58.61'N	136˚58.13'E	0.183	0.07
19-Jul-10	08:19	13˚59.99'N	136˚57.16'E	0.145	0.06
19-Jul-10	21:45	12˚59.91'N	136˚57.25'E	0.193	0.06
20-Jul-10	11:13	12˚00.11'N	136˚56.43'E	0.151	0.03
21-Jul-10	01:28	11˚00.56'N	136˚56.68'E	0.212	0.06
21-Jul-10	14:50	10˚00.13'N	136˚58.09'E	0.242	0.04
22-Jul-10	02:57	9˚00.78'N	136˚57.52'E	0.229	0.06
22-Jul-10	17:19	7˚59.83'N	136˚58.61'E	0.339	0.06
23-Jul-10	14:29	7˚00.36'N	136˚58.13'E	0.510	0.05
2-Aug-10	02:38	7˚01.80'N	136˚59.66'E	0.105	0.10
4-Aug-10	11:23	3˚45.89'N	140˚14.74'E	-0.111	0.04
5-Aug-10	00:09	3˚00.95'N	140˚57.80'E	-0.104	0.06
5-Aug-10	17:49	1˚59.73'N	141˚58.66'E	-0.099	0.05
7-Aug-10	03:43	0˚59.99'N	141˚58.33'E	-0.024	0.09
7-Aug-10	12:11	0˚29.74'N	141˚57.93'E	-0.060	0.06
7-Aug-10	14:37	0˚14.75'N	141˚59.47'E	0.633	0.13
7-Aug-10	21:35	0˚00.34'N	141˚57.14'E	0.288	0.14
8-Aug-10	14:29	0˚59.78'S	141˚57.93'E	0.147	0.13
9-Aug-10	16:39	2˚00.22'S	141˚57.71'E	-0.033	0.14
10-Aug-10	22:56	1˚58.91'N	141˚59.16'E	-0.124	0.05
11-Aug-10	09:50	2˚11.62'N	140˚57.94'E	-0.101	0.05
11-Aug-10	22:08	2˚24.47'N	139˚58.34'E	-0.064	0.06
12-Aug-10	11:12	2˚35.48'N	138˚59.16'E	-0.071	0.05
13-Aug-10	01:37	2˚47.76'N	137˚59.88'E	-0.068	0.05
13-Aug-10	17:37	2˚59.39'N	136˚59.57'E	-0.009	0.07
14-Aug-10	09:46	4˚00.91'N	136˚57.92'E	-0.050	0.04
15-Aug-10	00:09	4˚59.68'N	136˚59.26'E	-0.014	0.06
15-Aug-10	18:15	5˚58.61'N	136˚56.93'E	-0.004	0.05
16-Aug-10	08:51	6˚59.93'N	136˚58.48'E	-0.009	0.04

Table B.5.3. Results of the fluorescence value of the sensor at the start and end of each leg(0 : deionized water, 10 : 0.1ppm Rhodamine solution).

	Start			End		
	Date [UTC]	0	10	Date [UTC]	0	10
1 Leg	6-Jul-10 08:30	0	10.000	27-Jul-10 05:00	0	8.296
2 Leg	1-Aug-10 04:30	0	10.000	20-Aug-10 01:32	0	8.438

6. *Acoustic Doppler Current Profiler*

(1) Personnel

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(2) Instruments and Methods

The instrument used was the hull-mounted 38kHz Ocean Surveyor ADCP (Teledyne RD Instruments, Inc., USA; hereafter TRDI). The transducer of the system was installed in a dome at 3 m left of center and 13 m aft of the bow at the water line. The firmware version was 23.17 and the data acquisition software was TRDI/VMDAS Version. 1.46. The instrument was used in water-tracking mode during the operations, and was recording each ping raw data in 20 m × 60 bin from about 36 m to 1200 m in depth. Sampling interval was variable as short as possible and typically 6.4 seconds. GPS navigation data and ship's gyrocompass data were recorded with the ADCP data. In addition to the raw data, 60 seconds and 300 seconds averaged data were stored as short time average (STA) and long time average (LTA) data, respectively. Current field based on the gyrocompass was used to check the operation and the performance on board.

(3) Performance and quick view of the ADCP data on board

The performance of the ADCP instrument was almost good throughout the cruise, and current profiles were usually reached about 1000m. We monitored the profiles and currents based on LTA data in this cruise on board. The ADCP had been installed on the R/V Ryofu Maru just before the cruise, so the scale factor and misalignment angle (*Joyce*, 1989) to ADCP firmware for Leg 1 were set 1.0 and 0.0, respectively. The scale factor and misalignment for Leg 2 and Leg 3 were set 1.0012 and −1.0627, respectively, based on the calibration constants evaluated

by the Leg 1 data.

(4) Data Processing

LTA data were processed by using CODAS (Common Oceanographic Data Access System) software, developed at the University of Hawaii (http://currents.soest.hawaii.edu/docs/doc/index.html). We use a standard CODAS processing including a PC time correction, a sound-speed correction based on the thermistor temperature at the transducers, and an amplitude and phase calibration constant applied to the measured velocities.

Calibration constants to be applied were evaluated for each leg using the water track data. For Leg 1, the amplitude and phase were 1.0012 and −1.0627, respectively, and for Leg 2 and Leg 3, those were 1.0005 and −0.5528, respectively. Figure B.6.1 shows surface current at the depth of 36 m during the cruise.
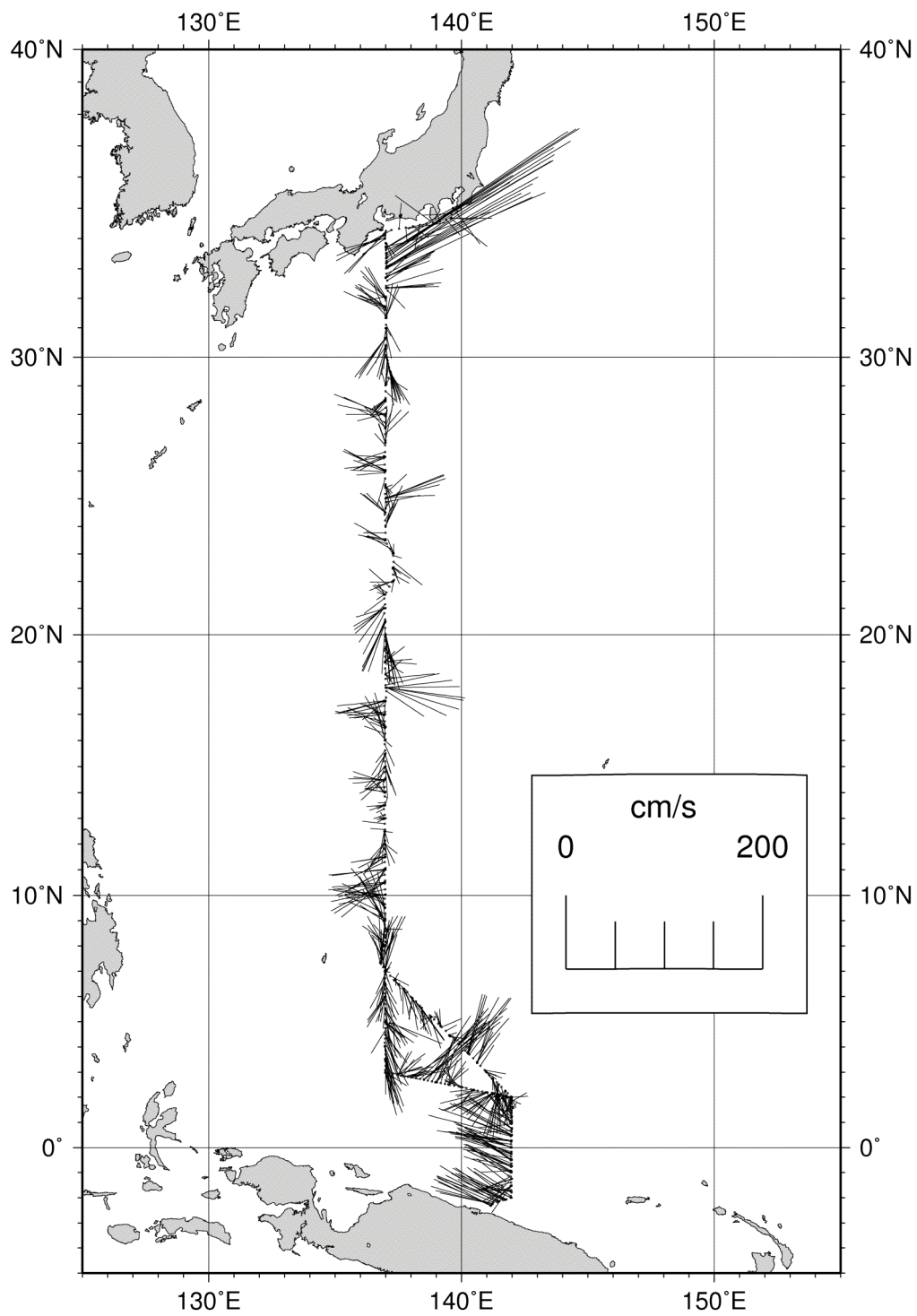
Figure B.6.1. Surface current at the depth of 36 m.

Reference

Joyce, T. M. (1988): On in-situ "calibration" of shipboard ADCPs. *J. Atmos. Oceanic Technol., 6*, 169-172.

C. Hydrographic Measurement Techniques and Calibration

1. CTD/O2 Measurements

13 December 2013

(1) Personnel

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(2) CTD Traction Winch and Motion Compensated Crane Arrangements

The CTD/O$_2$ system was deployed by using a Traction Winch System with ca. 7000m of 8.03 mm armored cable (Tyco Electronics, USA) and a Motion Compensated Crane (Dynacon, Inc., USA). The system was installed on the *R/V Ryofu Maru* in March, 2010 (Photo C1.1).
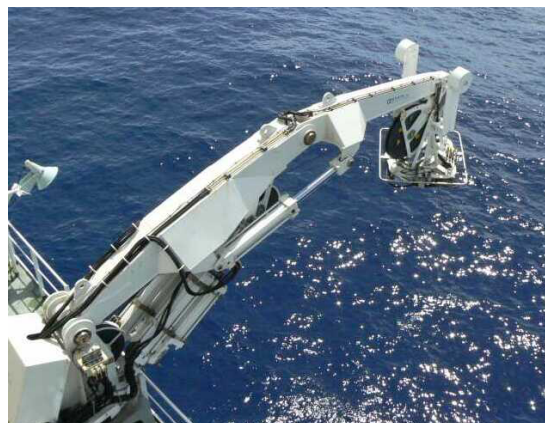
Photo C1.1. (Left) The Traction Winch and (right) Motion Compensated Crane.

(3) Overview of the CTD/O$_2$ system

The CTD/O$_2$ system, SBE 911plus system (Sea-Bird Electronics, Inc., USA), was used for entire cruise. The system is consisted of a SBE 9plus underwater unit and a SBE 11plus deck unit. The SBE 11plus deck unit is a rack-mountable interface which supplies DC power to under

water unit, decodes serial data stream, formats data under microprocessor control, and passes the data to a computer. The real time serial data from the underwater unit is sent to the deck unit. The deck unit decodes the serial data and sends them to a personal computer to display and a storage in a file using SEASAVE data acquisition software (SEASAVE-Win32, version 7.18).

The SBE 911plus system controls 36-position SBE 32 Carousel Water Sampler (Photo C1.2). The Carousel with a custom frame accepts 10-liter Niskin bottles (General Oceanics, Inc., USA). The SBE 9plus was mounted horizontally in the 36-position carousel frame. Two set of SBE's temperature (SBE 3plus) and conductivity (SBE 4C) sensor modules were used with the SBE 9plus underwater unit. Two modular units of underwater housing pump (SBE 5T) flush water through sensor tubing at a constant rate independent of the CTD's motion (Photo C1.3). Two dissolved oxygen sensors (RINKO III: JFE Advantech Co., Ltd., Japan; http://www.jfe-alec.co.jp/html/english_top.htm) were mounted on CTD housing, by the side of primary T/C sensors (Photo C.1.3). Auxiliary sensors, Deep Ocean Standards Thermometer (SBE 35) and an altimeter (PSA-916D: Teledyne Benthos, Inc., USA) were also used with the SBE 9plus underwater unit. The SBE 35 was mounted at the center of CTD between two pumps and the altimeter was mounted at the same height of pressure sensor of SBE 9plus.
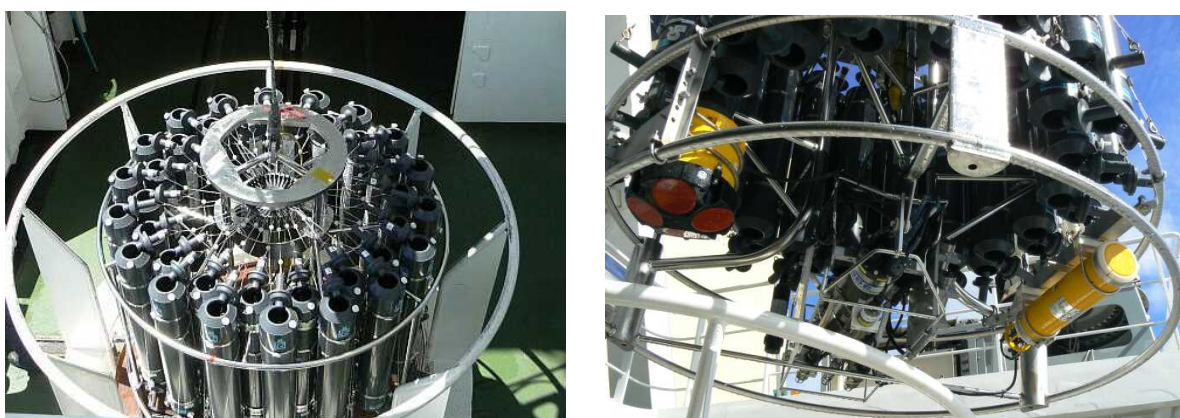
Photo C1.2. The CTD/O_2 system (left) top view and (right) bottom view.
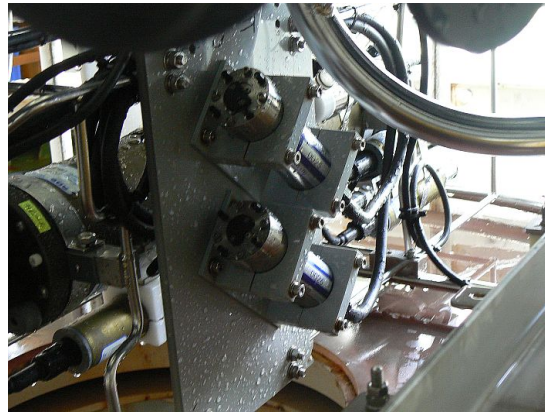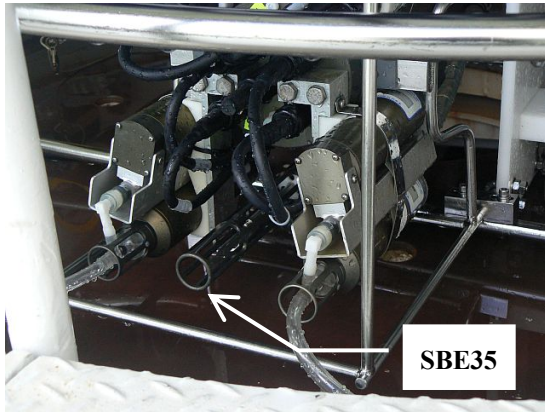
Photo C1.3.　(left) SBE 9plus CTD with SBE35 and (right) RINKO III.

Table C.1.1. Specification and serial number of the CTD/O2 measurements system components.

Deck unit	Serial Number				
SBE 11plus（SBE）	0648				

Under water unit	Serial Number	Range	Accuracy	Stability	Resolution
SBE 9plus (SBE)	35560	0 to 10000 psi	0.015 %(FS)	0.002%FS/year	0.001 % (FS)
	(Pressure: 0764)	0 to 6800 dbar	1.0 dbar	0.2 dbar/year	0.1 dbar

Temperature	Serial Number	Range	Accuracy	Stability	Resolution
SBE 3plus (SBE)	4923 (primary)	-5 to 35 ℃	0.001 ℃	0.0002 ℃/month	0.0002 ℃
	4199 (secondary)				

Conductivity	Serial Number	Range	Accuracy	Stability	Resolution
SBE 4C (SBE)	3670 (primary)	0 to 7 S/m	0.0003 S/m	0.0003 S/m/month	0.00004 S/m
	2842 (secondary)				

Pump	Serial Number				
SBE 5T (SBE)	3887 (primary)				
	5501 (secondary)				

Oxygen	Serial Number	Range	Linearity	Response time	Resolution
RINKO III (JFE)	25 (primary, foil number:144)	0 to 200% (saturation)	±2% (FS)	≤ 1 second	0.01 to 0.04 %
	26 (secondary, foil numner:144)				

Water sampler	Serial Number		
SBE 32 (SBE)	0734		

Altimeter	Serial Number	Range	Resolution
PSA-916D (TB)	1267	0 to 100 m	1 cm

Water Sampling Bottle			
Niskin Bottle (GO)	・10-Liter	・Bottle O-ring: Viton	
	・No TEFRON coating	・Stainless spring	

SBE: Sea-Bird Electronics Inc., USA　JFE: JFE Advantech Co., Ltd., Japan

GO: General Oceanics, Inc., USA　TB: Teledyne Benthos, Inc., USA

(4)　Pre-cruise calibration

(4.1) Pressure

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

S/N 0764, 25 May 2010

$$c_1 = -4.318853e+04$$
$$c_2 = -4.853949e-01$$
$$c_3 = 1.294200e-02$$
$$d_1 = 3.706500e-02$$
$$d_2 = 0.000000e+00$$
$$t_1 = 3.005385e+01$$
$$t_2 = -4.407111e-04$$
$$t_3 = 4.098190e-06$$
$$t_4 = 1.662250e-09$$
$$t_5 = 0.000000e+00$$

Pressure coefficients are first formulated into

$$c = c_1 + c_2 \times U + c_3 \times U^2$$
$$d = d_1 + d_2 \times U$$
$$t_0 = t_1 + t_2 \times U + t_3 \times U^2 + t_4 \times U^3 + t_5 \times U^4$$

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

$$U(degrees\,Celsius) = M \times (12\,bit\,pressure\,temperature\,compensation\,word) - B$$

The following coefficients were used for S/N 0764 in SEASOFT:

$$M=1.289080e–02$$

$$B=–8.282450e+00$$

 (in the underwater unit system configuration sheet dated on 25 May, 2010)

Finally, pressure is computed as

$$P(psi) = c \times (1 - t_0^2/t^2) \times \left\{1 - d \times (1 - t_0^2/t^2)\right\}$$

where *t* is pressure period (μsec).

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

The pressure sensor drift is known to be primarily an offset drift at all pressures rather than a change of span slope. The following coefficients for the sensor drift correction were also used in SEASOFT:

$$Slope=0.999930$$

$$Offset=–0.56680$$

The drift–corrected pressure is computed as

$$Drift\,corrected\,pressure(dbar) = slope \times (computed\,pressure\,in\,dbar) + offset$$

(4.2) Temperature (SBE 3plus)

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

S/N 4923(primary), 26 May 2010

g = 4.35306322e–03

h = 6.39215989e–04

i = 2.11728148e–05

j = 1.77647263e–06

f_0 = 1000.000

S/N 4199(secondary), 26 May 2010

g = 4.39450115e–03

h = 6.49623486e–04

i = 2.38724882e–05

j = 2.21735485e–06

f_0 = 1000.000

Temperature (ITS-90) is computed according to

$$Temperature(ITS-90) = \frac{1}{g + h \times \ln(f_0/f) + i \times \ln^2(f_0/f) + j \times \ln^3(f_0/f)} - 273.15$$

where f is the instrument frequency (Hz).

Time drift of the SBE 3plus temperature sensors based on the laboratory calibrations is shown in Figure C.1.1.
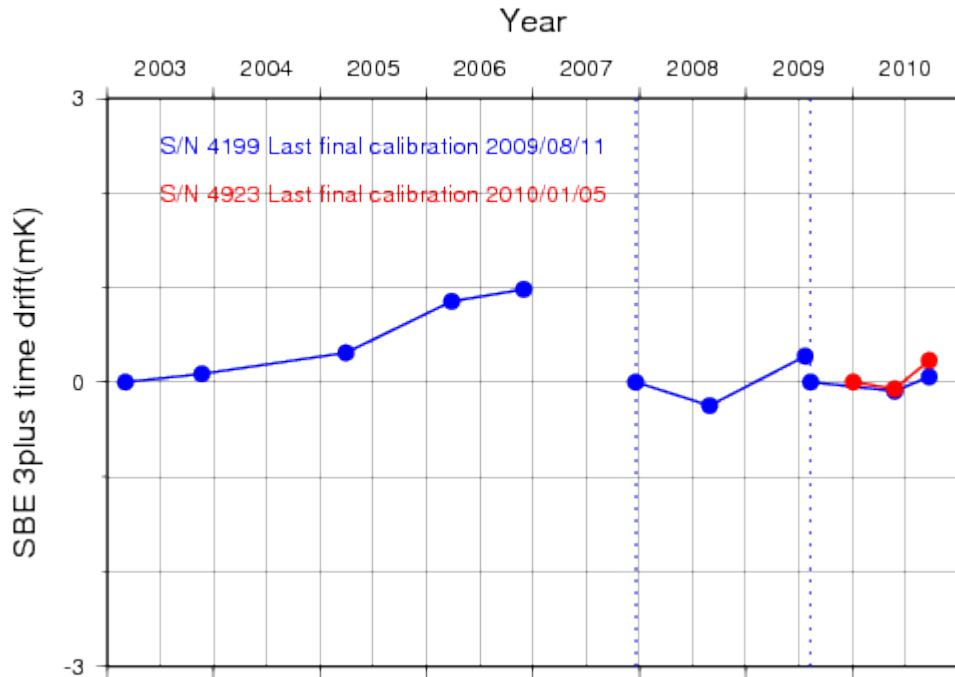
Figure C.1.1. Time drift of the SBE 3plus temperature sensors (S/N 4923 and 4199) based on laboratory calibrations performed by SBE, Inc. The secondary sensor (S/N4199) was resecured the temperature probe retaining nut in December 2007, and replaced the main piston O-rings in August 2009

(4.3) Conductivity (SBE 4C)

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

S/N 3670(primary), 26 May 2010

$$g = -1.02022781e+001$$
$$h = 1.57745207e+000$$
$$i = -2.48735605e-003$$
$$j = 2.86313468e-004$$
$$CP_{cor} = -9.57e-08$$
$$CT_{cor} = 3.25e-06$$

C1-7

S/N 2842(secondary), 26 May 2010

$$
\begin{aligned}
g &= -1.01321263e+001 \\
h &= 1.38952824e+000 \\
i &= 2.52094473e-004 \\
j &= 4.58018677e-005 \\
CP_{cor} &= -9.57e-08 \\
CT_{cor} &= 3.25e-06
\end{aligned}
$$

Conductivity of a fluid in the cell is expressed as:

$$C(S/m) = \left(g + h \times f^2 + i \times f^3 + j \times f^4\right) / \left\{10 \times \left(1 + CT_{cor} \times t + CP_{cor} \times p\right)\right\}$$

where f is the instrument frequency (kHz), t is the water temperature (degrees Celsius) and p is the water pressure (dbar).

(4.4) Deep Ocean Standards Thermometer (SBE 35)

In the first place a newly manufactured SBE 35 is first calibrated in a temperature controlled bath against Standard Platinum Resistance Thermometer, and this calibration is referred as the Linearization Calibration. In the next place SBE 35 is calibrated to generate slope and offset coefficients that correct for the time drift from the Linearization Calibration. This calibration is referred Fixed Point Calibrations. Pre-cruise sensor calibrations were performed at SBE, Inc., USA. The following coefficients were stored in EEPROM:

S/N 0069, 23 October, 2006(1st step: Linearization Calibration)

$$
\begin{aligned}
a_0 &= 4.96812728e-003 \\
a_1 &= -1.39341438e-003 \\
a_2 &= 2.06596098e-004 \\
a_3 &= -1.14827915e-005 \\
a_4 &= 2.44200422e-007
\end{aligned}
$$

Linearized temperature (ITS–90) is computed according to

$$Linearized\,temperature(ITS-90) = 1/\{a_0 + a_1 \times \ln(n) + a_2 \times \ln^2(n) + a_3 \times \ln^3(n) + a_4 \times \ln^4(n)\} - 273.15$$

where $\boldsymbol{n}$ is the instrument output. Then the SBE 35 is certified by measurements in thermodynamic fixed-point cells of the Triple Point of Water (TPW: 0.0100 degrees Celsius) and Gallium Melt Point (GaMP: 29.7646 degrees Celsius). The slow time drift of the SBE 35 is adjusted by periodic recertification corrections.

S/N 0069, 21 August, 2009 (2nd step: Fixed Point Calibration)

Slope=0.999998

Offset=0.000258

Temperature (ITS-90) is calibrated according to

$$Temperature(ITS-90) = slope \times (Linearized\ temperature) + offset$$

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. In this cruise NCYCLES was set to 2.

(5) Data processing

(5.1) Data Collection

CTD system was powered on at least five minutes in advance of the operation and was powered off after CTD came up from the surface.

The package was lowered into the water from the port side and held about 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 0.6 m/s approximately to 50m (or more when wave height was high), then the package was stopped to turn on the heave compensator of the crane. The package was lowered again at a rate of 0.9 m/s to the bottom. For the up cast, the package was lifted at a rate of 0.9 m/s except for bottle firing stops. At each bottle firing stops, the bottle was fired after waiting for about 30 seconds and the package was stayed at least 10 seconds for measurement of the SBE 35 after firing. At 50 m from the surface, the package was stopped to turn off the heave compensator of the crane.

Water samples were collected using a 36-position SBE 32 Carousel Water Sampler with 10-liter Niskin bottles.

The SBE11plus deck unit received the data signal from the CTD. Digitized data were forwarded to a personal computer running the SEASAVE data acquisition software (*SEASAVE-Win32, version 7.18*). Temperature, conductivity, salinity, oxygen and descent/ascent rate profiles were displayed in real–time with the package depth, altimeter reading and sound speed. Differences in temperature, salinity, and oxygen between primary and secondary sensor were also displayed in order to monitor the status of sensors. Note that oxygen data were displayed and monitored in voltage (0–5V).

Altimeter (PSA-916D) was mounted at the same height of pressure sensor of SBE 9plus (Photo C1.4). The altimeter detected the sea floor at 100 of 124 stations, the average distance of beginning detecting the sea floor was 26.4m, and that of final detection of sea floor was 13.8m. The summary of detection of PSA-916D was shown in Figure C.1.2.
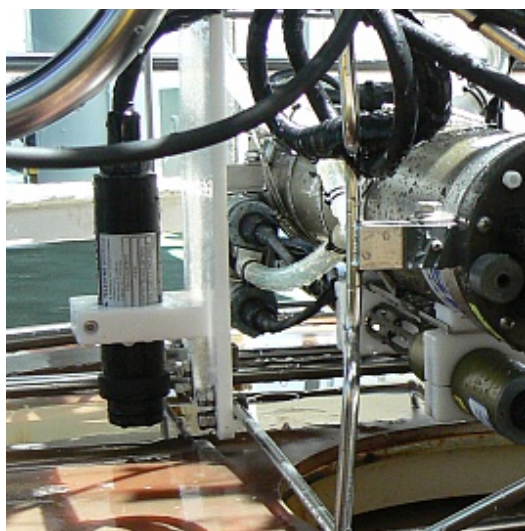
Photo C.1.4. The location of PSA-916D.
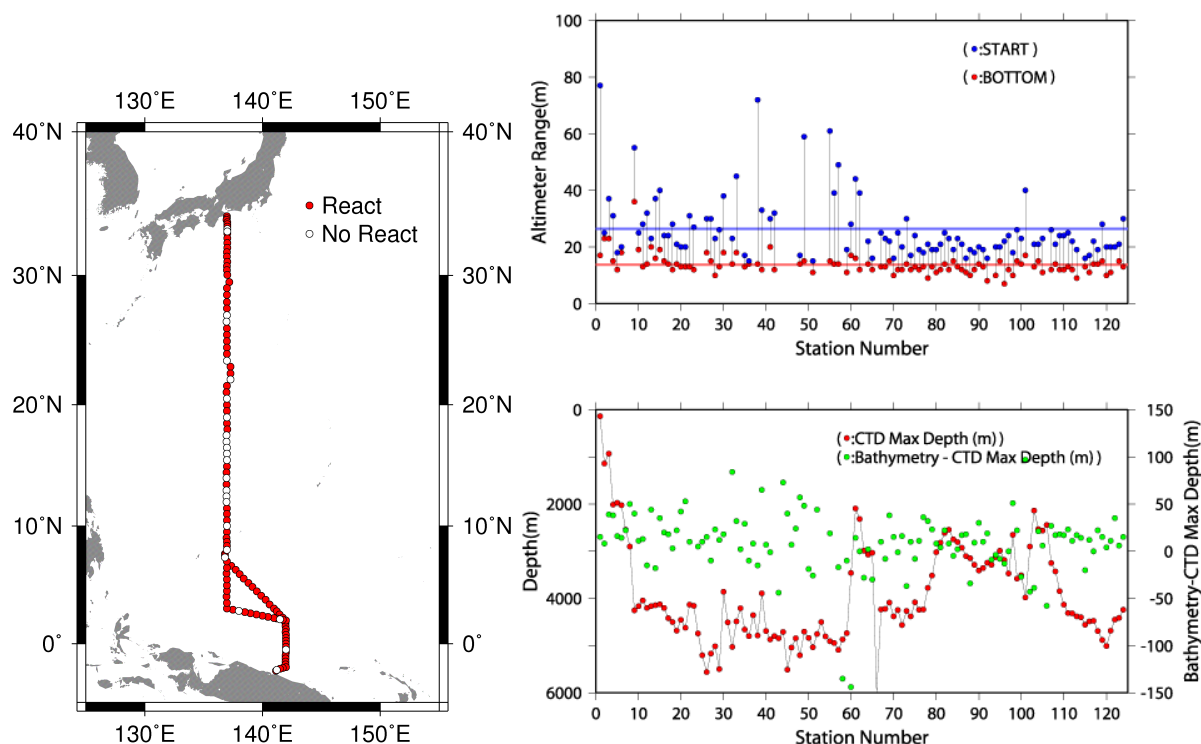
Figure C.1.2. The summary of detection of PSA-916D. The left panel shows the stations of detection, the right panel shows the relationship among PSA-916D, bathymetry and CTD depth.

(5.2) Data Processing

SEASOFT (*SEASOFT-Win32, version 7.18*) 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 personal computer. Raw data are acquired from instruments and are stored as unmodified data. The conversion module ***DATCNV*** uses 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.

We made the original module for the process of RINKO III and JMA's report. The following

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

DATCNV converted the raw data to engineering unit data such as scan number, pressure, temperatures, conductivities, RINKO III voltages, time in Julian days, pump status, and flag. ***DATCNV*** also extracted bottle information where scans were marked with the bottle confirm bit during acquisition. The duration was set to 2.0 seconds, and the offset was set to 0.0 seconds.

DECKP_OFF (original module) cancelled the deck pressure and after this module, spikes in temperature and salinity were eliminated manually.

RINKO_hystoff (original module) cancelled the hysteresis of RINKO III using the method of SBE 43 (Sea-Bird Electronics, 2009) .

SECT_IN (original module) found the first and last scan numbers while pump was activated, and made the surface data while pump was not activated for down cast.

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

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.

ALIGNCTD converted the time-sequence of RINKO III sensor outputs into the pressure sequence to ensure that all calculations were made using measurements from the same parcel of water. RINKO III sensor output delays 1 second compared to pressure, temperature and conductivity.

ALIGNROS (original module) replace the RINKO III output of the bottle to that of all scan data applied ***ALIGNCTD*** module.

BOTTOLESUM created a summary of the bottle data. The bottle position, date, time were output as the first two columns. Salinities, pressure, temperatures, conductivities and oxygen voltage were averaged over 2.0 seconds.

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.

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

BINAVG averaged the data into 1dbar 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 could exist in every dbar.

RSC2ASC (original module) made the data set from 1dbar to the bottom of observation.
The RINKO III processes (original module) to make down and up cast data in every dbar were performed after those processes.

(6) Post–cruise calibration

(6.1) Pressure

The CTD pressure sensor offset in the period of this cruise is estimated from the pressure readings on the ship deck. In order to get the calibration data for the pre-cast pressure sensor drift, the CTD deck pressure was averaged over five scan pressure data after the CTD system had been stable on the deck.

Deck pressure was used to cancel the CTD pressure sensor offset in CTD data processing. Time series of the CTD deck pressure is shown in Figure C.1.3. Tendencies of CTD deck pressure and air pressure were almost similar during the cruise.
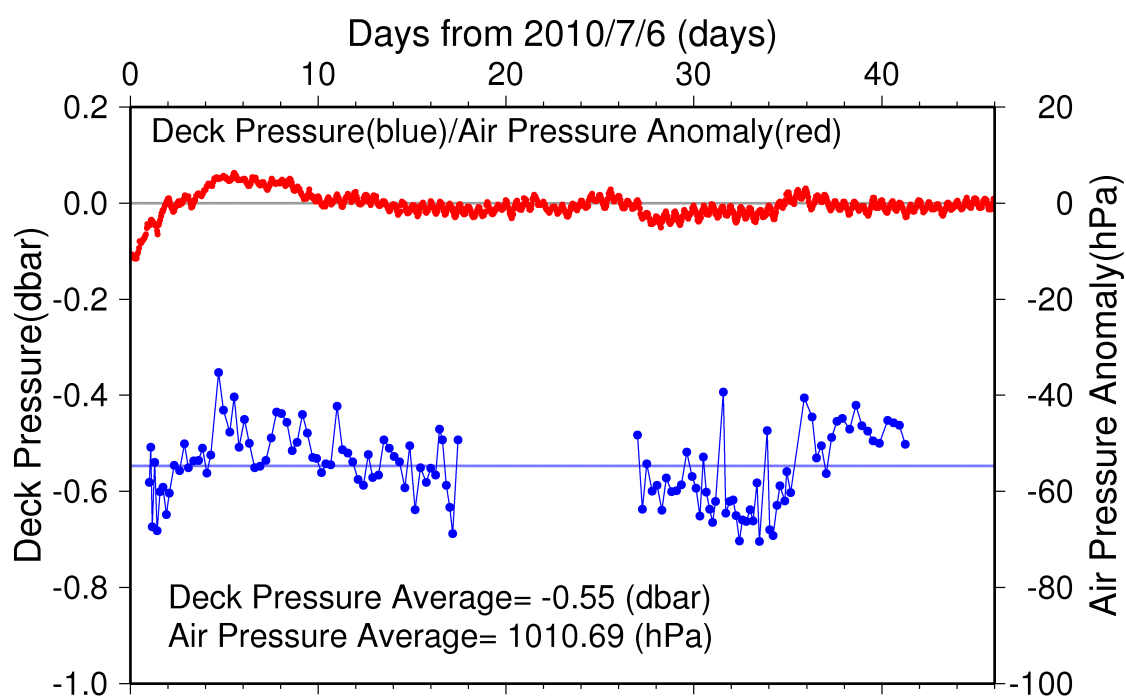
Figure C.1.3. Time series of the CTD deck pressure. Red line indicates atmospheric pressure anomaly. Blue line and dots indicate pre-cast deck pressure and average.

Post-cruise sensor calibrations were performed at SBE, Inc., USA. The pressure sensor drift is known to be primarily an offset drift at all pressures rather than a change of span slope.

S/N 0764, 27 September 2010

Slope = 0.999940

Offset = –0.55550

The pressure sensor drift was estimated to be 0.07 dbar at the pressure of 6000 dbar. The pressure sensor drift was small, so post-cruise calibration is not applied.

(6.2) Temperature

*Budeus and Schneide*r (1998) noted that the CTD temperature sensor (SBE 3plus) showed a pressure sensitivity. The pressure sensitivity for a SBE 3plus sensor is usually less than +2 mK/6000 dbar. It is somewhat difficult to measure this effect in the laboratory and the difficulty is one of the primary reasons to use the SBE 35 at sea for critical work. Also SBE 3plus measurements may be affected by viscous heating (about +0.5 mK) that occurs in a TC duct and does not occur for un–pumped SBE 35 measurements (*Larson and Pederson,* 1996). Furthermore, the SBE 35 calibrations have some uncertainty (about 0.2 mK) and SBE 3plus calibrations have some uncertainty (about 1 mK). So the practical corrections for CTD temperature data can be made by using a SBE 35, correcting the SBE 3plus to agree with the SBE 35 (*Uchida et al.,* 2007).

Post-cruise sensor calibration for the SBE 35 was performed at SBE, Inc., USA.

S/N 0069, 03 October 2010 (2nd step: fixed point calibration)

Slope=1.000009

Offset=0.000313

The discrepancy between the CTD temperature and the SBE 35 temperature is considered to be a function of pressure and time. But the time drift correction is regarded as 0 due to following reasons; 1) The time drift of the SBE 3plus estimated to be as –0.00094 K/year for S/N 4923, –0.00044 K/year for S/N 4199 and that of SBE 35 is estimated to be as +0.01 mK during cruise according to pre-cruise and post-cruise calibrations performed at SBE, 2).

Effect of the viscous heating is assumed to be constant. Since the pressure sensitivity is thought to be constant in time at least during observation period, the CTD temperature is calibrated as

$$Calibrated\ temperatrue = T - (c_0 + c_1 \times P)$$

where T is the CTD temperature in degrees Celsius, P is pressure in dbar and c_0, c_1 are calibration coefficients.

The calibration is performed for the primary and secondary temperature data. The CTD data created by the software module ***BOTTLESUM*** are used. (The deviation of CTD temperature from the SBE35 temperature at depth shallower than 1900 dbar is large for determining the coefficients with sufficient accuracy since the vertical temperature gradient is too large in the

regions. So the coefficients are determined by least squares method using the data for the depth deeper than 1900 dbar). The temperature calibration summary is listed in Table C.1.1 at Pressure $\geq$ 1900dbar. We adopted secondary conductivity sensor (S/N 2842), so secondary temperature sensor (S/N4199) is adopted.

Table C.1.1. Temperature Calibration summary (Pressure $\geq$ 1900dbar).

S/N	Num	c_0 (K)	c_1 (K/dbar)	Average (K)	STD (K)	Note
4923	620	5.2348920e–4	2.3591956e–7	0.0000	0.0002	Leg 1
4923	378	5.8598217e–4	2.3668426e–7	0.0000	0.0002	Leg 2
4199	620	2.0889685e–4	2.4549467e–7	0.0000	0.0002	Leg 1
4199	378	2.3835674e–4	2.3980066e–7	0.0000	0.0002	Leg 2
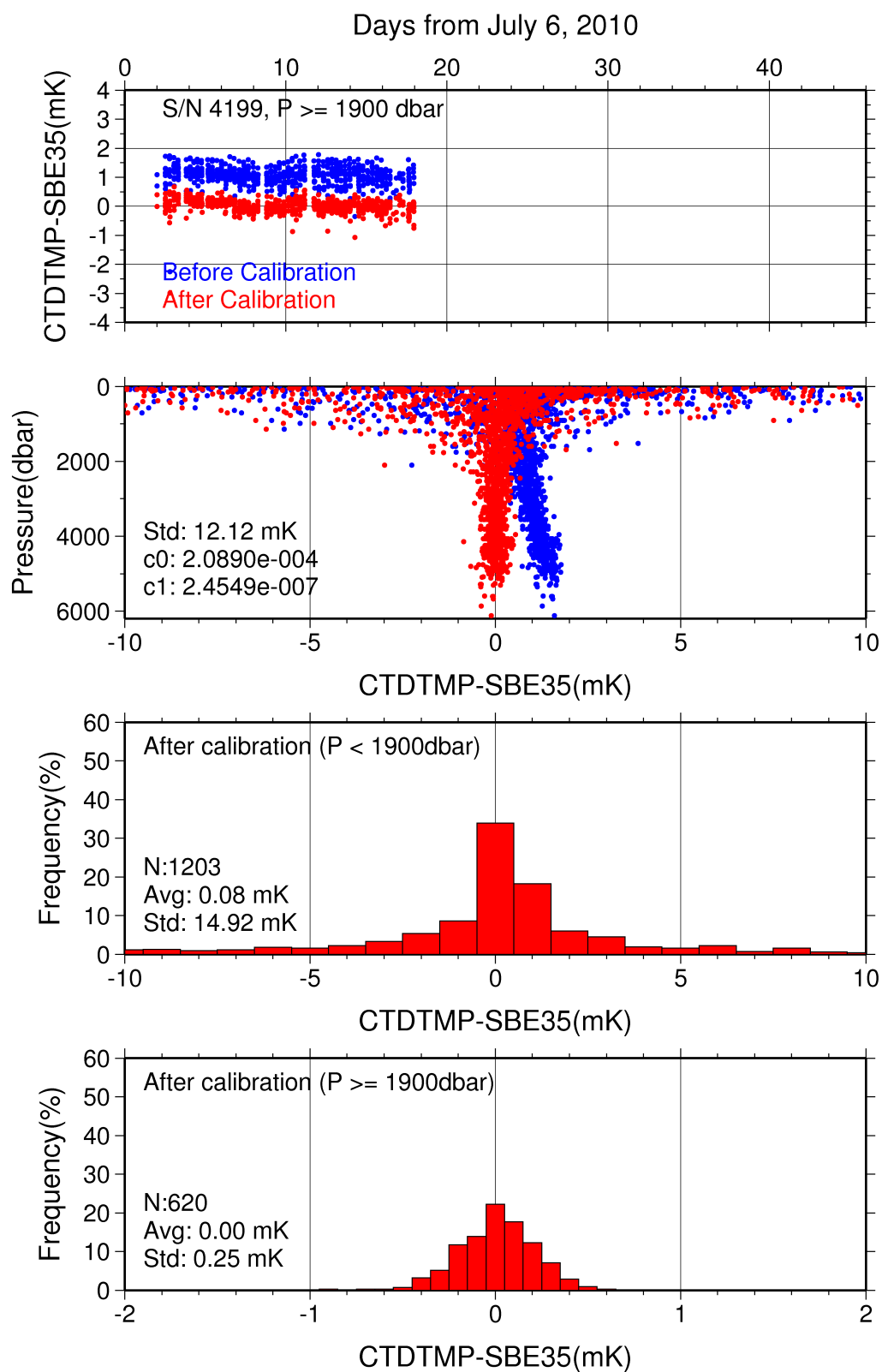
Figure C.1.4. Difference between the CTD temperature (secondary) and the Deep Ocean Standards thermometer (SBE35) at Leg 1. Blue and red dots indicate before and after the calibration using SBE35 data respectively. Lower two panels show histogram of the difference after calibration.
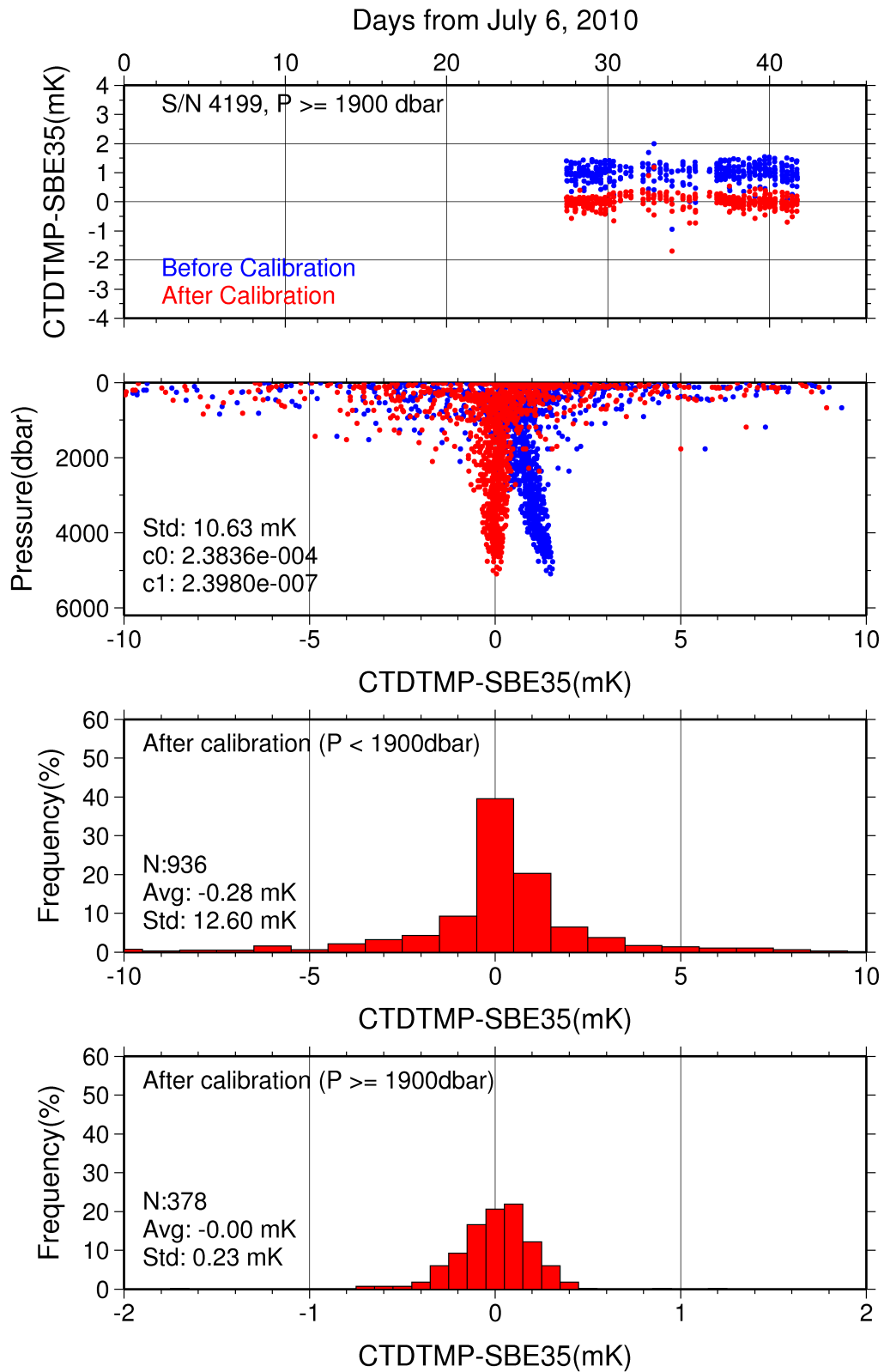
Figure C.1.5. Difference between the CTD temperature (secondary) and the Deep Ocean Standards thermometer (SBE35) at Leg 2. Blue and red dots indicate before and after the calibration using SBE35 data respectively. Lower two panels show histogram of the difference after calibration.

(6.3) Salinity

The CTD salinity is computed from pressure, conductivity and temperature according to algorithm of the Practical Salinity Scale of 1978 (PSS78). The discrepancy between the CTD conductivity and the bottle conductivity is considered to be a function of pressure and time according to *McTaggart et al.* (2010).

Post–cruise sensor calibrations were performed in September 2010 at SBE, Inc., USA. According to the conductivity calibration report, the drifts since pre-cruise calibration was – 0.00090 /month in PSS78 at 3.0 S/m for primary sensor (S/N3670), so the effect of SBE 4C drift during the cruise was estimated to be less than 0.002 in PSS78. However the time coefficient was set to zero in this cruise because the calibration was performed considering the sudden station-dependent shifts of the CTD conductivity and other calibration coefficients included the effect of slow drift by calibration grouping. So the CTD conductivity is calibrated as below.

$$Calibrated\,Conductivity = C - (\sum_{i=0}^{I} c_i \times C^i + \sum_{j=1}^{J} p_j \times P^j)$$

where C is the CTD conductivity and c_i and p_j are calibration coefficients. Coefficient sets of each (I, J) combination was calculated by least square method between CTD conductivity and the bottle conductivity data except for bad bottle data. In calculated coefficient sets, the best (I, J) combination are determined by referring to AIC (*Akaike*, 1974). According to *McTaggart et al.* (2010), maximum of I and J are 2.

The discrepancy between the calibrated CTD conductivity and the bottle conductivity was within 0.0001 S/m for each sensor. The results of post–cruise calibration for the CTD salinity (S/N 2849) are summarized in Figure C.1.6. The calibration coefficients and the data (Num) used for the calibration are listed in Table C.1.2, and the calibration summary are listed in Table C.1.3 and C.1.4 for S/N 3670 and S/N 2842, respectively. Secondary sensor (S/N 2842) is adopted because of large time drift of primary sensor (S/N 3670).

Table C.1.2. Conductivity Calibration Coefficient Summary.

S/N	Num	c_0(mS/m)	c_1	c_2(mS/m)	Stations
			p_1(mS/dbar)	p_2(mS/m/dbar^2)	
3670	1274	1.5107e–3	–7.4144e–5	0.0000e+0	Stn. 1 – 67
			6.6856e–7	–8.3866e–11	
3670	308	2.2680e-3	–8.0696e–5	0.0000e+0	Stn. 68 – 83, Stn. 105 – 107
			–1.2437e–8	0.5038e–11	
3670	608	1.0048e-3	–7.6991e–5	0.0000e+0	Stn. 84 – 104, Stn. 108 – 124
			3.9031e–7	–4.2466e–11	
2849	2195	2.1693e-3	–5.5359e–5	0.0000e+0	Stn. 1 – 124
			8.3709e–7	–7.6495e–11	

Table C.1.3. Conductivity Calibration Summary for S/N 3670.

Stations	Pressure < 1900dbar			Pressure ≥ 1900 dbar		
	Num	Average (mS/cm)	Std (mS/cm)	Num	Average (mS/cm)	Std (mS/cm)
Stn. 1 – 67	830	0.0000	0.0022	444	–0.0000	0.0006
Stn. 68 – 83, 105 – 107	211	0.0000	0.0024	94	0.0000	0.0004
Stn. 84 – 104, 108 – 124	411	0.0000	0.0023	197	-0.0000	0.0005

Table C.1.4. Conductivity Calibration Summary for S/N 2842.

Stations	Pressure < 1900dbar			Pressure ≥ 1900 dbar		
	Num	Average(mS/cm)	Std(mS/cm)	Num	Average(mS/cm)	Std(mS/cm)
Stn. 1 – 124	1455	0.0000	0.0022	740	–0.0000	0.0004
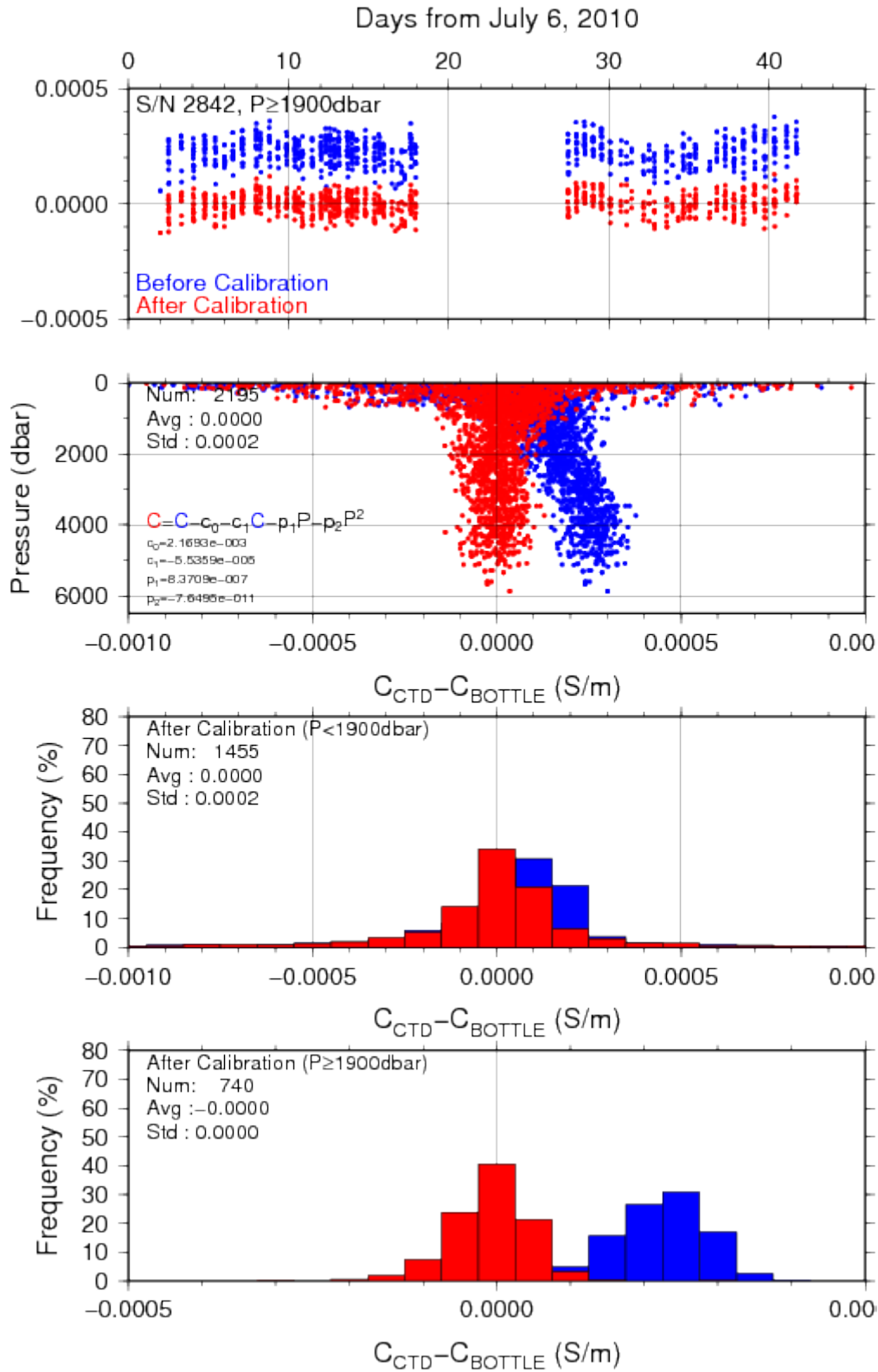
Figure C.1.6. Difference between the CTD conductivity (secondary) and the bottle conductivity. Blue and red dots indicate before and after the calibration using bottle data respectively. Lower two panels show histogram of the difference before and after calibration.

(6.4) Oxygen

RINKO III (JFE Advantech Co., Ltd., Japan) is based on the ability of selected substance to act as dynamic fluorescence quenchers. RINKO III model is designed to use with a CTD system which accept an auxiliary analog sensor, and is designed to operate down to 7000 m. The CTD oxygen is calculated using RINKO III output (voltage) by the Stern–Volmer equation, according to a method by *Uchida et al.* (2008). The formulas are as follows:

$$P_0 = 1.0 + c_4 \times t$$
$$P_c = c_5 + c_6 \times v + c_7 \times T + c_8 \times T \times v$$
$$K_{sv} = c_1 + c_2 \times t + c_3 \times t^2$$
$$coef = (1.0 + c_9 \times P / 1000)^{1/3}$$
$$[O_2] = \left\{ (P_0 / P_c - 1.0) / K_{sv} \times coef \right\}$$

Where **P** is the pressure in dbar, **t** is the potential temperature, **v** is RINKO output voltage in volt, **T** is elapsed time of the sensor from the beginning of first station in calculation group in day and **$[O_2]$** is the dissolved oxygen saturation, dissolved oxygen is calculated from **$[O_2]$**, **potential temperature** and **salinity** by *Garcìa and Gordon* (1992) in µmol/kg. Calibration coefficients (**c_1–c_9**) are determined by minimizing difference between CTD oxygen and bottle dissolved oxygen by quasi-newton method (*Shanno,* 1970).

In general, the calibration was performed for each Leg. But in this cruise, both RINKO III had large time drift especially in the early part of Leg 1, we could not solve on **c_7** and **c_8**. Worse yet, bottle dissolved oxygen data were flagged bad due to the problem of titration (please refer to C3 - (15)) in the latter part of Leg1 (Stn. 58 - 67). To avoid extrapolation in the direction of **T** in the period when bottle dissolved oxygen data were flagged bad, the calibration was performed across Leg1 and Leg2. The calibration was performed only for primary sensor (S/N 25) because the output of secondary sensor (S/N 26) was very noisy during the cruise. Calibration coefficients are listed in Table C.1.5. The result of the calibration during cruise is shown in Figure C.1.7, the data summary is listed in Table C.1.6 and Table C.1.7.

Table C.1.5. Dissolved Oxygen Calibration Coefficients.

Stations	c_1	c_2	c_3	c_4	c_5
	c_6	c_7	c_8	c_9	
Stn. 1 – 29	1.89977	1.93812e–2	1.43624e–4	–6.661791e–4	–1.26432e–1
	3.07029e–1	–7.05462e–5	9.73313e–4	4.45363e–2	
Stn. 30 – 80	1.90512	2.00330e–2	1.50096e–4	–7.75255e–4	–1.27249e–1
	3.08390e–1	–5.89936e–4	8.77397e–4	4.23961e–2	
Stn. 81 – 124	1.76044	1.55258e–2	8.25974e–6	–1.65719e–3	–9.90824e–2
	3.06244e–1	1.44412e–4	4.13619e–4	4.51073e–2	

Table C.1.6. Dissolved Oxygen Calibration Summary.

	Pressure < 950dbar			Pressure ≥ 950dbar		
Stations	Num	Average of deviation (μmol/kg)	STD of deviation (μmol/kg)	Num	Average of deviation (μmol/kg)	STD of deviation (μmol/kg)
Stn. 1 – 29	245	–0.01	0.94	234	–0.01	0.33
Stn. 30 – 80	467	0.05	0.81	432	0.00	0.23
Stn. 81 – 124	435	–0.01	0.77	308	0.01	0.25
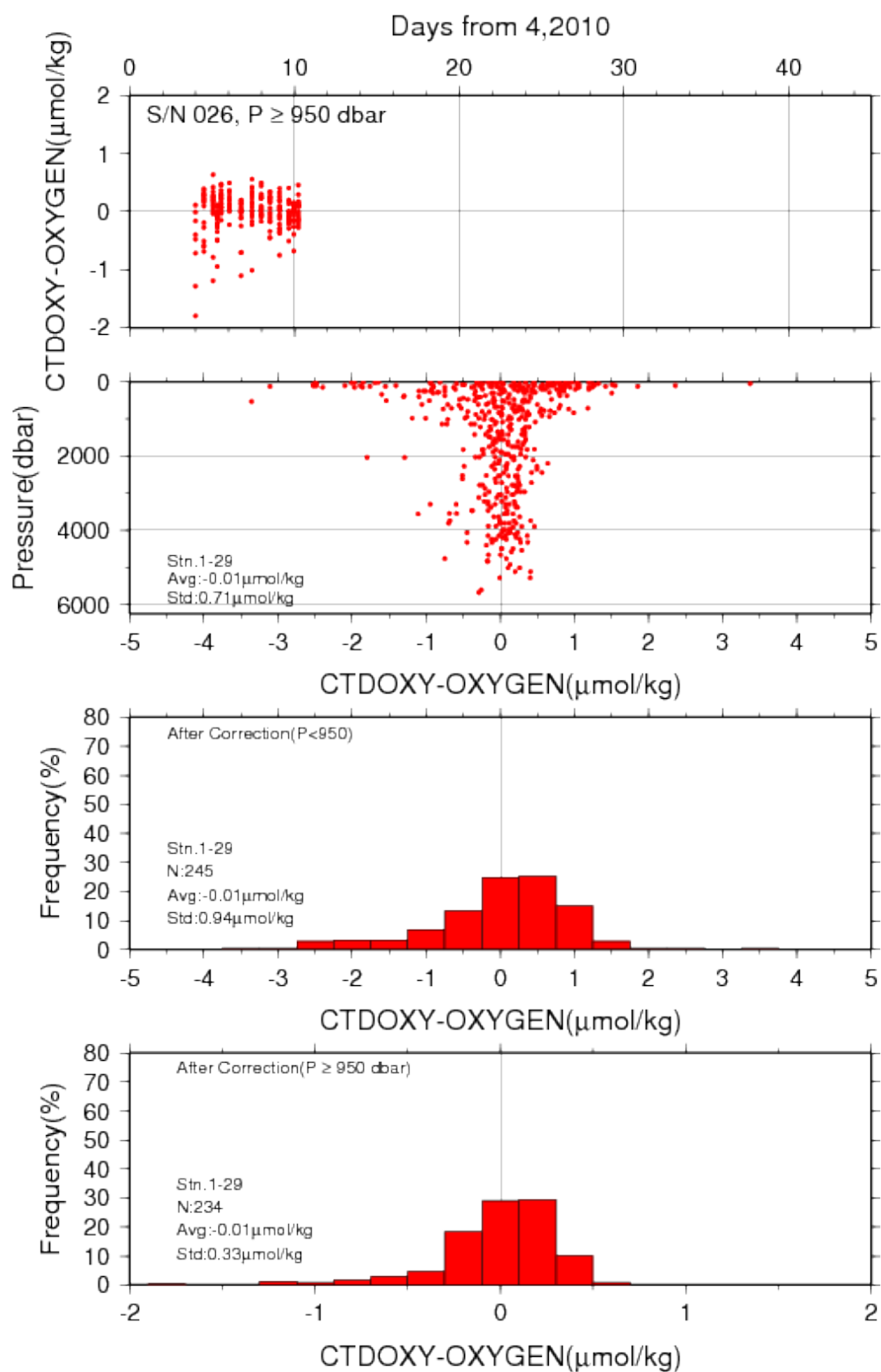
Figure C.1.7. Difference between the CTD oxygen and bottle dissolved oxygen in the early part of Leg 1. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.
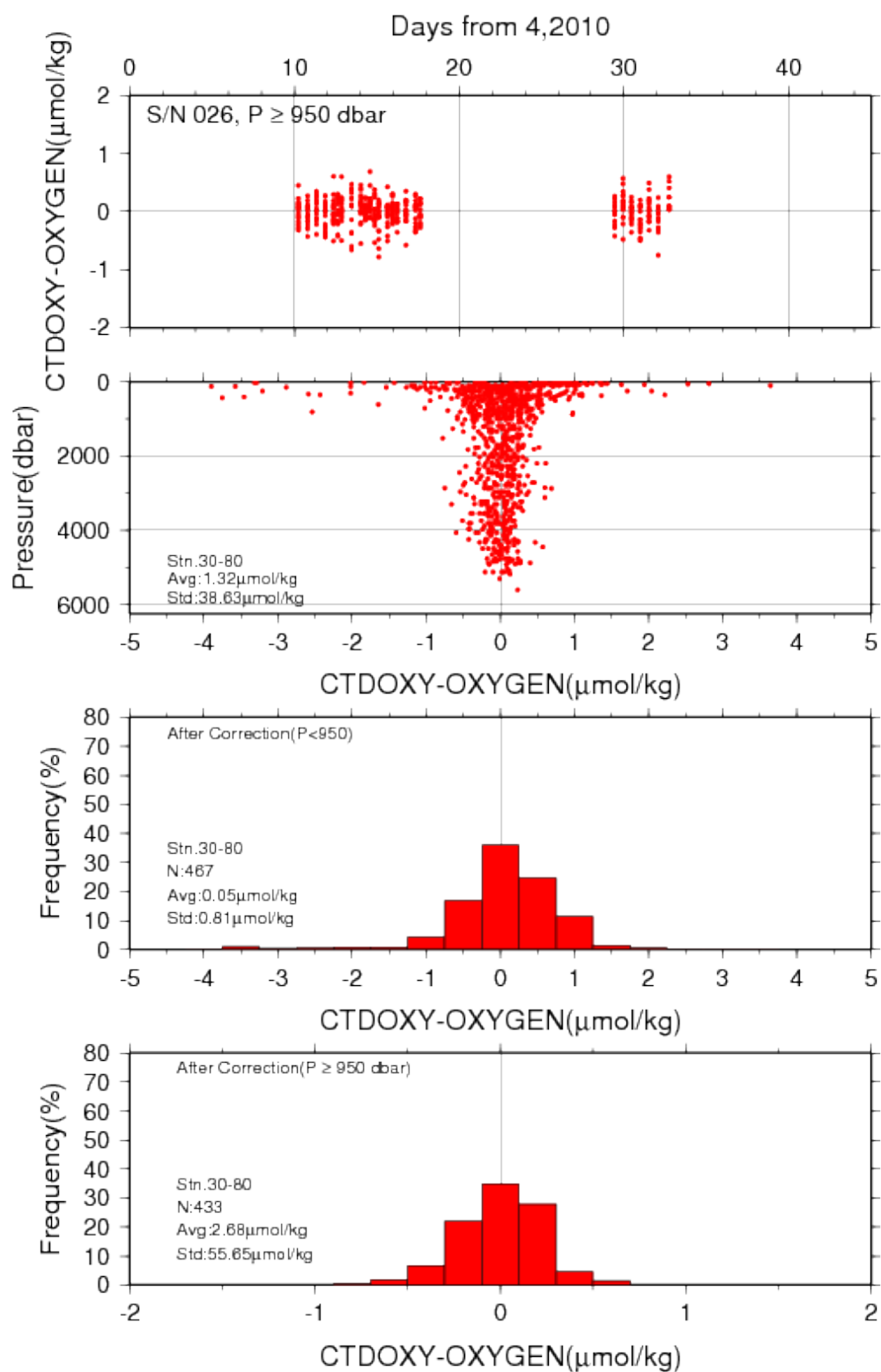
Figure C.1.8. Difference between the CTD oxygen and bottle dissolved oxygen across Leg 1 and Leg 2. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.
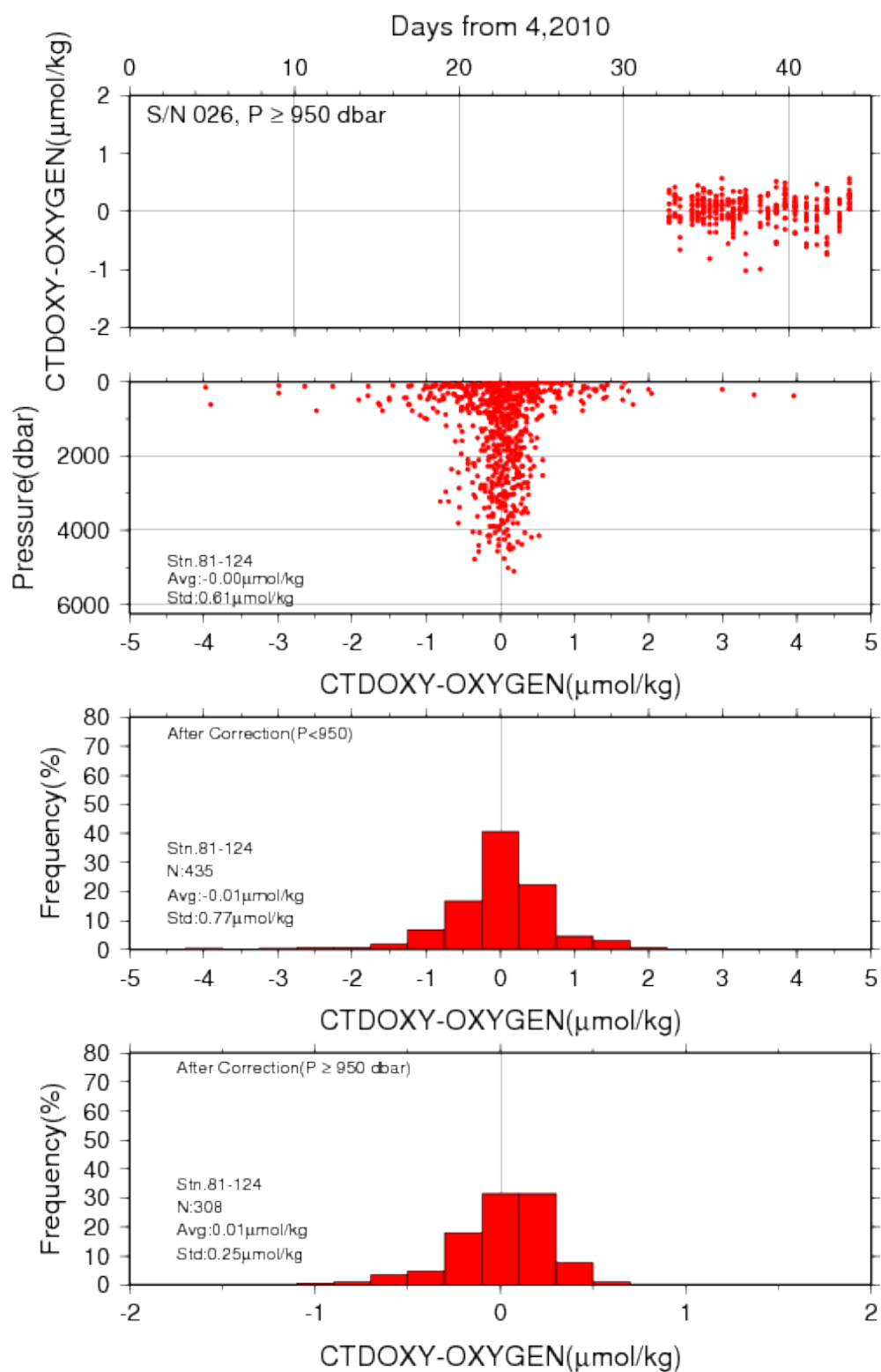
Figure C.1.9. Difference between the CTD oxygen and bottle dissolved oxygen in the latter part of Leg 2. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.

References

McTaggart, K. E., G. C. Johnson, M.C.Johnson, F.M.Delahoyde, and J.H.Swift (2010): The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and guidelines. IOCCP Report No *14*, ICPO Publication Series No. 134, version 1, 2010

Budeus. G., and W. Schneider (1998): In-situ temperature calibration: A remark on instruments and methods. *International WOCE Newsletter, No.30, WOCE International Project Office, Southampton, United Kingdom, 16-18.*

Larson, N., and A.M. Pedersen (1996): Temperature measurements in flowing water: Viscous heating of sensor tips. *Proc. of the First IGHEM Meeting, Montreal, QC, Canada, International Group for Hydraulic Efficiency Measurement. [Available online at http://www.seabird.com/technical_references/viscous.htm]*

Uchida, H., K. Ohyama, S. Ozawa, and M. Fukasawa (2007): In-situ calibration of the Sea-Bird 9plus CTD thermometer. *J. Atmos. Oceanic Technol.24, 1961-1967.*

Akaike, H. (1974): A new look at the statistical model identification. *IEEE Transactions on Automatic Control, 19:716 – 722.*

Uchida, H., T. Kawano, I. Kaneko, and M. Fukasawa (2008): In –situ calibration of optode-based oxygen sensors. *J. Atmos. Oceanic Technol., 25, 2271-2281.*

Garcìa, H. E., and L. I. Gordon (1992): Oxygen solubility in seawater: Better fitting equations. *Limnol. Oceanogr., 37, 1307-1312.*

Shanno, David F. (1970): Conditioning of quasi-Newton methods for function minimization. *Math. Comput. 24, 647-656. MR 42 #8905*

Sea-Bird Electronics (2009): SBE 43 dissolved oxygen (DO) sensor – hysteresis corrections, *Application note no. 64-3, 7 pp.*

2. *Bottle Salinity*

13 December 2013

(1) Personnel

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Tomoyuki KITAMURA (GEMD/JMA)

(2) Station occupied

A total of 68 stations (Leg 1: 40, Leg 2: 28) were occupied for bottle salinity. Station location and sampling layers of bottle salinity are shown in Figure C.2.1.
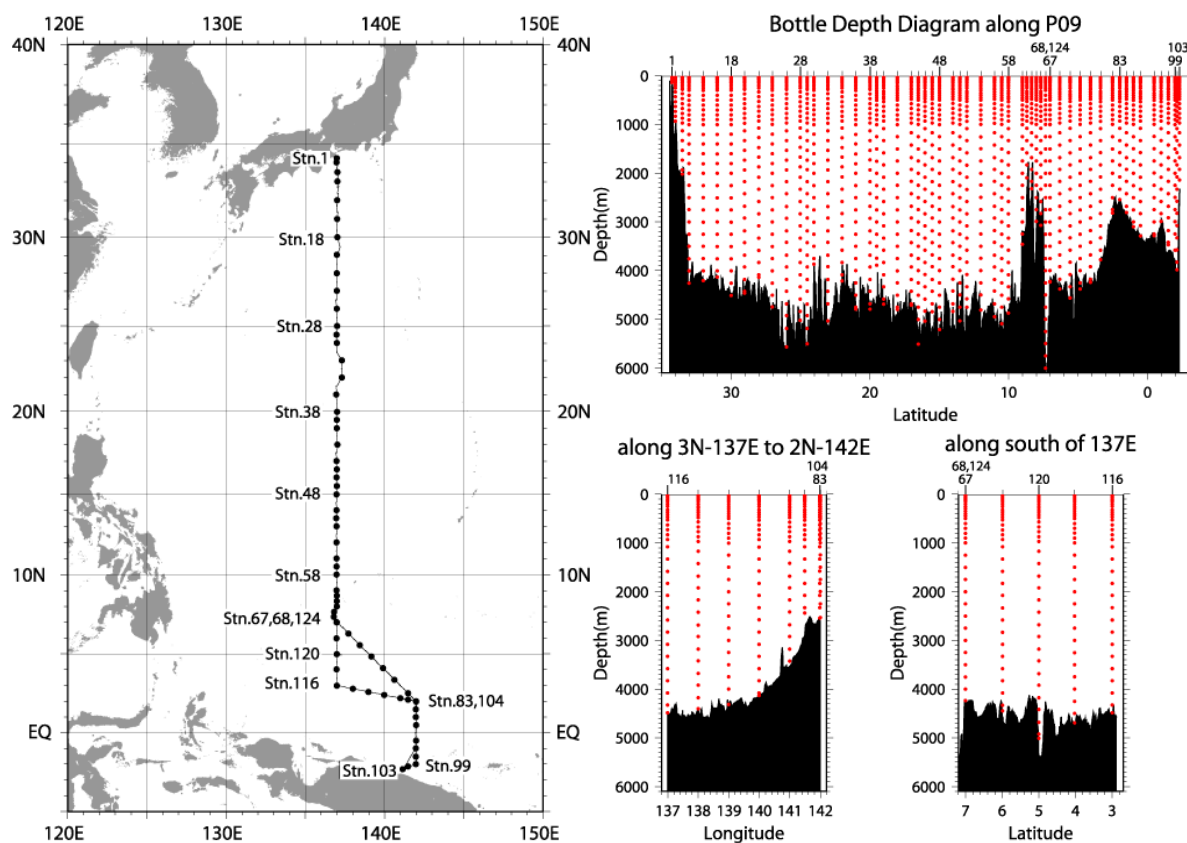
Figure C.2.1. Station location (left panel) and sampling layers of bottle salinity (right panel).

(3) Instruments and method

(3.1) Salinity sample collection

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

(3.2) Instruments and methods

The salinity analysis was carried out on AUTOSAL Laboratory Salinometer model 8400B (S/N69677; Guildline Instruments Ltd., Canada), 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 1 mK. The measurement system was almost same as *Aoyama et al* (2003). The salinometer was operated in a ship's laboratory air-conditioned at a bath temperature of 24 deg-C. Ambient temperature varied from approximately 21.5 to 23.5 deg-C, while bath temperature is very stable and varied within ± 0.001 deg-C. A measure of a double conductivity ratio of a sample is taken as a median of thirty-one readings. Data collection was started after 10 seconds and it took about 10 seconds to collect 31 readings by a personal computer. Data were sampled for the fourth and the fifth filling of the cell. In case the difference in the double conductivity ratio between this two fillings was smaller than 0.00003, the average value of the two double conductivity ratios was used to calculate the bottle salinity with the algorithm for the Practical Salinity Scale, 1978 (hereafter PSS-78; *UNESCO,* 1981). If the difference was greater than or equal to 0.00003, we measured the sixth filling of the cell. In case the double conductivity ratio of the sixth filling did not satisfy the criteria above, we measured the next filling of the cell and chose proper two fillings which satisfied the criteria. We continued these process at most ninth fillings.

(4) Result

Standardization control was set to 5.72 and all the measurements were done by this setting. During the whole measurement, readings of STANDBY were almost 6019 ± 0001 and those of ZERO were 0.00001 or 0.00002. We used IAPSO Standard Seawater batch P152 whose conductivity ratio was 0.99981 (double conductivity ratio is 1.99962) as the standard for salinity. We measured 2 or 3 bottles of P152 for each station, total amount was 187. If some readings of SSW bottle were extremely high or low, we measured another bottle of SSW.

Figure C.2.2 shows the history of ambient temperature, bath temperature, double conductivity ratio of standard sea water (P152) and time drift of P152 readings but for four bad bottles. In raw P152 readings, it was found offset and long-term variability. To remove long-term variability, raw P152 readings were corrected to label value 1.99962 in the least significant digit of readings. After the correction, SSW drift was steady within 1 digit of readings in each leg. The average of corrected SSW double conductivity ratio was 1.999621 and the standard deviation was 0.000010, which was equivalent to 0.0002 in salinity. The same correction was applied to sample readings. The correction of AUTOSAL drift for salinity measurements was from 0 to 2 digits of readings.

During measurement of a sample taken at Stn.28 (RF3676), one heater lamp of the salinometer was broken down so the result of measurement was omitted from salinity calibration.
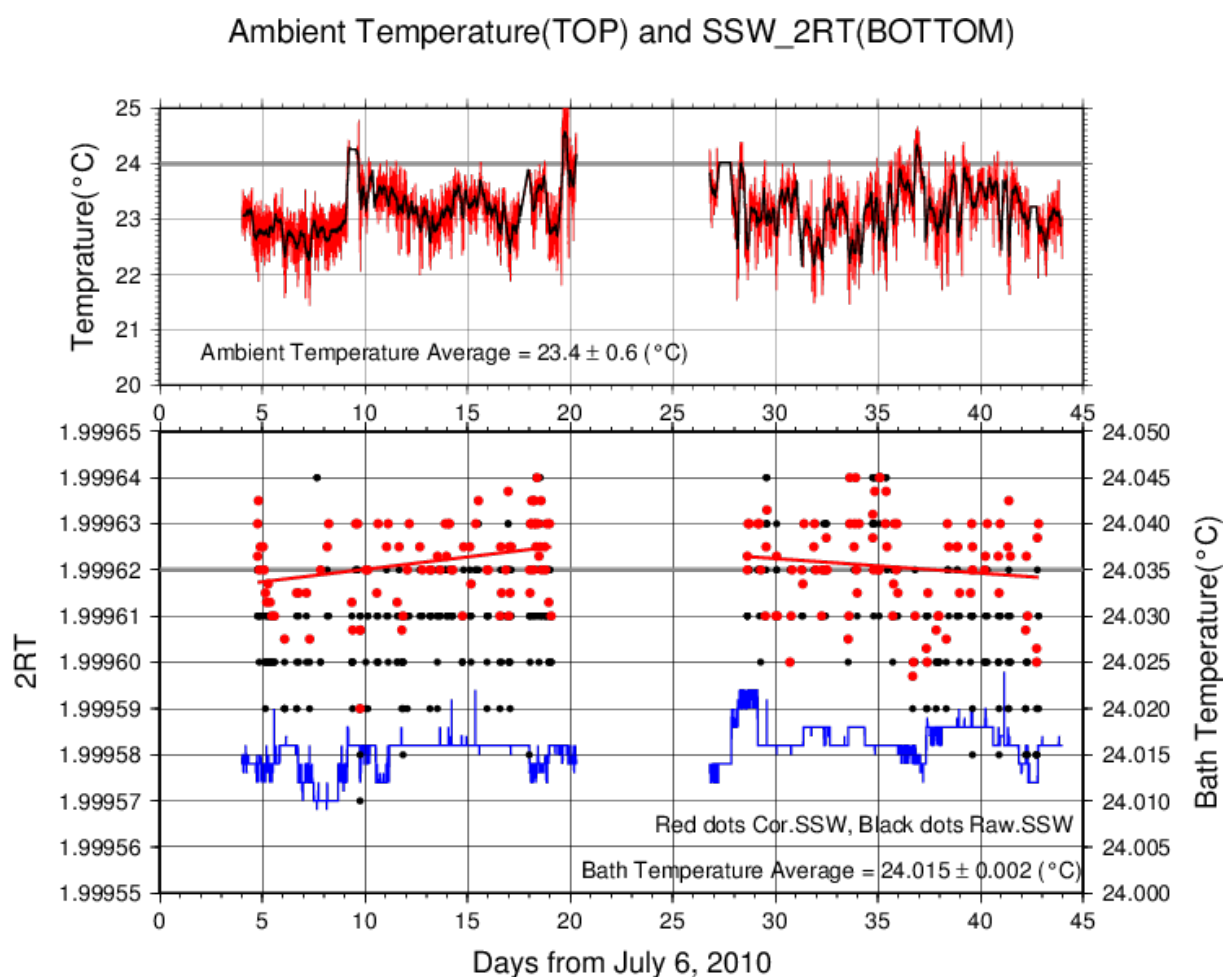
Figure C.2.2. The upper panel shows time-series of ambient temperature during cruise. The lower panel, black dots and red dots indicate raw and corrected time-series of the double conductivity ratio of the standard sea water (P152), red line indicate linear regression of corrected standard sea water for each leg, gray line indicate label value double conductivity ratio of P152 and blue line indicates time-series of bath temperature during cruise.

(5) Sub-Standard Water

We also used sub-standard seawater which was filtered by pore size of 10 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 possible sudden drift of the salinometer. During the whole measurements, there was no detectable sudden drift of the salinometer except for measurement of a sample taken at Stn.28 (RF3676).

(6) Replicate and Duplicate Samples

We took 267 pairs of replicate samples and 210 pairs of duplicate samples during the cruise. Figure C.2.3 and Figure C.2.4 show the absolute difference among replicate and duplicate samples in salinity, respectively. There were 30 bad measurements and 2 questionable measurements in replicate pairs and 23 bad measurements, 4 questionable measurements and 1 failure of sampling in duplicate pairs. Excluding those bad and questionable measurements, the mean absolute difference and standard deviation in 237 pairs of replicate samples was 0.0004 ± 0.0004 in salinity and that in 182 pairs of duplicate samples was 0.0005 ± 0.0006 in salinity. Note that standard deviation was calculated by a procedure (SOP23) in *DOE* (1994).

Table C.2.1. Summary of assigned quality control flags

Flag	Definition	Salinity
2	Good	1716
3	Questionable	34
4	Bad (Faulty)	290
6	Replicate measurements	237
Total number of samples		2277
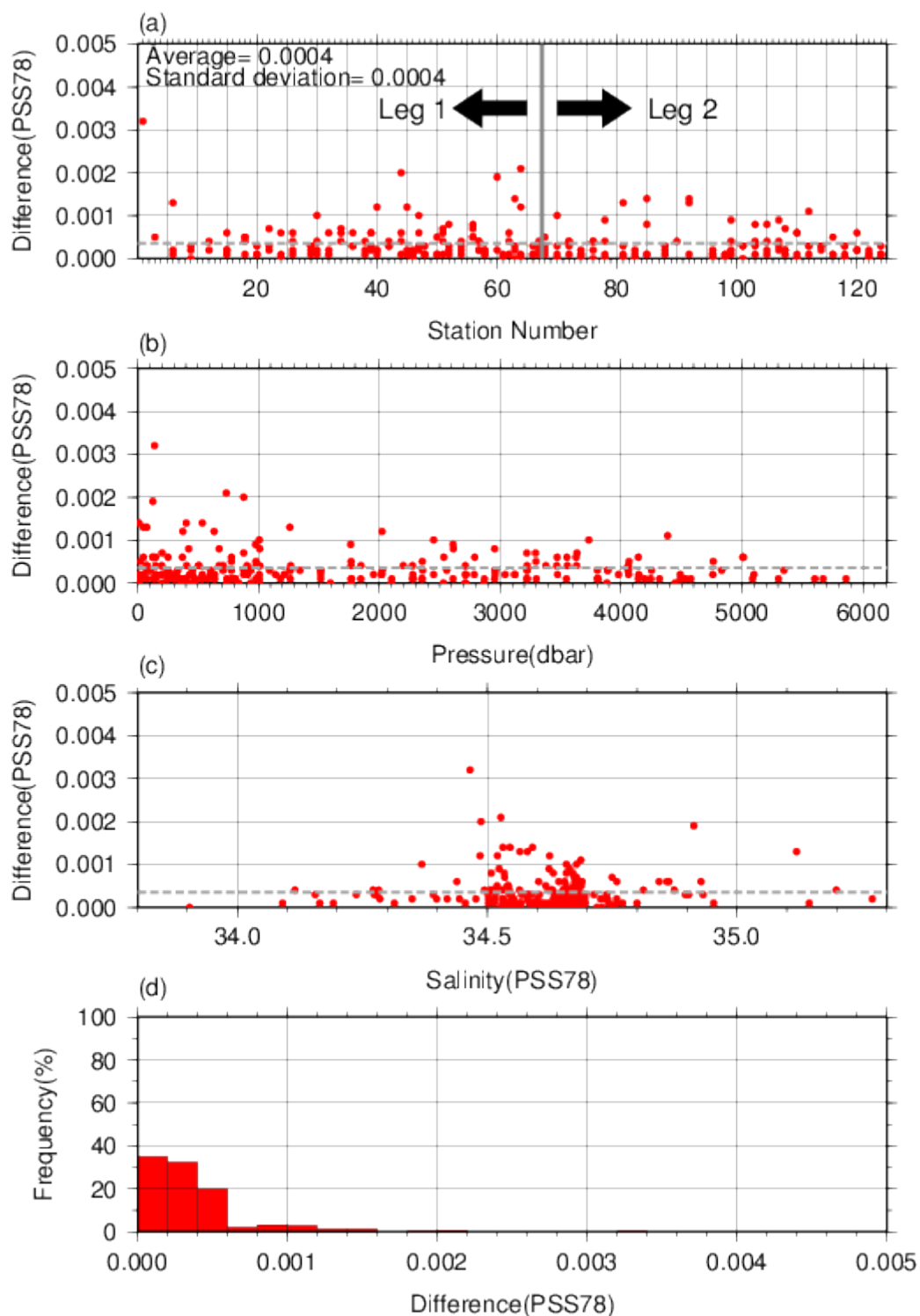
Figure C.2.3. Result of replicate samplings during this cruise against (a) station number, (b) sampling pressure and (c) salinity. Dotted line denotes the average of replicate samplings. Bottom panel (d) shows histogram of the result of replicate samplings.
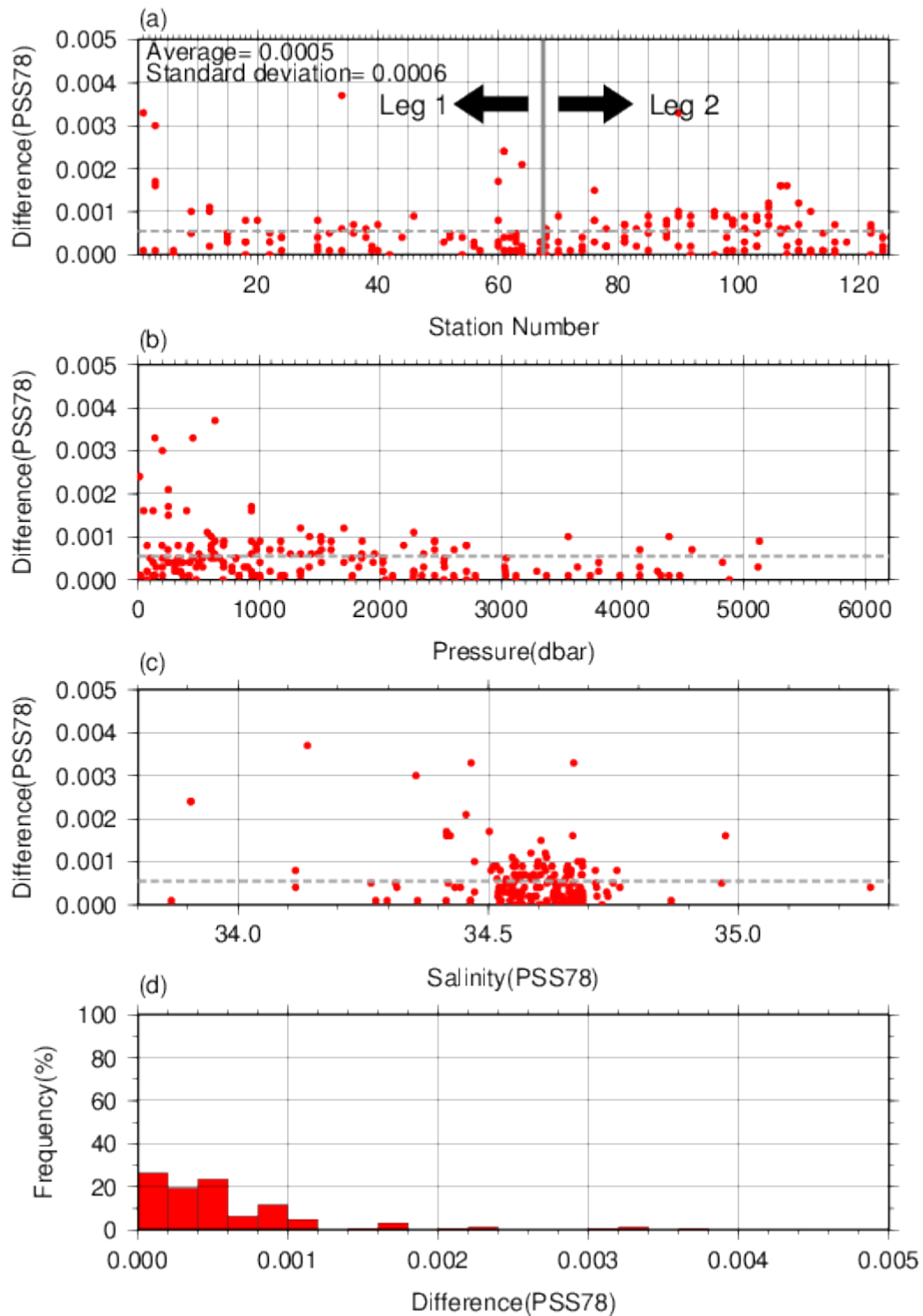
Figure C.2.4. Same as Fig.C.2.3 but for duplicate samplings.

References

Aoyama, M., T. Joyce, T. Kawano and Y. Takatsuki (2003): Standards seawater comparison up to P129. *Deep-sea Research, 1, Vol. 49, 1103-1114.*

UNESCO (1981): Tenth report of the Joint Panel on Oceanographic Tables and Standards. *UNESCO Tech. Papers in Mar. Sci., 36, 25 pp.*

DOE (1994): Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. *A.G. Dickson and C. Goyet (eds), ORNL/CDIAC-74.*

3. Bottle Oxygen

13 December 2013

(1) Personnel

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Sho HIBINO (GEMD/JMA)

(2) Station occupied

A total of 71 stations (Leg 1: 42, Leg 2: 29) were occupied for bottle oxygen. Station location and sampling layers of bottle oxygen are shown in Figure C.3.1.
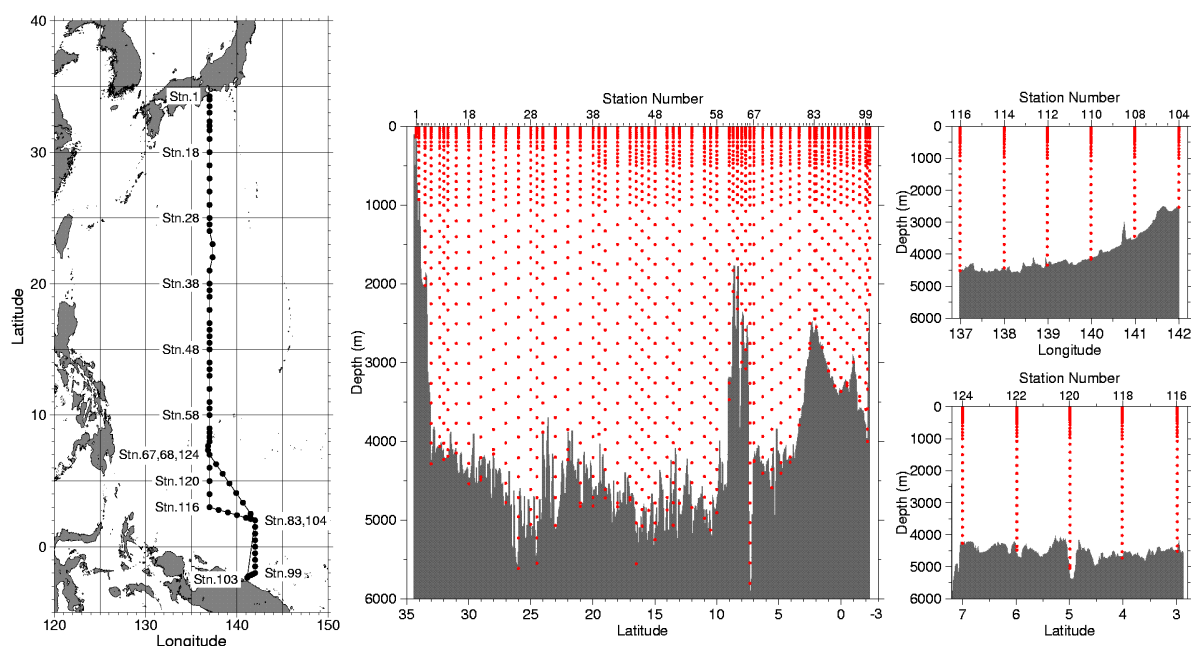
Figure C.3.1. Station location (left panel) and sampling layers of bottle oxygen (right panels).

(3) Reagents

· Manganous chloride solution (3 M) (Pickling Reagent-I)

Dissolved 600 g of $MnCl_2 \cdot 4H_2O$ in deionized water, then dilute the solution with deionized water to a final volume of 1 L. $MnCl_2 \cdot 4H_2O$ (Lot. CDP6460) used to make pickling reagent-I was guaranteed reagent manufactured by Wako Pure Chemical industries, Ltd.

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

Dissolved 320 g of NaOH in about 500 ml of deionized water, allow to cool, then add 600 g

NaI and dilute with deionized water to a final volume of 1 L. NaOH (Lot. STN1103) and NaI (Lot. STQ5226) used to make pickling reagent-II were guaranteed reagent manufactured by Wako Pure Chemical industries, Ltd.

· Sulfuric acid solution (5 M)

Slowly add 280 ml concentrated H_2SO_4 to roughly 500 ml of deionized water. After cooling the final volume should be 1 L. H_2SO_4 (Lot. KWK1803) used to make sulfuric acid solution was guaranteed reagent manufactured by Wako Pure Chemical industries, Ltd.

· Sodium thiosulfate (0.04 M)

Dissolved 50 g of $Na_2S_2O_3 \cdot 5H_2O$ and 0.4 g of Na_2CO_3 in deionized water, then dilute the solution with deionized water to a final volume of 5 L. $Na_2S_2O_3 \cdot 5H_2O$ (Lot. PER3227) and Na_2CO_3 (Lot.WKF1312) used to make sodium thiosulfate were guaranteed reagent manufactured by Wako Pure Chemical industries, Ltd.

·Potassium iodate (0.001667 M)

Dry high purity KIO_3 for two hours in an oven at 130°C. After weight out accurately KIO_3, dissolve it in deionized water in a 5 L flask. Concentration of potassium iodate is determined by a gravimetric method. KIO_3 (Lot. 62404E) used to make potassium iodate was manufactured by MERCK & CO., Inc., and a purity of KIO_3 that is traceable to NIST (National Institute of Standards and Technology) standard reference material is 99.75±0.05 %. The normality of the standard potassium iodate solution made by Merck reagent was corrected by the factor as 1.0026. Details about this correction are described in chapter C.3 (16).

(4) Instruments

Detector;

DOT-01X automatic photometric titrator manufactured by Kimoto Electronic Co. Ltd.

Burette for sodium thiosulfate;

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

Burette for potassium iodate;

Multipette stream 4986 and Combitip plus manufactured by eppendorf /10 ml of tip vessel Bottle top dispenser for pickling reagent-I and II;

Calibrex™ 520 manufactured by SOCOREX ISBA S.A.

(5) Seawater sampling

Following procedure is based on a determination method in IOCCP Report No.14 (*Langdon*, 2010). Seawater samples were collected from 10-liters Niskin bottles attached the CTD-system and a stainless steel bucket for the surface. Seawater for bottle oxygen measurement was transferred from the Niskin sample bottle and a stainless steel bucket to a volumetrically calibrated dry glass bottles (ca. 120 ml, standard deviation of calibration = 0.008 ml). At least three times volume of the glass of sample water was overflowed. Two reagent solutions (Reagent-I and II) of 1 ml (standard deviation of calibration = 0.003 ml) each were added immediately, sample temperature was then measured by a thermometer. After the stopper was inserted carefully into the glass, the sample glass was shaken vigorously to mix the content and to disperse the precipitate finely. The precipitate has settled at least halfway down the glass, the glass was then shaken again vigorously to disperse the precipitate. The sample glasses containing pickled samples were stored in a laboratory until they were titrated. To prevent air from entering the flask, deionized water was added to the neck of the flask after sampling.

(6) Sample measurement

At least 30 minutes after the re-shaking, the pickled samples were measured on board. 1 ml sulfuric acid solution and a magnetic stirrer bar were added into the sample glass 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 thermometer. The titrations were carried out using the titration apparatus, named DOT-01X. Dissolved oxygen concentration (μmol/kg) was calculated by the sample temperature at the fixation, CTD salinity, glass volume, and titrated volume of the sodium thiosulfate solution.

(7) Standardization

Concentration of sodium thiosulfate titrant (ca. 0.04 M) was determined by potassium iodate

solution. Table C.3.1 shows a list of potassium iodate solution used in this cruise. Using a calibrated volumetric dispenser, 10 ml (standard deviation of calibration = 0.006 ml) of the standard potassium iodate solution was added to a glass with 100 ml of deionized water. Then, 1 ml of sulfuric acid solution, and 1 ml of pickling reagent solution-II and I were added into the glass in order. Amount of titrated volume of sodium thiosulfate (usually 5 times measurements average) gave the molarity of the sodium thiosulfate titrant. Figure C.3.2 and Table C.3.2 show the results of the standardization during this cruise. The sodium thiosulfate titrant of each batch was a mean of titrated volume of sodium thiosulfate on each day and a standard deviation of a concentration at 20 °C of sodium thiosulfate on each day was an uncertainty caused by the standardization. A sodium thiosulfate of one batch was assumed to be one sodium thiosulfate titrant. The uncertainty of dissolved oxygen that caused by the standardization was estimated 0.01-0.13 %.

Table C.3.1. List of the standard potassium iodate solution in this cruise.

KIO_3 batch	Conc. at 20°C (N)
KIO_3_I	0.009980±0.000003
KIO_3_IV	0.009993±0.000003
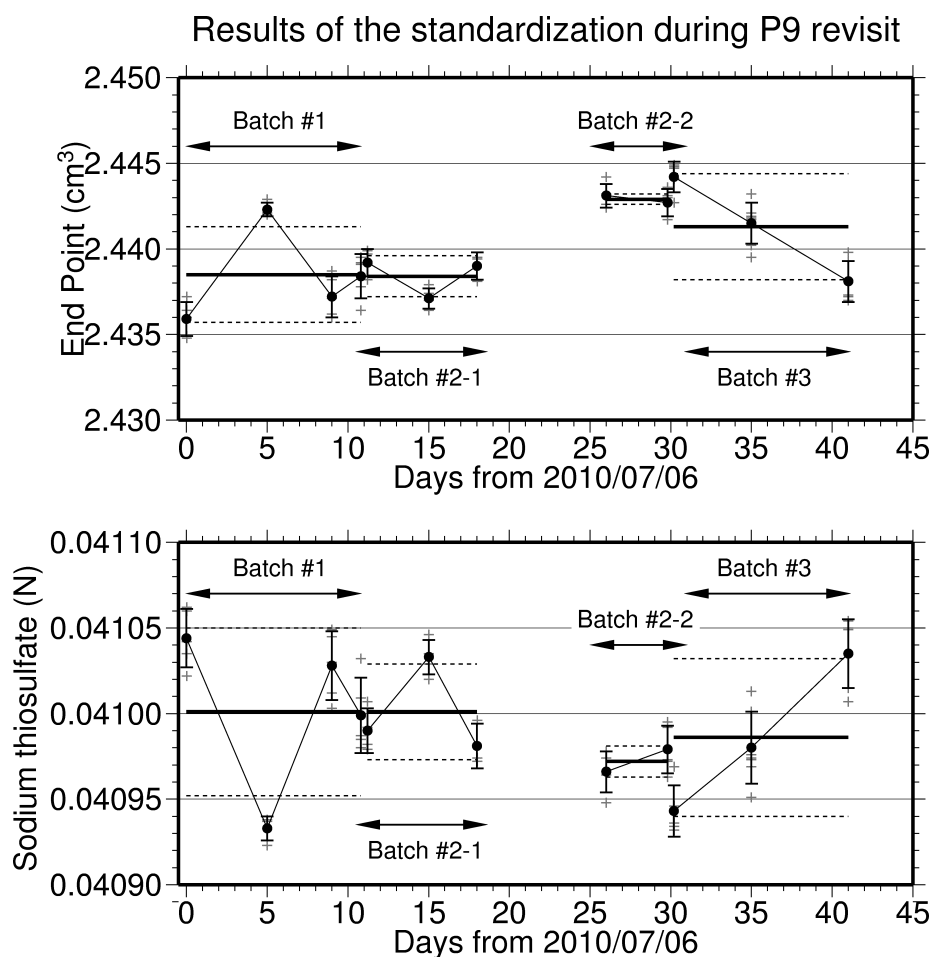
Figure C.3.2. Results of the standardization. Upper panel shows results of end point, bottom panel shows results of calculated concentration at 20°C of sodium thiosulfate. Crosses show each value for each standardization samples, and closed circles show the mean at each standardizations. Thick lines and dotted lines denote the means and 1 σ error for each batch of sodium thiosulfate, respectively.

Table C.3.2. Results of the standardization.

Leg	Date (UTC)	KIO$_3$ Batch	KIO$_3$ Bottle	Na$_2$S$_2$O$_3$ (ml) Batch	Na$_2$S$_2$O$_3$ (ml) End Point	Stations
1	2010/7/6	KIO$_3$_IV	2	#1	2.4359	Stn.1
	2010/7/11	KIO$_3$_IV	3	#1	2.4423		
	2010/7/15	KIO$_3$_IV	4	#1	2.4372	Stn.43
	2010/7/17	KIO$_3$_IV	5	#1	2.4384	
		Na$_2$S$_2$O$_3$_#1			2.4385±0.0028	
	2010/7/17	KIO$_3$_IV	5	#2	2.4392	Stn.44
	2010/7/21	KIO$_3$_IV	6	#2	2.4371		
	2010/7/24	KIO$_3$_IV	7	#2	2.4390	Stn.67
		Na$_2$S$_2$O$_3$_#2_1			2.4384±0.0012	
2	2010/8/1	KIO$_3$_IV	9	#2	2.4431	Stn.68-
	2010/8/5	KIO$_3$_IV	10	#2	2.4427	Stn.84
		Na$_2$S$_2$O$_3$_#2_2			2.4429±0.0003	
	2010/8/5	KIO$_3$_IV	10	#3	2.4442	Stn.93
	2010/8/10	KIO$_3$_IV	11	#3	2.4415		
	2010/8/16	KIO$_3$_IV	12	#3	2.4381	Stn.105
		Na$_2$S$_2$O$_3$_#4			2.4413±0.0031	

(8) Determination of the blank

The oxygen in the pickling reagents-I (1 ml) and II (1 ml) was assumed to be 7.6 x 10^{-8} mol (*Murray et al.*, 1968). The blank from the presence of redox species apart from oxygen in the reagents (the pickling reagents-I, II, and the sulfuric acid solution) was determined as follows. Using a calibrated volumetric dispenser, 1 ml of the standard potassium iodate solution was added to a glass with 100 ml of deionized water. Then, 1 ml of sulfuric acid solution, and 1 ml of pickling reagent solution-II and I were added into the glass in order. First, the sample was titrated to the end-point by sodium thiosulfate solution. Then, the sample was titrated again to the end-point after added a further 1 ml of the standard potassium iodate solution. The blank was determined by difference between the first (1 ml of KIO$_3$) titrated volume of the sodium thiosulfate and the second (2 ml of KIO$_3$) one. Because reagents set were prepared two sets (set A and B), the blank in each sets were determined. Usually, the results of 5 times blank determinations were averaged (Table C.3.3). The standard deviation of the blank determination during this cruise was 0.0010 (set A) and 0.0011 (set B) ml, c.a. 0.02 %.

Table C.3.3. Result of the blank determinations.

Date (UTC)	$Na_2S_2O_3$ Batch	Blank (ml)		Samples (stations)
		Set A	Set B	
2010/7/6	#1	0.0008	0.0004	Stn.1-Stn.12
2010/7/9	#1	0.0014	0.0029	Stn.13-Stn.18
2010/7/11	#1	0.0024	0.0029	Stn.19-Stn.26
2010/7/13	#1	0.0018	0.0013	Stn.27-Stn.32
2010/7/15	#1	0.0021	0.0023	Stn.33-Stn.42
2010/7/17	#2	0.0015	0.0020	Stn.43-Stn.57
2010/7/21	#2	0.0015	0.0015	Stn.58-Stn.67
2010/8/1	#2	0.0042	0.0042	Stn.68-Stn.83
2010/8/5	#3	0.0028	0.0031	Stn.84-Stn.103
2010/8/10	#3	0.0027	0.0033	Stn.104-Stn.124

(9) Reagent blank

The blank determined in section (8), pure water blank ($V_{blk, dw}$) can be represented by equation (i),

$$V_{blk, dw} = V_{blk, ep} + V_{blk, reg} \qquad (i)$$

where

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

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

Here, the reagent blank ($V_{blk, reg}$) was determined by following procedure. 1 ml of the standard potassium iodate solution and 100 ml of deionized water were added to two glasses each. 1 ml of sulfuric acid solution, pickling reagent solution-II and I each were added into the first glass in order. Then, two times volume of the reagents (2 ml of sulfuric acid solution, pickling reagent solution-II and I each) was added to the second glass. The reagent blank was determined by difference between the first (3 ml of the total reagent volume added) titrated volume of the sodium thiosulfate and the second (6 ml of the total reagent volume added) one. We also carried out experiments for three and four times volume of the reagents. The results are shown in Figure

C.3.3.

The relation between difference of the titrant ($Na_2S_2O_3$) volume and the volume of the reagents added ($V_{reagent}$) is expressed by equation (ii),

$$\text{Difference of the titrant volume} = -0.0023 V_{reagent} \qquad \text{(ii)}$$

$V_{blk, reg}$ was estimated to be about -0.007 ml, suggesting that about 0.04 μmol of reductants was contained in every 3 ml of the reagents added.
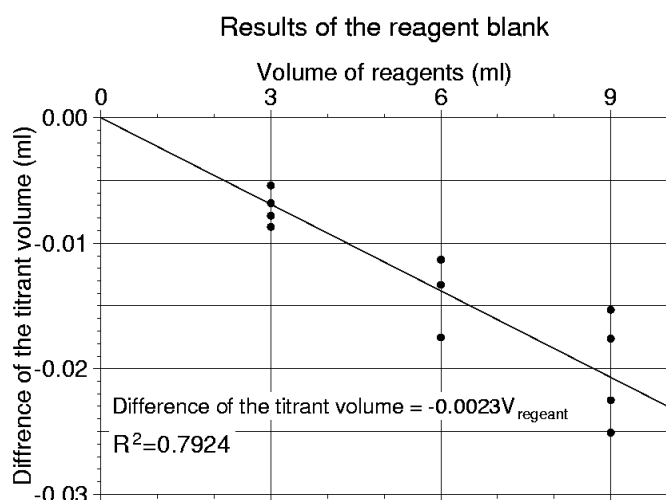
Figure C.3.3. Blank (ml) due to redox species apart from oxygen in the reagents.

(10) Sample blank

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

$$V_{blk, sw} = V_{blk, spl} + V_{blk, dw} \qquad \text{(iii)}$$

If the pure water blank ($V_{blk, dw}$) that is determined in section (9) is identical both in pure water and in seawater, the difference between the seawater blank and the pure water one gives the sample blank ($V_{blk, spl}$).

Here, $V_{blk, spl}$ was determined by following procedure. Seawater sample was collected in the calibrated volumetric glass (c.a. 120 ml) without the pickling. Then 1 ml of the standard

potassium iodate solution, sulfuric acid solution, and pickling reagent solution-II and I each were added into the glass in order. Additionally, a glass contained 100 ml of deionized water and 1 ml of the standard potassium iodate solution, sulfuric acid solution, pickling reagent solution-II and I was prepared. The difference of the titrant volumes of the seawater glass and the deionized water one gave the sample blank ($V_{blk, spl}$).

We measured vertical profiles of the sample blank at 3 stations (Table C.3.4). The sample blank ranged from 0.17 to 1.96 μmol/kg and its vertical and horizontal variations are large. This result does not agree to reported values ranged from 0.4 to 0.8 μmol/kg (*Culberson et al.*, 1991). It does not have been known about the magnitude and variability of the seawater blank, so this result should be discussed carefully. Ignorant of the sample blank will cause systematic errors in the oxygen calculations, but these errors are expected to be the same to all investigators and not to affect the comparison of results from different investigators (*Culberson*, 1994).

Table C.3.4. Results of the sample blank determinations during this cruise.

Station: Stn.75 4.45˚N/139.53˚E		Station: Stn.111 2.50˚N/139.50˚E		Station: Stn.115 2.91˚N/137.50˚E	
Pres. (dbar)	Blank (μmol/kg)	Pres. (dbar)	Blank (μmol/kg)	Pres. (dbar)	Blank (μmol/kg)
10.3	0.17	10.3	0.35	25.3	0.91
50.6	1.03	103.5	0.74	100.8	0.63
101.7	0.54	201.2	1.04	302.0	0.95
251.5	–	381.9	0.70	503.2	1.09
634.7	0.61	483.8	1.76	1,008.8	0.98
838.0	0.90	675.1	1.96	1,514.0	0.75
1,596.4	0.56	978.3	0.98	2,020.6	1.29
2,611.7	0.82	1,940.0	1.39	3,038.5	1.44
3,631.6	0.71	2,955.6	1.11	4,060.8	1.29
4,142.7	0.84	4,382.1	–	4,574.2	0.90

(11) Replicate sample measurement

Replicate samples were carried out at every bottle oxygen observation stations. Total amount of the replicate sample pairs in good measurement (flag=6) was 234, and total amount of the removed pair (flag=3 or 4) was 14. The average and the standard deviation of the replicate measurement during this cruise were 0.17±0.17 μmol/kg. The standard deviation was calculated by a procedure (SOP23) in *DOE* (1994). The difference between the replicate sample pairs did not depended on sampling pressure, measurement date and concentration of sample (Figure C.3.4). The averages and the standard deviations during Leg 1 and Leg 2 were 0.17±0.17 (n=127) and 0.18±0.16 (n=107) μmol/kg, respectively.
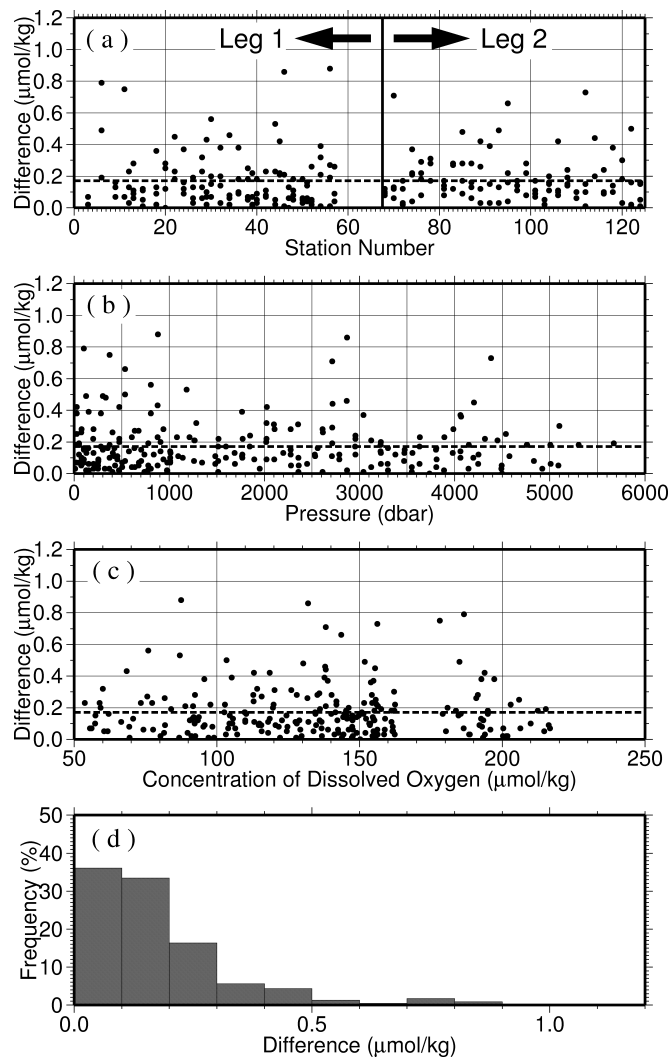
Figure C.3.4. Result of replicate samplings during this cruise against (a) station number, (b) sampling pressure and (c) concentration of dissolved oxygen. Dotted line denotes the average of replicate samplings. Bottom panel (d) shows histogram of the result of replicate samplings.

(12) Duplicate sample measurement

Duplicate samples that were seawater samples from two Niskin sample bottles that were collected at same depth were carried out at almost every bottle oxygen observation stations also. Total amount of the duplicate sample pairs in good measurement (flag=2) was 156, and total amount of the removed pair (flag=3 or 4) was 16. The average and the standard deviation of the duplicate measurement during this cruise were 0.22 ± 0.21 μmol/kg. The difference between the duplicate sample pairs did not depended on measurement date and concentration of sample, but the results of the duplicate measurement on surface and subsurface (above 1,000 dbar) were large (Figure C.3.5). We thought that this reason was because water mass on a surface and a subsurface was not similar compared with that of an intermediate and a deep layer. The averages and the standard deviations during Leg 1 and Leg 2 were 0.26 ± 0.24 (n=60) and 0.20 ± 0.18 (n=96) μmol/kg, respectively.
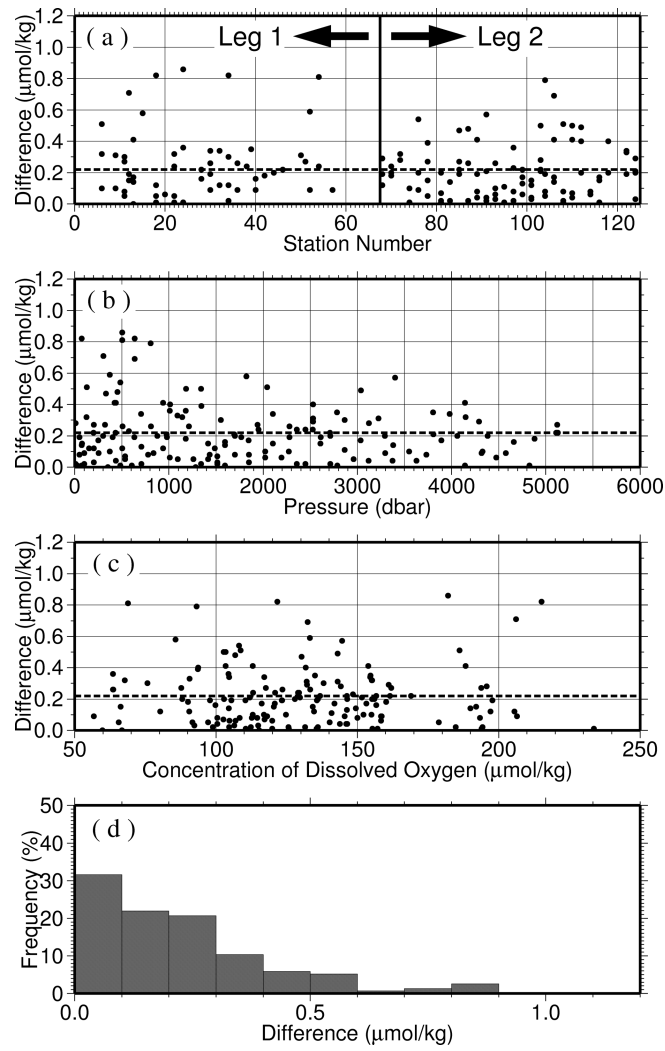
Figure C.3.5. Result of duplicate samplings during this cruise against (a) station number, (b) sampling pressure and (c) concentration of dissolved oxygen. Dotted line denotes the average of duplicate samplings. Bottom panel (d) shows histogram of the result of duplicate samplings.

(13) Mutual comparison between each standard potassium iodate

During the cruise, we performed the mutual comparison between two standard potassium iodate of difference Lot. in order to confirm the accuracy of our oxygen measurement and the bias of a standard potassium iodate. We measured concentration of a KIO_3 (KIO_3_I) against another KIO_3 (KIO_3_IV), and checked the difference between measurement value and theoretical one (Table C.3.5, Figure C.3.6). Error weighted means of measurement results of KIO_3_I were 0.009947 ± 0.000012 N. The averaged value of the KIO_3_I was so close to the theoretical value (0.009955 ± 0.000003 N) that was prepared in laboratory. A good agreement among two standard potassium iodate confirmed that there was no systematic shift in our oxygen measurements during this cruise.

Table C.3.5. Results of mutual comparison of KIO_3_I against KIO_3_IV

Date (UTC)	KIO_3 Batch	Measurement Value (N)
2010/7/6	$KIO_3\_I\_4$	0.009982 ± 0.000013
2010/7/11	$KIO_3\_I\_5$	0.009966 ± 0.000011
2010/7/15	$KIO_3\_I\_6$	0.009970 ± 0.000011
2010/7/17	$KIO_3\_I\_7$	0.009968 ± 0.000012
2010/7/17	$KIO_3\_I\_7$	0.009964 ± 0.000012
2010/7/21	$KIO_3\_I\_8$	0.009977 ± 0.000012
2010/7/24	$KIO_3\_I\_9$	0.009978 ± 0.000013
2010/8/1	$KIO_3\_I\_10$	0.009981 ± 0.000011
2010/8/5	$KIO_3\_I\_11$	0.009968 ± 0.000011
2010/8/5	$KIO_3\_I\_11$	0.009966 ± 0.000013
2010/8/10	$KIO_3\_I\_12$	0.009983 ± 0.000012
2010/8/16	$KIO_3\_I\_13$	0.009982 ± 0.000012
Weighted Mean		0.009973 ± 0.000012
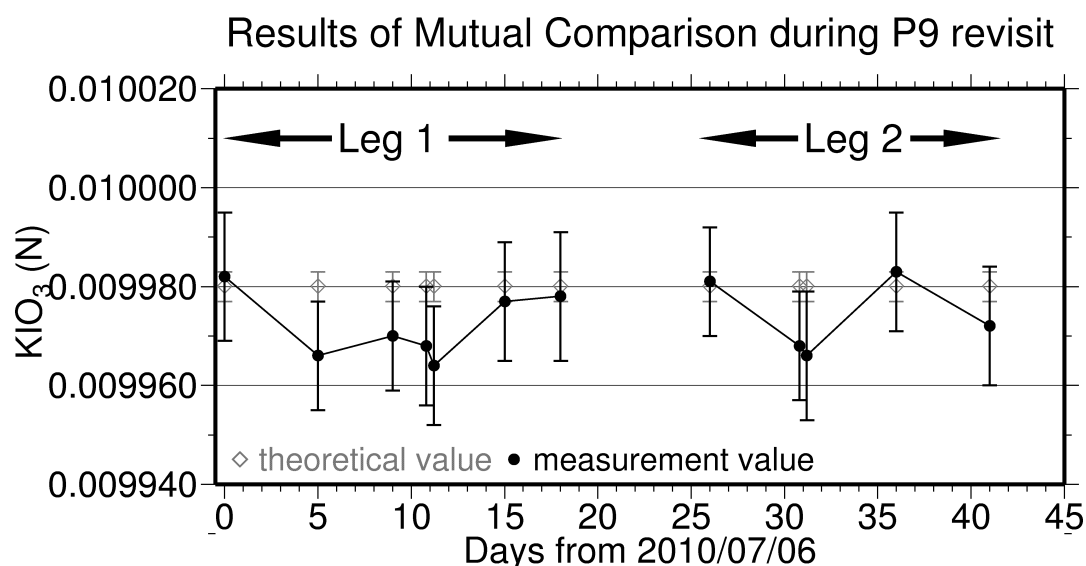
Figure C.3.6. Results of mutual comparison of KIO_3_I against KIO_3_IV. Closed circles show mean of measurement value with 1 σ error at each mutual comparison, and gray opened diamonds and error bar show the theoretical value and the uncertainty of the standard potassium iodate.

(14) Quality control flag assignment

Quality flag values were assigned to oxygen measurements using the code defined in IOCCP Report No.14 (*Swift*, 2010). Measurement flags of 2 (good), 3 (questionable), 4 (bad), 5 (not reported), and 6 (replicate measurement) have been assigned (Table C.3.6). The replicate data were averaged and flagged 6 if both of them were flagged 2. If either of them was flagged 3 or 4, a datum with "younger" flag was selected. For the choice between 2, 3, or 4, we basically followed a flagging procedure as listed below:

a. Vertical sections against pressure and potential density were drawn. Any points not lying on a generally smooth curve were noted.

b. Dissolved oxygen was then plotted against potential temperature, salinity and nutrients. If a datum deviated from a group of plots, it was flagged 3.

c. If a datum was deviated from the mean ±3σ on the section, datum flag was degraded from 2 to 3, or from 3 to 4.

d. We Compared bottle oxygen with CTD oxygen at the sampling depth. If a datum deviated from CTD oxygen, datum flag was degraded from 2 to 3, or from 3 to 4.

e. If the bottle flag was 4 (did not trip correctly), a datum was flagged 4 (bad). If the bottle

flag was 3 (leaking) or 5 (unknown problem), a datum was flagged based on steps a, b, c, and d.

Table C.3.6. Summary of assigned quality control flags.

Flag	Definition	Number
2	Good	2353
3	Questionable	326
4	Bad (Faulty)	52
5	Not reported	1
6	Replicate measurements	234[*]
	Total number of samples	2732[*]

*Samples of flag 6 are counted as flag 2

(15) Problems

A leak of sodium thiosulfate from a joint of burette was revealed at the standardization after Stn.67. From the comparison between bottle oxygen and the oxygen sensor (RINKO III manufactured by JFE Advantech Co. Ltd.), it was thought that this problem had happened from Stn.58 (Figure C.3.7). The data between Stn.58 and Stn.67 were flagged 3 or 4.
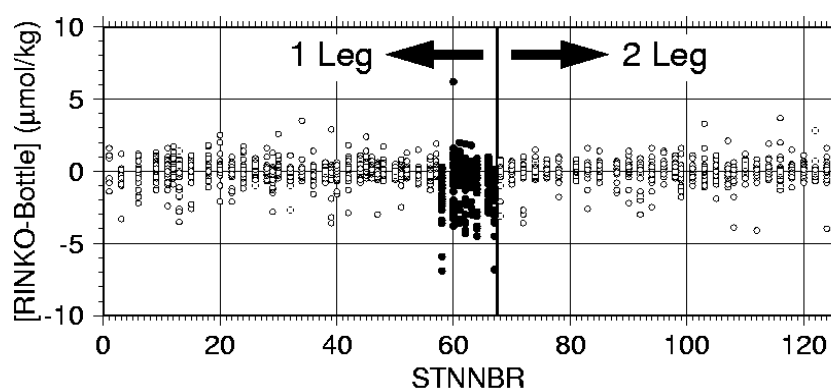
Figure C.3.7. Comparison between bottle oxygen and RINKO III. Closed circles show data between Stn.58 and Stn.67.

(16) Correction of a standard potassium iodate made by Merck reagent

We have conducted the inter-laboratory comparison of the standard potassium iodate solution between JMA and Japan Agency for Marine-Earth Science and Technology (JAMSTEC) in order to ensure the comparability of dissolved oxygen concentration in sea water since 2010. Moreover, we also conducted the inter-laboratory comparison of the standard potassium iodate solution between JMA and Scripps Institution of Oceanography (SIO) on board R/V *Melville* in May 2013. Table C.3.7 shows pure KIO_3 reagents used in each laboratory.

The results of inter-laboratory comparisons are summarized as follows. The standard potassium iodate solution made by Merck reagent shows a systematic difference to the solutions made from Wako reagent and Alfa Aesar reagent. On the other hand, the standard potassium iodate solution made by National Metrology Institute of Japan (NMIJ) reagent has no significant difference to the standard solutions made from Wako reagent and Alfa Aesar reagent (Table C.3.8 and Figure C.3.8).

The measured normality of standard potassium iodate solution made by Merck reagent based on the nominal normality of NMIJ reagent is higher (0.26±0.12%) than the nominal normality (Figure C.3.9). From t-test, this difference is significant. Thus, the normality of the standard potassium iodate solution made by Merck reagent should be corrected by the factor as 1.0026 from the result of the inter-laboratory comparison studies conducted by JMA.

Table C.3.7. List of pure KIO_3 reagent used in each institution

Institution	Company	Lot.	Purity (%)
JMA	Merck	62404E	99.75 (2010~2011)
		92404G	99.74 (2011~)
	NMIJ	CRM 3006-a	99.973 (2012~)
JAMSTEC	Wako	EPR3227	>99.95
SIO	Alfa Aesar	B05N35	99.4 ~ 100.4

Table C.3.8 The results of standard potassium iodate solution inter-comparison.

Date	measured (N)	Uncertainty (N)	Nominal (N)	Uncertainty[***] (N)	Ratio (measured/nominal)
(1) normality of the standard potassium iodate solution made by *Wako* versus *Merck* at JMA					
2010/5/23	0.009985	0.000008[*]	—	—	—
2010/5/29	0.010004	0.000007[*]	—	—	—
2010/12/18	0.009983	0.000009[*]	—	—	—
2011/6/22	0.009981	0.000013[*]	0.010014	—	0.9967
2011/6/22	0.009978	0.000013[*]	0.010014	—	0.9964
2011/6/22	0.009986	0.000012[*]	0.010014	—	0.9972
2011/6/22	0.009981	0.000012[*]	0.010014	—	0.9967
2011/6/22	0.009984	0.000013[*]	0.010014	—	0.9970
2011/6/22	0.009988	0.000012[*]	0.010014	—	0.9974
2012/5/28	0.009993	0.000008[*]	0.010009	—	0.9984
2012/5/28	0.009986	0.000009[*]	0.010010	—	0.9976
2012/5/28	0.009989	0.000008[*]	0.010012	—	0.9977
2012/5/28	0.009986	0.000009[*]	0.010012	—	0.9974
2012/5/28	0.009989	0.000008[*]	0.010012	—	0.9977
2012/5/28	0.009990	0.000008[*]	0.010012	—	0.9978
2013/6/10	0.009976	0.000009[*]	0.010002	—	0.9974
2013/6/10	0.009979	0.000009[*]	0.010002	—	0.9977
2013/6/10	0.009974	0.000009[*]	0.010002	—	0.9972
Mean ratio of the measured normality versus the nominal normality = **0.9974 ± 0.0005**					
(2) normality of the standard potassium iodate solution made by *Wako* versus *NMIJ* at JMA					
2012/5/28	0.010015	0.000008[*]	0.010009	—	1.0006
2012/5/28	0.010008	0.000009[*]	0.010010	—	0.9998
2012/5/28	0.010012	0.000008[*]	0.010012	—	1.0000
2012/5/28	0.010008	0.000009[*]	0.010012	—	0.9996
2012/5/28	0.010011	0.000008[*]	0.010012	—	0.9999
2012/5/28	0.010013	0.000008[*]	0.010012	—	1.0001
2013/6/10	0.010001	0.000009[*]	0.010002	—	0.9999
2013/6/10	0.010003	0.000010[*]	0.010002	—	1.0001
2013/6/10	0.009999	0.000009[*]	0.010002	—	0.9997
Mean ratio of the measured normality versus the nominal normality = **1.0000 ± 0.0003**					

*: The standard uncertainty estimated theoretically by precision of burette, etc.

**: The standard deviation of 4-5 times measurements

***: The standard uncertainty by gravimetric method

Table C.3.8 (continued)

Date	measured (N)	Uncertainty (N)	Nominal (N)	Uncertainty[***] (N)	Ratio (measured/nominal)
(3) normality of the standard potassium iodate solution made by *Merck* versus *Wako* at JAMSTEC					
2010/7/14	0.009976	—	0.009955	0.000003	1.0021
2010/7/14	0.009990	—	0.009972	0.000003	1.0018
2010/7/14	0.009990	—	0.009972	0.000003	1.0018
2010/7/14	0.010002	—	0.009977	0.000003	1.0025
2010/9/3	0.009994	—	0.009967	0.000003	1.0027
2010/9/3	0.009979	—	0.009952	0.000003	1.0027
2011/5/30	0.010250	—	0.010233	0.000003	1.0017
2011/5/30	0.010168	—	0.010154	0.000003	1.0014
2011/5/30	0.010017	—	0.010001	0.000003	1.0016
2011/5/31	0.010573	—	0.010546	0.000003	1.0026
2011/5/31	0.010571	—	0.010546	0.000003	1.0024
2011/5/31	0.010856	—	0.010840	0.000003	1.0015
2012/4/24	0.010168	0.000005[**]	0.010148	0.000003	1.0020
2012/4/24	0.010049	0.000004[**]	0.010031	0.000003	1.0018
2012/4/24	0.010050	0.000004[**]	0.010031	0.000003	1.0019
2012/4/25	0.010112	0.000004[**]	0.010094	0.000003	1.0018
2012/4/25	0.010189	0.000005[**]	0.010162	0.000003	1.0027
2012/4/25	0.010018	0.000004[**]	0.010001	0.000003	1.0017
2013/5/21	0.010010	0.000003[**]	0.009989	0.000003	1.0021
2013/5/21	0.010012	0.000003[**]	0.009989	0.000003	1.0023
2013/5/21	0.010006	0.000004[**]	0.009989	0.000003	1.0017
2013/5/21	0.010014	0.000004[**]	0.009990	0.000003	1.0024
2013/5/21	0.010011	0.000005[**]	0.009990	0.000003	1.0021
2013/5/21	0.010002	0.000005[**]	0.009990	0.000003	1.0012
Mean ratio of the measured normality versus the nominal normality = **1.0020 ± 0.0004**					
(4) normality of the standard potassium iodate solution made by *NMIJ* versus *Wako* at JAMSTEC					
2012/4/25	0.009997	0.000004[**]	0.009997	0.000001	1.0000
2013/5/19	0.009995	0.000004[**]	0.009994	0.000001	1.0001
2013/5/19	0.009994	0.000006[**]	0.009994	0.000001	1.0000
2013/5/19	0.009980	0.000003[**]	0.009994	0.000001	0.9986
2013/5/21	0.009981	0.000003[**]	0.009994	0.000001	0.9987
Mean ratio of the measured normality versus the nominal normality = **0.9995 ± 0.0008**					

*: The standard uncertainty estimated theoretically by precision of burette, etc.

**: The standard deviation of 4-5 times measurements

***: The standard uncertainty by gravimetric method

Table C.3.8 (continued)

Date	measured (N)	Uncertainty (N)	Nominal (N)	Uncertainty[***] (N)	Ratio (measured/nominal)
(5) normality of the standard potassium iodate solution made by *Merck* versus *Alfa Aesar* at SIO					
2013/5/10	0.010023	—	0.009996	0.000003	1.0027
2013/5/10	0.010062	—	0.010033	0.000003	1.0029
2013/5/10	0.010050	—	0.010033	0.000003	1.0017
Mean ratio of the measured normality versus the nominal normality = **1.0024 ± 0.0006**					
(6) normality of the standard potassium iodate solution made by *NMIJ* versus *Alfa Aesar* at SIO					
2013/5/10	0.009994	—	0.009994	0.000001	1.0000
2013/5/10	0.009990	—	0.009994	0.000001	0.9996
Mean ratio of the measured normality versus the nominal normality = **0.9998 ± 0.0003**					

*: The standard uncertainty estimated theoretically by precision of burette, etc.

**: The standard deviation of 4-5 times measurements

***: The standard uncertainty by gravimetric method
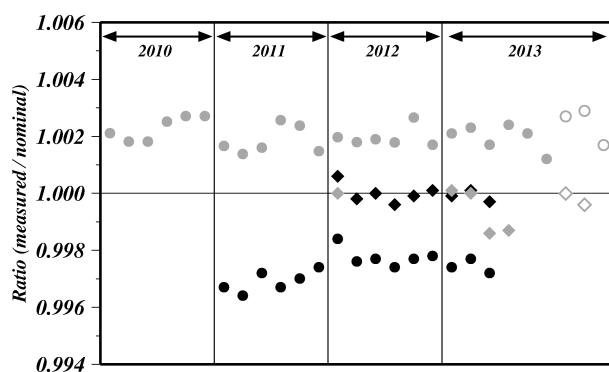
Figure C.3.8 Results of standard potassium iodate solution inter-laboratory comparison among
JMA, JAMSTEC and SIO. Black (Gray) closed circles denote measured/nominal ratio of
Wako (Merck) versus Merck (Wako), and black (gray) closed diamonds denote
measured/nominal ratio of Wako (NMIJ) versus NMIJ (Wako). Gray open circles (diamonds)
denote measured/nominal ratio of Merck (NMIJ) versus Alfa Aesar.
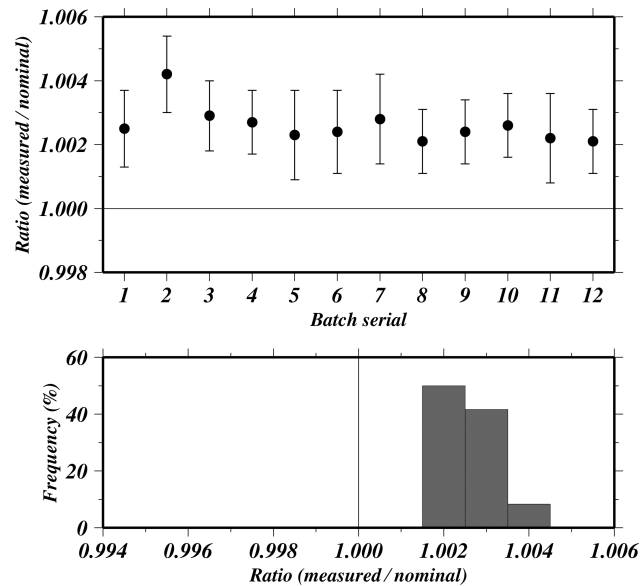
Figure C.3.9. Results of inter-comparison between Merck and NMIJ. Upper panel shows measured/nominal ratio of Merck versus NMIJ for each standard potassium iodate solution batch serial, and lower panel shows the histogram of its ratios.

(17) Uncertainty in Oxygen data of this cruise

The reproducibility in this cruise determined by replicate samples and duplicate samples in section (11) and (12) was 0.17±0.17 μmol/kg and 0.22±0.21 μmol/kg. Bottle oxygen data in this cruise were calculated based on IOCCP Report No.14 (*Langdon*, 2010). In these results, various uncertainties were included (ex. standardization, calibration of glass bottles, precision of burette etc.). Considering these uncertainty that can be estimated theoretically, it was estimated that the standard uncertainty of bottle oxygen data in this cruise is about 0.43 μmol/kg. However, it is impossible to estimate an accurate uncertainty because there is no reference material.

(18) Results

(18.1) Comparison at cross-stations during this cruise

Cross-stations during this cruise were two stations. The one was located at 2°N/142°E, the another was located 7°N/137°E.

At stations of Stn.83 (RF3731) and Stn.104 (RF3755), hydrocast sampling for dissolved oxygen

was conducted two times at interval of about five days. Dissolved oxygen profiles of the two hydrocasts agreed well (Figure C.3.10). We compared interpolated data, because the sampling layers of the two hydrocasts were difference. In the layers deeper than 2000 dbar, difference of interpolated data between the two hydrocasts was calculated to be about 1.23±0.30 μmol/kg. In these layers, difference of the oxygen sensor between the two hydrocasts was also about 1.1±0.6 μmol/kg.

At stations of Stn.67 (RF3715), Stn.68 (RF3716), and Stn.124 (RF3772), hydrocast sampling for dissolved oxygen was conducted three times. Interval between the first and the second was about a week, interval between the second and the third was about two weeks. Dissolved oxygen profiles between the second and third hydrocasts agreed well, but the data of the first hydrocast had slightly larger than that of second and third hydrocast because of a leak of sodium thiosulfate from a joint of the burette (Figure C.3.7). In the layers deeper than 2000 dbar, difference between the second and third hydrocast was calculated to be about 0.11±0.64 μmol/kg.
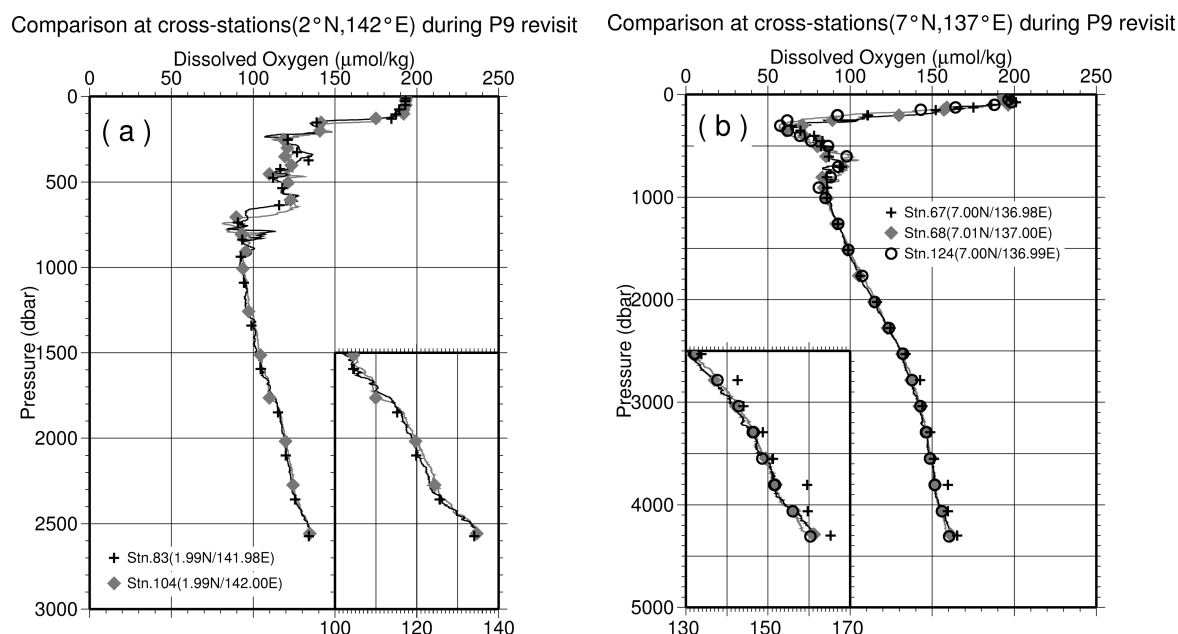
Figure C.3.10. Comparison of dissolved oxygen profiles between the first hydrocast (pluses), the second one (gray diamonds) and the third one (circles) at the cross-stations of (a) 2°N/142°E and (b) 7°N/137°E. Lines denote the profiles of the oxygen sensor.

(18.2) Comparison at cross-stations of WHP-P2 section in 1994 and 2004

We compared our oxygen data and one of WHP-P2 at a cross point, around 30°N/137°E. WHP-P2 line was observed two times, first in 1994 by *R/V Shoyo* belonged to Maritime Safety Agency of Japan (MSA) (present Japan Coast Guard (JCG)) and repeated in 2004 by *R/V Melville* belonged to Scripps Institution of Oceanography (SIO). Dissolved oxygen profiles between one in this cruise and in 2004 agreed well (Figure C.3.11), and the difference blow 2000 dbar is 0.70±0.74 µmol/kg. But it was found that oxygen data in this cruise were significantly lower than those in 1994 in deep layers, the differences below 2000 dbar is –4.18±2.71µmol/kg. This difference should be discussed carefully.

(18.3) Comparison at cross-stations of WHP-P3 section in 1985 and 2005/06

We compared our oxygen data and one of WHP-P3 at a cross point, around 24°N/137°E. WHP-P3 line was observed two times, first in 1985 by *R/V Thomas G. Thompson* belonged to SIO and repeated in 2005/06 by *R/V Mirai* belong to Japan Agency for Marine-Earth Science and Technology (JAMSTEC). Dissolved oxygen profiles between one in this cruise and in 2005/06 agreed well (Figure C.3.11). The differences between oxygen data below 2000 dbar in this cruise and these in 1985, or in 2005/06 are –1.39±0.56, 0.28±1.14 µmol/kg, respectively. For the comparison with oxygen data in 1985, the offset value is larger than reported adjustments, about minus 0.3 µmol/kg (*Johnson et al.*, 2001; *Gouretski and Jancke*, 2001). For the comparison with oxygen data in 2005/06, it should also be noted that the relatively large difference in deep layer ranged from about 1,000 to 2000 dbar. Though it might be caused by the slight difference of the observation position, it is necessary to discussed it carefully.
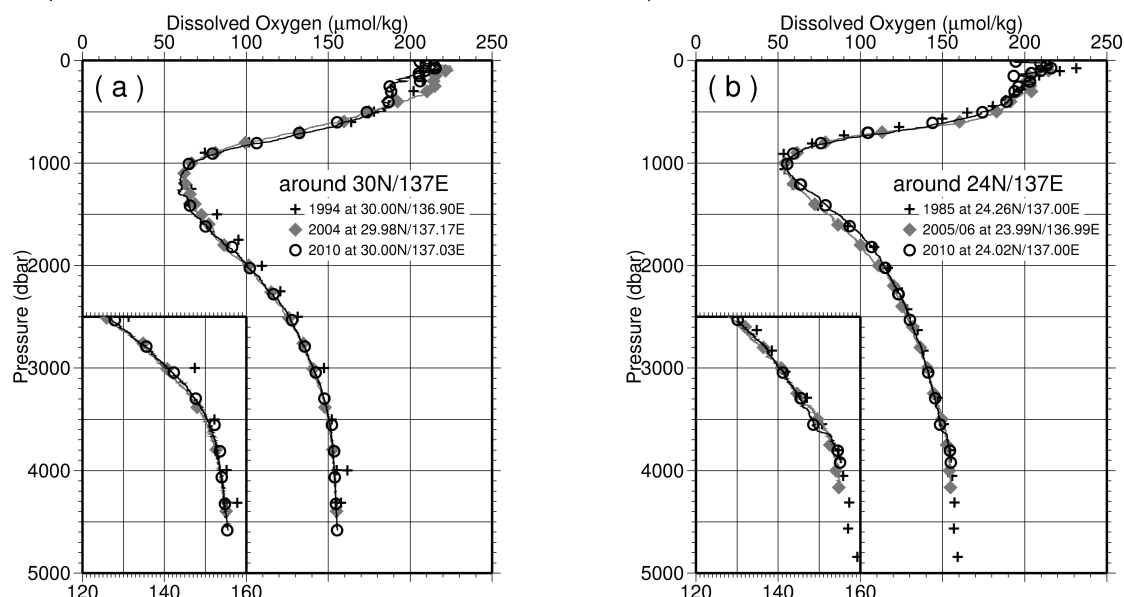
Figure C.3.11. Comparison of dissolved oxygen profiles at cross-stations of (a) WHP-P2 and (b) WHP-P3. Pluses, gray diamonds and opened circles show the first observation, the second one and this cruise, respectively. Lines denote the profiles of the oxygen sensor.

(18.4) Comparison with WHP-P9 oxygen data in 1994

We compared oxygen data in this cruise and one of WHP-P9 in 1994. In deep layers in a wide region, dissolved oxygen have been decreased from 1994 (Figure C.3.12). Below 2000 m, the difference in average is calculated in -1.38 ± 2.28 µmol/kg (Figure C.3.13). This offset value is closed to reported adjustments, about -1 µmol/kg for dissolved oxygen data of WHP-P9 (*Johnson et al.*, 2001; *Gouretski and Jancke*, 2001). Therefore, it was thought that oxygen measurements in this cruise were conducted correctly.
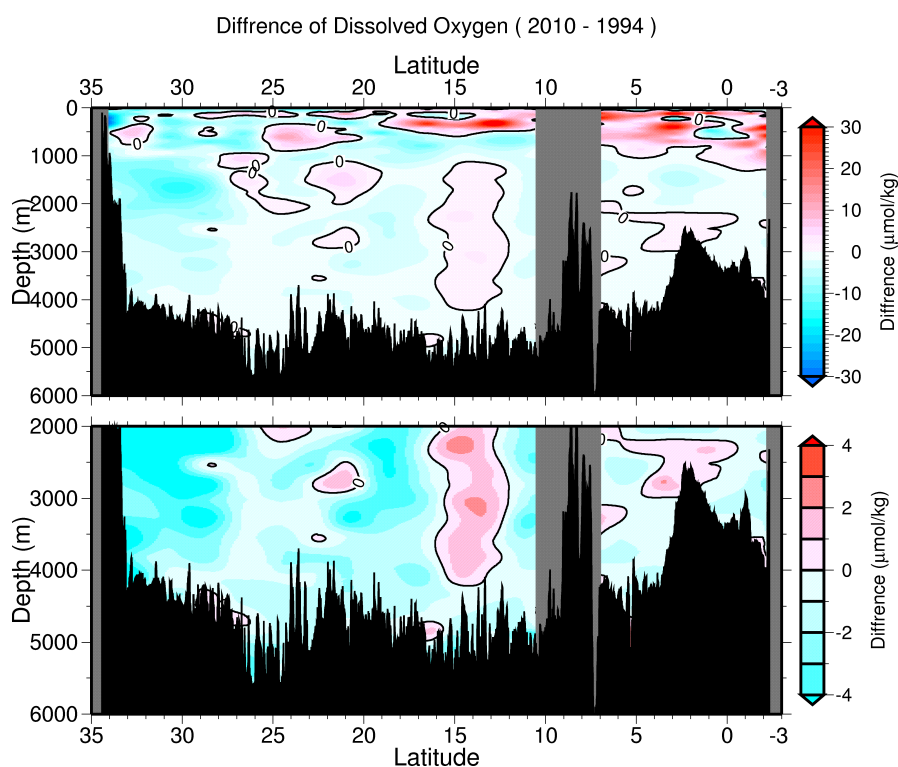
Figure C.3.12. Difference of dissolved oxygen between 2010 and 1994 against water depth.
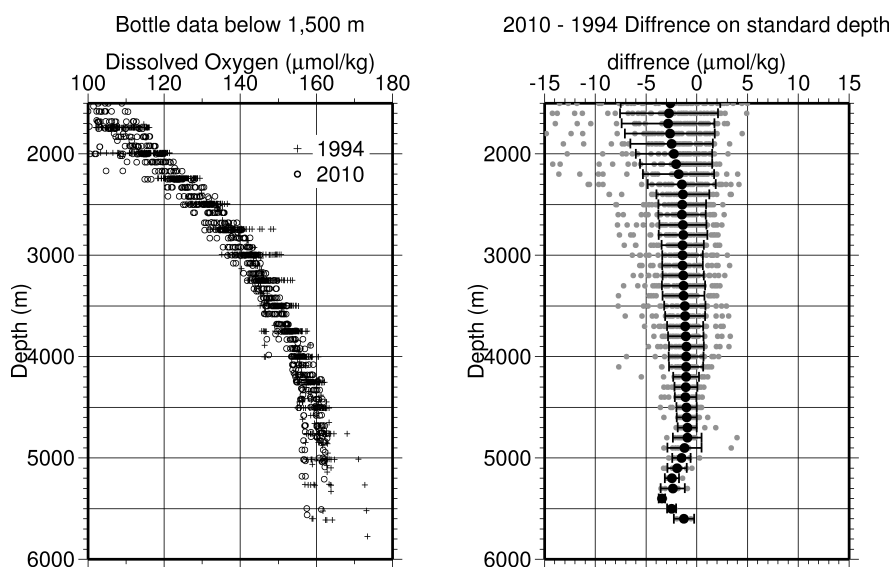
Figure C.3.13. Bottle oxygen data in 1994 (pluses) and 2010 (circles) below 1500 m (left panel) and difference of dissolved oxygen on the standard depth (right panel). Black closed circles denote mean of the differences with 1 σ error.

References

Cullberson, A.H. (1994), Dissolved oxygen, in *WHPO Pub. 91-1 Rev. 1*, November 1994, Woods Hole, Mass., USA.

Cullberson, A.H., G. Knapp, M.C. Stalcup, R.T. Williams, and F. Zemlyak (1991), A comparison of methods for the determination of dissolved oxygen in seawater, *WHPO Pub. 91-2*, August 1991, Woods Hole, Mass., USA.

DOE (1994), Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. A.G. Dickson and C. Goyet (eds), ORNL/CDIAC-74.

Gouretski, V.V. and K. Jancke (2001), Systematic errors as the causes for an apparent deep water property variability: global analysis of the WOCE and historical hydrographic data, *Prog. Oceanogr.*, *48*, 337-402.

JAMSTEC, WHP P03 REVISIT DATA BOOK (2001), edited by T. Kawano and H. Uchida, JAMSTEC

Johson, G.C., P.E. Robbins, and G.E. Hufford (2001), Systematic adjustments of hydrographic sections for internal consistency, *J. Atomos. Oceanic Technol.*, *18*, 1234-1244.

Murray, C.N., J.P. Riley and T.R.S. Wilson (1968), The solubility of oxygen in Winkler reagents used for the determination of dissolved oxygen, *Deep-Sea Res., 15*, 237-238

Langdon, C. (2010), Determination of dissolved oxygen in seawater by Winkler titration using the amperometric technique, *IOCCP Report No.14, ICPO Pub. 134, 2010 ver.1*

Swift, J. H. (2010): Reference-quality water sample data: Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.14, ICPO Pub. 134, 2010 ver.1*

4. Nutrients

Updated 8 July 2020

(1) Personnel

Kazuhiro SAITO (GEMD/JMA)

Hiroyuki FUJIWARA (GEMD/JMA)

Takahiro KITAGAWA (GEMD/JMA)

(2) Station occupied

A total of 104 stations (Leg1: 61, Leg2: 43) were occupied for nutrients. Station location and sampling layers of nutrients are shown in Figure C.4.1.
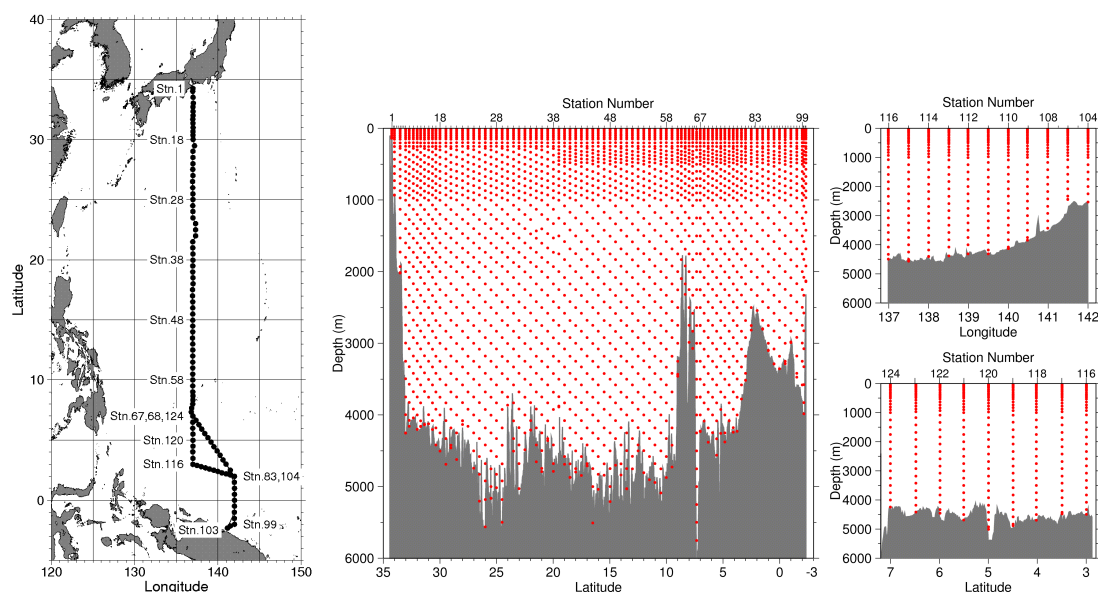
Figure C.4.1. Station location (left) and sampling layers (right) of nutrients.

(3) Instrument and Method

(3.1) Analytical detail using Auto Analyzer III systems (BLTEC)

The nutrients analyses were carried out on 4-channel Auto Analyzer III (BLTEC). Measured Parameters are nitrate + nitrite, nitrite, phosphate and silicate.

Nitrate + nitrite and nitrite are analyzed according to the modification method of *Armstrong* (1967). 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-1-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.

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.

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

The flow diagrams and reagents for each parameter are shown in Figures C.4.2-C.4.5.

(3.2) Nitrate Reagents

Ammonium chloride (buffer), 0.7 M (0.04 % w/v);

Dissolve 190 g Ammonium chloride, NH_4Cl, in ca. 5000 ml of milli-Q water, add about 5 ml Ammonia (aq.), adjust pH 8.2-8.5.

Sulfanilamide, 0.06 M (1 % w/v);

Dissolve 5 g Sulfanilamide, $4-NH_2C_6H_4SO_3H$, in 430 ml milli-Q water, add 70 ml concentrated HCl. After mixing, 1 ml Brij-35 (22 % w/w) is added.

N-1-Naphtylethylene-diamine dihydrochloride (NEDA), 0.004 M (0.1 % w/v);

Dissolve 0.5 g NEDA, $C_{10}H_7NH_2CH_2CH_2NH_2 \cdot 2HCl$, in 500 ml milli-Q water.

1ch
Nitrate + Nitrite

WHT/WHT debubble

waste ←

20T 10T 10T   5T   BLK/BLK   air

Cd tube   YEL/YEL   ammonium chloride(buffer)

ORG/WHT   sample or base sea water

BLK/BLK   air

ORG/WHT   sulfanilamide

ORG/WHT   N-1-Naphtylethylene-diamine

GRY/GRY   C/M

waste ←

waste

Colorimeter

1.5mm(I.D) × 15mm flow cell

530nm
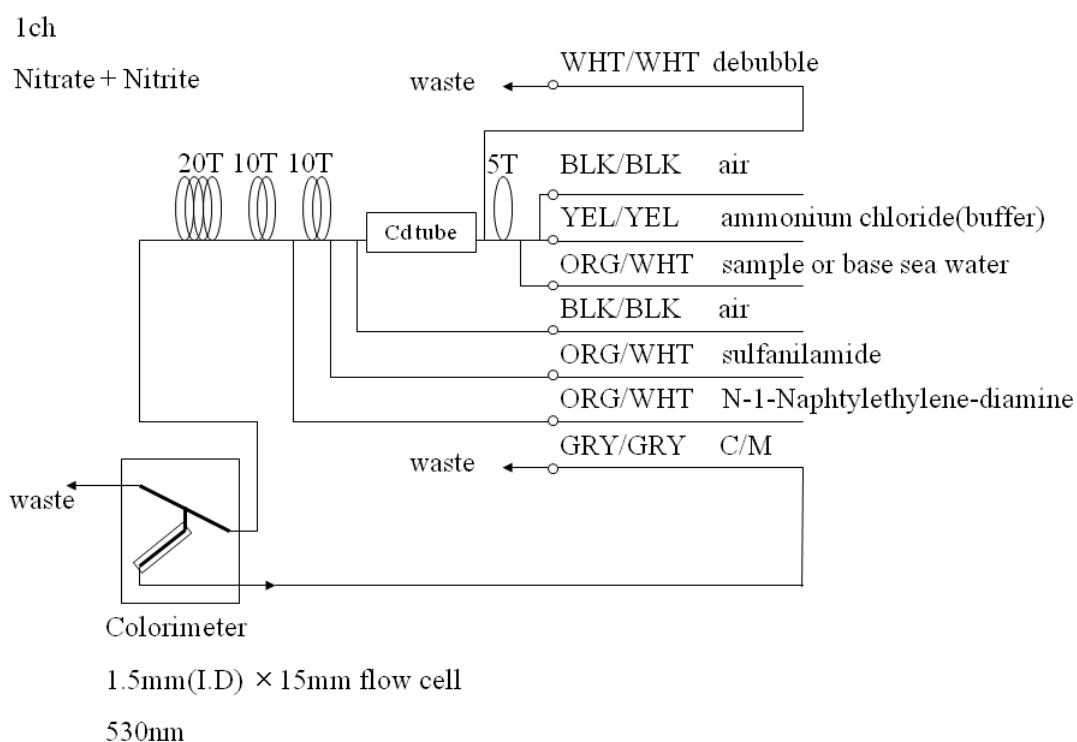
Figure C.4.2. 1ch. (Nitrate + Nitrite) Flow diagram.

(3.3) Nitrite Reagents

Sulfanilamide, 0.06 M (1 % w/v);

Dissolve 5 g Sulfanilamide, $4-NH_2C_6H_4SO_3H$, in 430 ml milli-Q water, add 70 ml concentrated HCl. After mixing, 1 ml Brij-35 (22 % w/w) is added.

N-1-Naphtylethylene-diamine dihydrochloride (NEDA), 0.004 M (0.1 % w/v);

Dissolve 0.5 g NEDA, $C_{10}H_7NH_2CH_2CH_2NH_2 \cdot 2HCl$, in 500 ml milli-Q water.

ch2
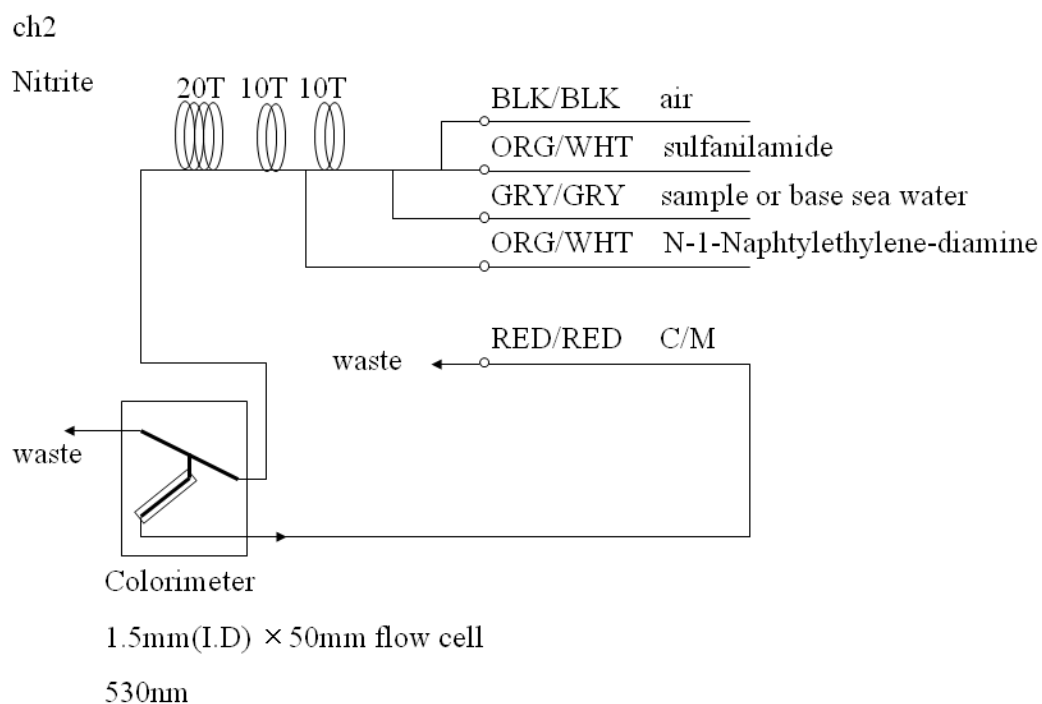
Nitrite

Figure C.4.3. 2ch. Nitrite Flow diagram.

(3.4) Phosphate Reagents

Ammonium molybdate, 0.005 M (0.6 % w/v);

Dissolve 3 g Ammonium molybdate(VI) tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, and 0.05 g Potassium antimonyl tartrate, $C_8H_4K_2O_{12}Sb_2\cdot3H_2O$, in 400 ml milli-Q water and add 100 ml H_2SO_4 (12.6N). After mixing, 2 ml Sodium dodecyl sulfate (15 % solution in water) is added.

L(+)-Ascorbic acid, 0.08 M (1.5 % w/v);

Dissolve 4.5 g L(+)-Ascorbic acid, $C_6H_8O_6$, in 300 ml milli-Q water. After mixing, 10 ml Acetone is added. Freshly prepared before every measurement.
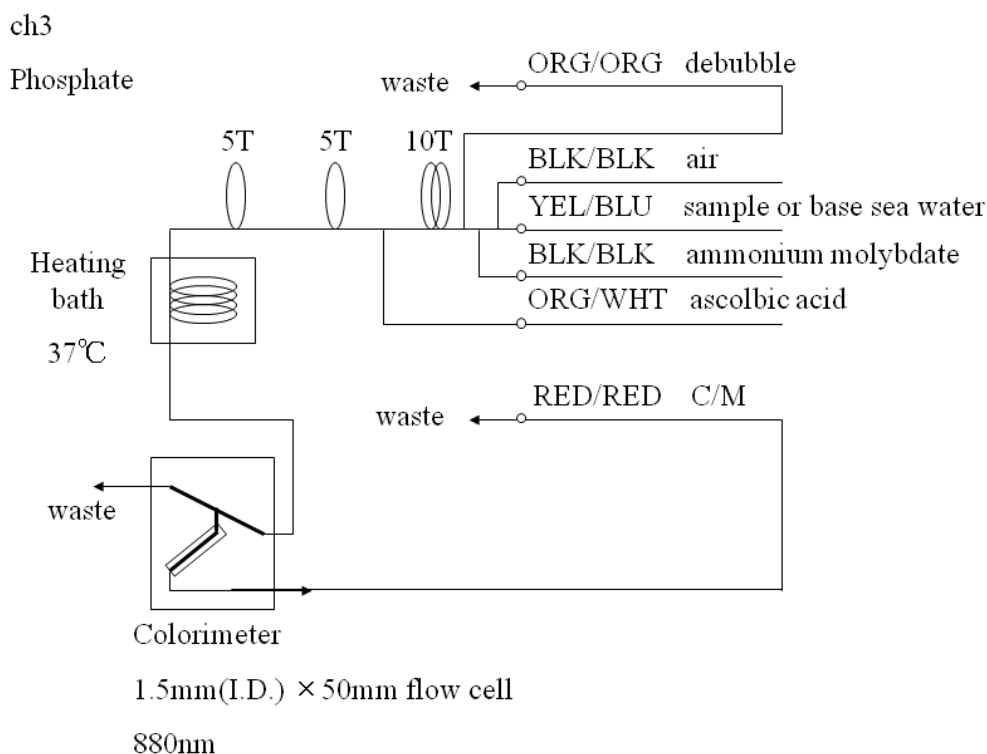
Figure C.4.4. 3ch. Phosphate Flow diagram.

(3.5) Silicate Reagents

Ammonium molydate, 0.005 M (0.6 % w/v);

Dissolve 3 g Ammonium molybdate (VI) tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in 495 ml milli-Q water and added 5 ml H_2SO_4 (12.6N). After mixing, 2 ml Sodium dodecyl sulfate (15 % solution in water) is added.

Oxalic acid, 0.4 M (5 % w/v);

Dissolve 25 g Oxalic acid dihydrate, $(COOH)_2 \cdot 2H_2O$, in 500 ml milli-Q water.

L(+)-Ascorbic acid, 0.08 M (1.5 % w/v);

Dissolve 4.5 g L(+)-Ascorbic acid, $C_6H_8O_6$, in 300 ml milli-Q water. After mixing, 10 ml Acetone is added. Freshly prepared before every measurement.

```
ch4
Silicate            5T      10T      5T
                                          BLK/BLK    air
                                          ORG/YEL    sample or base sea water
Heating                                   WHT/WHT  ammonium molydate
bath                                      ORG/ORG  oxalic acid
                                          WHT/WHT  ascolbic acid
37℃                                       YEL/YEL    C/M
                              waste  ◄
waste

Colorimeter
1.5mm(I.D.) ×15mm flow cell
820nm
```
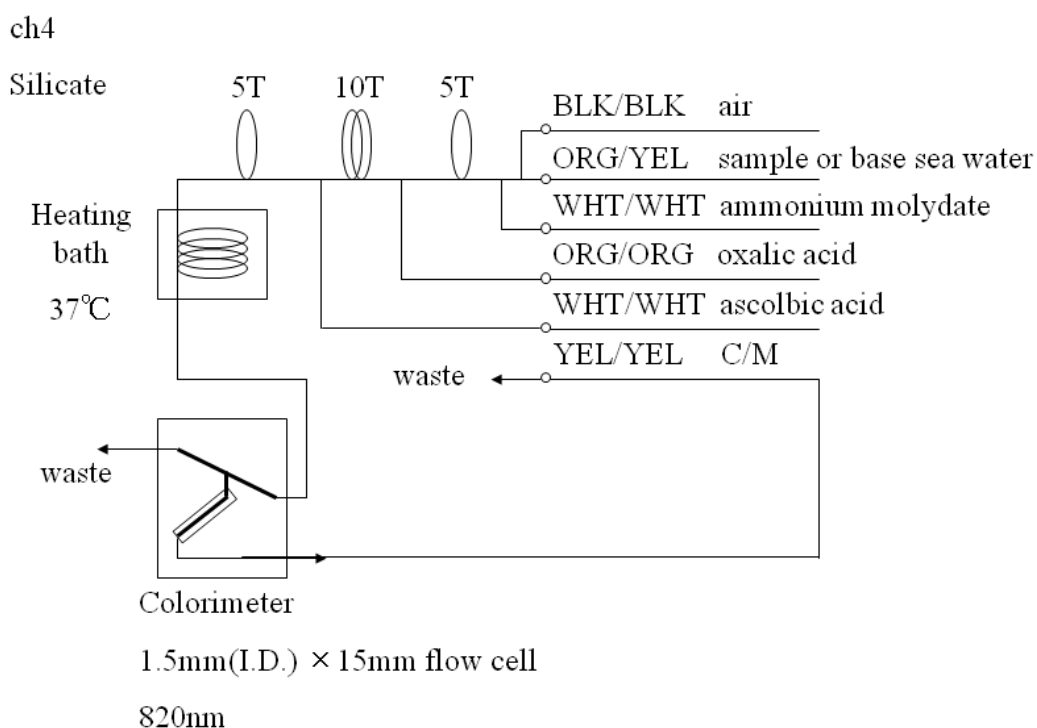
Figure C.4.5. 4ch. Silicate Flow diagram.

(3.6) Sampling procedures

Seawater samples were collected from 10-liters Niskin bottle attached CTD-system and a stainless steel bucket for the surface. Sampling of nutrients followed that oxygen and trace gases. Samples were drawn into 10 ml polymethylpenten vials with 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 immediately after collection.

(3.7) Data processing

Raw data from Auto Analyzer III were recorded at 1-second interval and were treated as follows;

- Calculate 11-second moving average.

- Check the shape of each peak and position of peak values taken, and then change the positions

of peak values taken if necessary.

- Baseline correction was done basically using liner regression.

- Reagent blank correction was done basically using liner regression.

- Carry-over correction was applied to peak heights of each sample.

- Sensitivity correction was applied to peak heights of each sample.

- Refraction error correction was applied to peak heights of each seawater sample.

- Calibration curves to get nutrients concentration were assumed quadratic expression.

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

- Convert data from $\mu mol/l$ to $\mu mol/kg$.

(4) Nutrients standards

(4.1) Volumetric Laboratory Ware of in-house standards

All volumetric ware used were gravimetrically calibrated. Polymethylpenten volumetric flasks were gravimetrically calibrated at the temperature of use within 3 - 4 K.

Volumetric flasks

The weights obtained in the calibration weightings were corrected for the density of water and air buoyancy.

Pipettes and pipettors

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

(4.2) Reagents, general considerations

Specifications

For nitrate standard, "potassium nitrate 99.995 suprapur" provided by Merck, CAS No. : 7757-79-1, was used.

For phosphate standard, "potassium dihydrogen phosphate anhydrous 99.995 suprapur" provided by Merck, CAS No. : 7778-77-0, was used.

For nitrite standard, "sodium nitrite GR for analysis ACS,Reag. Ph Eur" provided by Merck, CAS No. : 7632-00-0, was used.

For the silicate standard, we use "Silicon standard solution traceable to SRM from NIST SiO_2

in NaOH 0.5 mol/L 1000 mg/L Si CertiPUR" provided by Merck, which lot number is HC814662 is used. The silicate concentration is certified by NIST-SRM3150 as 999 mg/L with the expanded uncertainty of 5 mg/L (k=2). However, we used concentration corrected with factor as 0.975. Details about this correction are described in chapter C4 (10).

Ultra pure water

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

Low Nutrient Seawater (LNSW)

Surface water having low nutrient concentration was taken and filtered using 10 μm pore size membrane filter. This water is stored in 20 liter flexible container with paper box.

(4.3) Concentrations of nutrients for A, B and C standards

Concentrations of nutrients for A, B and C standards are set as shown in Table C.4.1. The C standard is prepared according recipes as shown in Table C.4.2. All volumetric laboratory tools were calibrated prior the cruise as stated in subsection (4.1). 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. The calibration curves for each run were obtained using 4 levels, C-1, C-2, C-3 and C-4.

Table C.4.1. Nominal concentrations of nutrients for A, B and C standards.

Unit: μmol/l

	A	B	C-1	C-2	C-3	C-4 (Full scale)
NO_3	26200	520	LNSW*	1/3 Full scale	2/3 Full scale	43.4
NO_2	12500	250	LNSW*	1/3 Full scale	2/3 Full scale	2.0
PO_4	2040	40.5	LNSW*	1/3 Full scale	2/3 Full scale	3.2
Si	35600	1950	LNSW*	1/3 Full scale	2/3 Full scale	155

Table C.4.2. Working calibration standard recipes.

C Std.	B-1 Std.	B-2 Std.
C-4 (Full scale)	20 ml	2 ml
	LNSW*	C-4 (Full scale)
C-1	30 ml	0 ml
C-2	20 ml	10 ml
C-3	10 ml	20 ml

B-1 Std.: Mixture of nitrate, phosphate and silicate.

B-2 Std.: Nitrite.

LNSW*: 22 ml milli-Q water in 250 ml volumetric flask, and LNSW add to marked line.

(4.4) Renewal of in-house standard solutions

In-house standard solutions as stated in (4.3) were renewed as shown in Table C.4.3.

Table C.4.3. Timing of renewal of in-house standards.

NO3, NO2, PO4, Si	Renewal
A-1 Std. (NO_3)	no renewal
A-2 Std. (NO_2)	no renewal
A-3 Std. (PO_4)	no renewal
A-4 Std. (Si)	commercial prepared solution
B Std.	
B-1 Std.	maximum 9 days
B-2 Std.	maximum 14 days

C Std.	Renewal
mixture of B-1 and B-2 Std.	Every measurement

B-1 Std.: Mixture of nitrate, phosphate and silicate.

B-2 Std.: nitrite.

(5) Use of RMNS

The reference material of nutrients in seawater (hereafter RMNS), which was prepared by the General Environmental Technos Co. Ltd. (Kanso Technos), was used every analysis at each hydrographic station. According to *Aoyama et al*. (2010), the RMNS homogeneity is 0.1 % - 0.2 % in high concentration range, and stability is 48 - 71 months. By the use of RMNSs for the analysis of seawater, it is expected to secure stable comparability and uncertainty of data. If RMNS will be certified in the future, the traceability of our analysis value will be secured. *Aoyama et al.* (2010) assigned nutrients concentrations for RMNS lot BA, AX, BE and AZ as shown in Table C.4.4.

Table C.4.4. INSS assigned concentration of RMNSs.

Unit: μmol/kg

	Nitrate	Phosphate	Silicate
RMNS-BA	0.07±0.01	0.061±0.007	1.61±0.07
RMNS-AX	21.44±0.05	1.614±0.006	58.05±0.12
RMNS-BE	36.70±0.04	2.662±0.005	99.20±0.08
RMNS-AZ	42.36±0.06	3.017±0.005	133.93±0.11

(5.1) RMNSs for this cruise

One hundred and five set of RMNS lots BA and BE were prepared to use every analysis at each hydrographic station. BA and BE were renewed every run. To check the inter-bottle consistency of RMNS, we re-measured the RMNS in the next analysis run. Sixteen of RMNS lots AX and AZ were prepared to use every 2 to 4 analysis and renewed every 2 or 3 runs in principle. The RMNS bottles were stored at a wet laboratory in the ship, where the temperature was maintained around 26 deg-C.

(5.2) Assigned concentration of RMNSs

We assigned nutrients concentrations for RMNS lots BA, AX, BE and AZ as shown in Table C.4.5 based on the analysis during the cruise. The measured concentration of RMNS lot BE

during the cruise are shown in Figures C.4.6–C.4.8 as quality control charts. The concentration variations in these figures represent largely differences of the in-house standard. At Stn.25, one bottle of RMNS lot BE, No. 0138, showed obviously low concentrations. The measured values of all parameters were ca. 2% lower than expected. The concentrations of another bottle of RMNS lot BE, which was also analyzed in previous run, showed a good agreement with expected value. So, we neglected the result of No. 0138 of RMNS lot BE. At Stn.58, nitrate + nitrite concentration of BA No. 0756 had also shown unexpected low value, so it was neglected too.

The concentrations of RMNSs were in close agreement with expected values within the range of uncertainty except for the phosphate.

Table C.4.5. Assigned concentration of RMNSs.

Unit: μmol/kg

	Nitrate + Nitrite	Phosphate	Silicate
RMNS-BA	0.07±0.03	0.02±0.00	1.64±0.11
RMNS-AX	21.89±0.08	1.59±0.01	59.67±0.38
RMNS-BE	36.77±0.11	2.64±0.01	101.85±0.36
RMNS-AZ	42.42±0.13	2.98±0.01	137.29±0.29

Note: N(BA: Nitrate + Nitrite, Silicate)=104, N(BA: Phosphate)=105, N(BE: Nitrate + Nitrite, Phosphate)=104, N(BE: Silicate)=103, N(AX,AZ)=45.
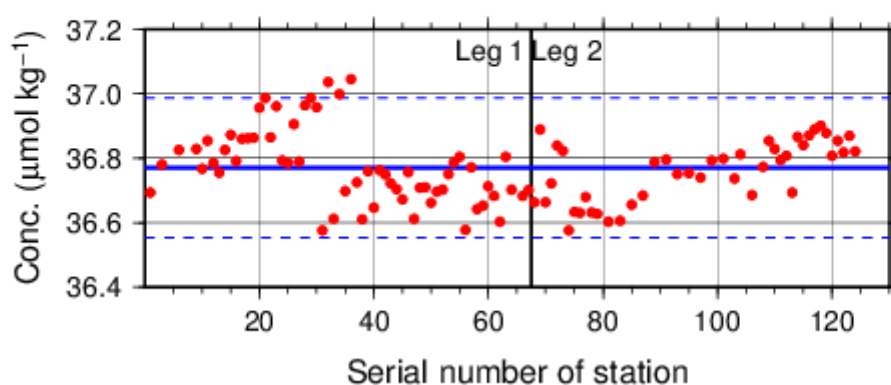
Figure C.4.6. Result of RMNS lot BE concentrations of nitrate + nitrite during the cruise.
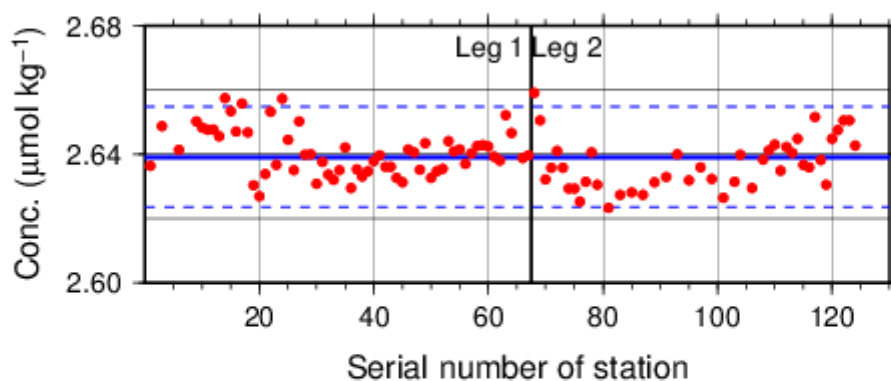
Figure C.4.7. Result of RMNS lot BE concentrations of phosphate during the cruise.
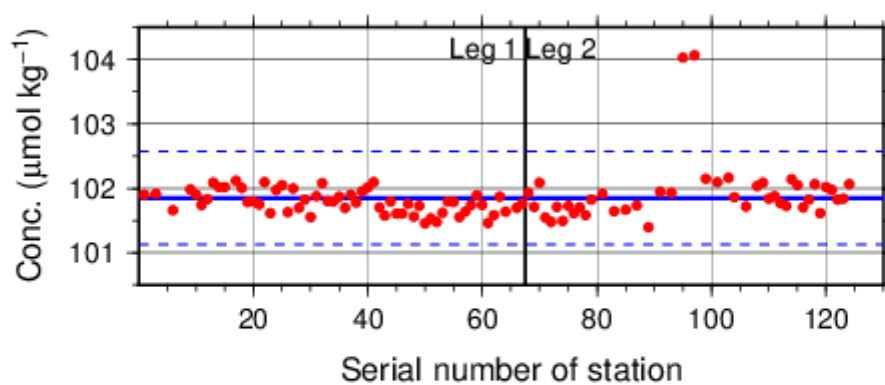
Figure C.4.8. Result of RMNS lot BE concentrations of silicate during the cruise.

(5.3) Relative standard deviation of RMNSs measurement

The relative standard deviation of lot BA, AX, BE and AZ throughout the cruise are shown in Table C.4.6.

Table C.4.6. Relative standard deviation of RMNSs lot BA, AX, BE and AZ measurements
in each run throughout cruise.

	Nitrate + Nitrite CV %	Phosphate CV %	Silicate CV %
RMNS-BA	41.03	16.02	6.47
RMNS-AX	0.35	0.43	0.31
RMNS-BE	0.30	0.30	0.19
RMNS-AZ	0.31	0.31	0.17

Note: N(BA: Nitrate + Nitrite, Silicate)=104, N(BA: Phosphate)=105, N(BE: Nitrate + Nitrite,
Phosphate)=104, N(BE: Silicate)=103, N(AX,AZ)=45.

(6) Quality control

(6.1) Precision of nutrients analyses during the cruise

Precision of nutrients analyses during the cruise was evaluated based on 5 or 6 measurements
of the C-4 (full scale) standard in each run. Summary of precisions are shown in Table C.4.7.
During this cruise, analytical precisions were 0.11 % for nitrate, 0.16 % for phosphate and
0.09 % for silicate in terms of mean of precision, respectively. The time series of precision are
shown in Figure C.4.9 - C.4.11.

Table C.4.7. Summary of precisions during the cruise.

	Nitrate + Nitrite CV %	Phosphate CV %	Silicate CV %
Median	0.11	0.14	0.08
Mean	0.11	0.16	0.09
Maximum	0.32	0.38	0.31
Minimum	0.03	0.03	0.01
Number	105	105	104
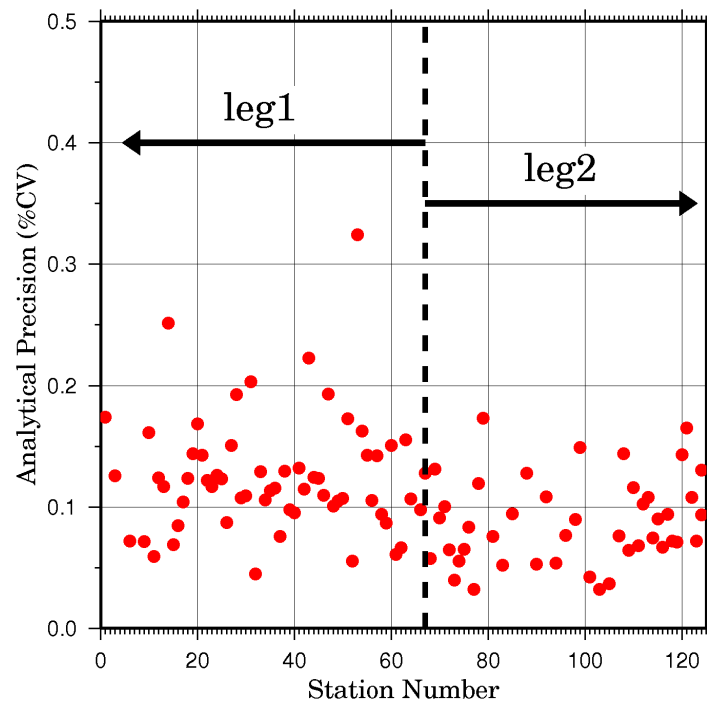
Figure C.4.9. Time series of precision of nitrate + nitrite.
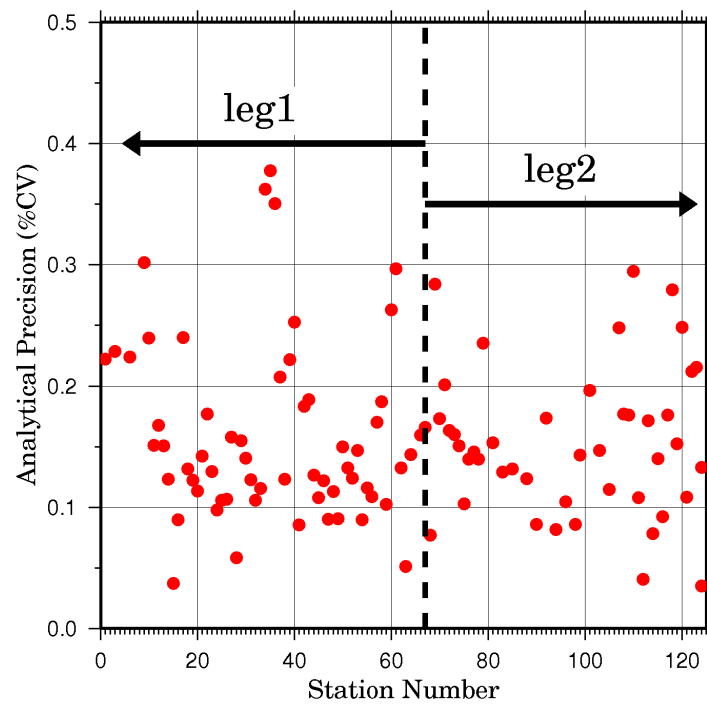
Figure C.4.10. Time series of precision of phosphate.
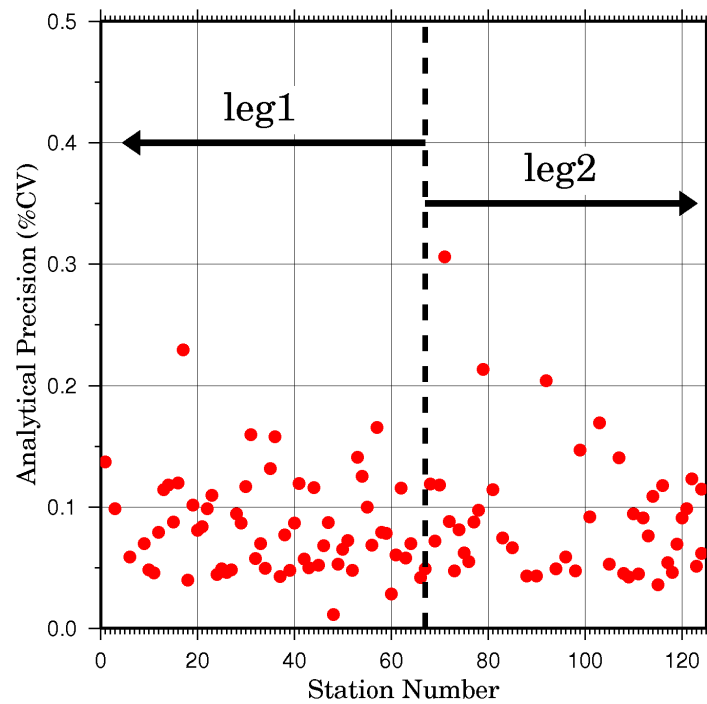
Figure C.4.11. Time series of precision of silicate.

(6.2) Replicate sample measurement

Replicate samples were analyzed at every hydrographic station. Total amount of the replicate sample pairs was 405. Summary of replicate sample measurements are shown in Table C.4.8, and Figure C.4.12 - C.4.14. During this cruise, the average difference and standard deviation of replicate measurement were 0.038±0.036 μmol/kg for nitrate + nitrite, 0.004±0.004 μmol/kg for phosphate and 0.140±0.139 μmol/kg for silicate, respectively.

Table C.4.8. Average difference of replicate samples in each run throughout cruise.

Unit: μmol/kg

Nitrate + Nitrite	Phosphate	Silicate
0.038±0.036	0.004±0.004	0.140±0.139

Note: N=403(nitrate, phosphate), N=399(silicate) at flag 2.

Figure C.4.12. Result of nitrate + nitrite replicate samplings (N=403) during RF10-05 against (a) station number, (b) sampling pressure, (c) concentration and (d) histogram of the result of replicate samplings.
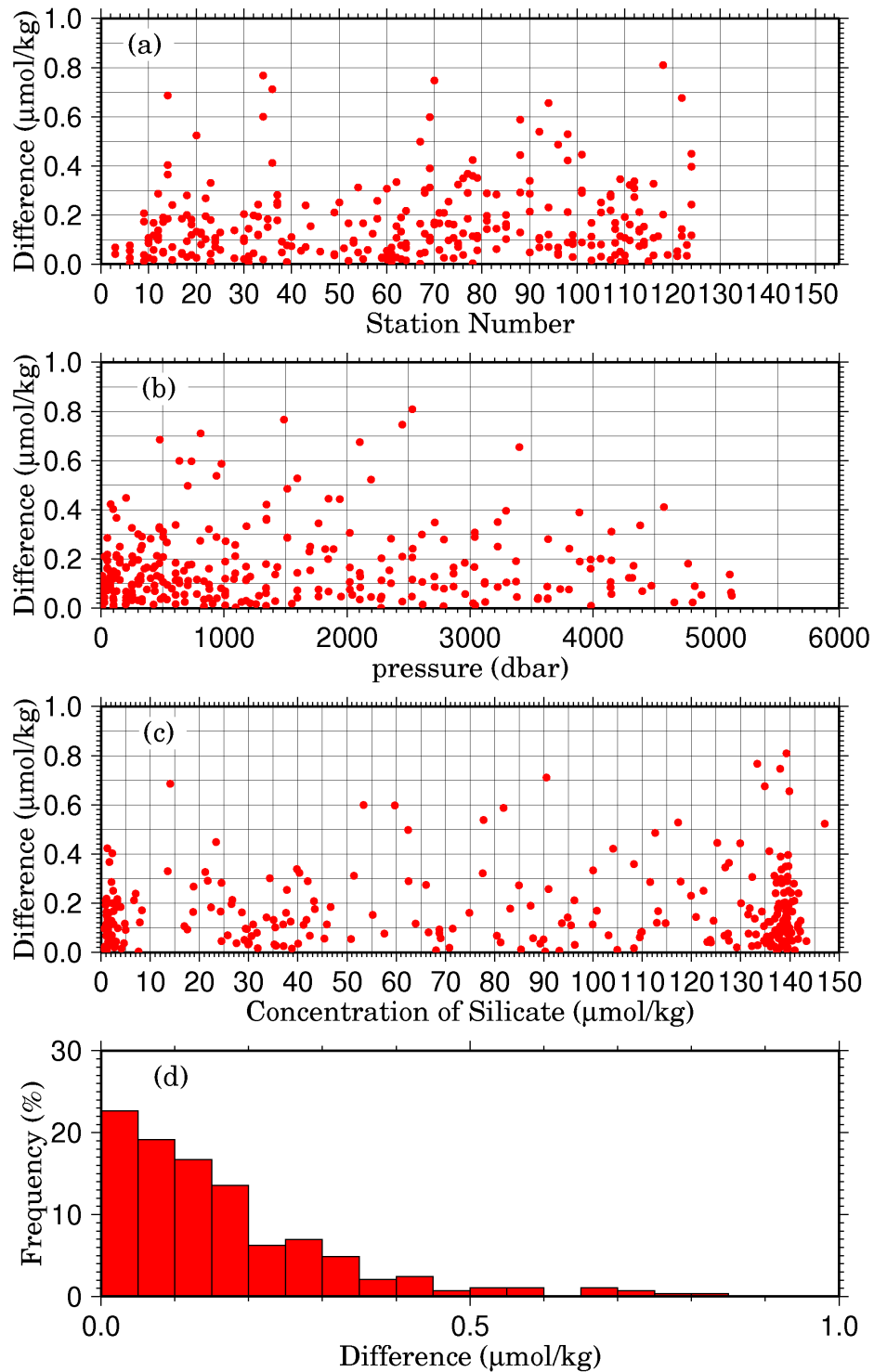
RF1005_PO₄ Result of Replicate Sampling (N=403)
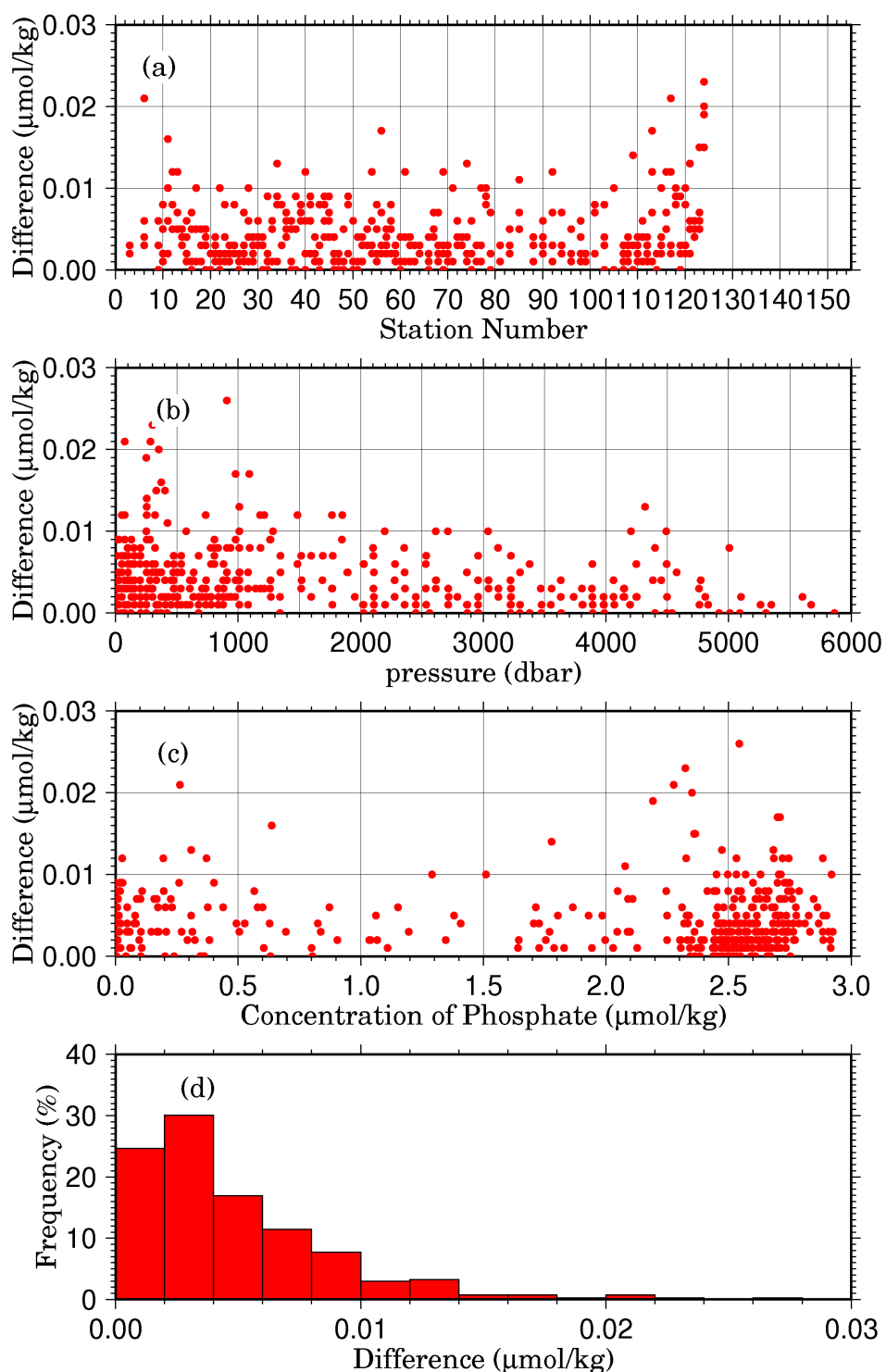
Figure C.4.13. Result of phosphate replicate samplings (N=403) during RF10-05 against (a) station number, (b) sampling pressure, (c) concentration and (d) histogram of the result of replicate samplings.

RF1005_SiO$_2$ Result of Replicate Sampling (N=399)
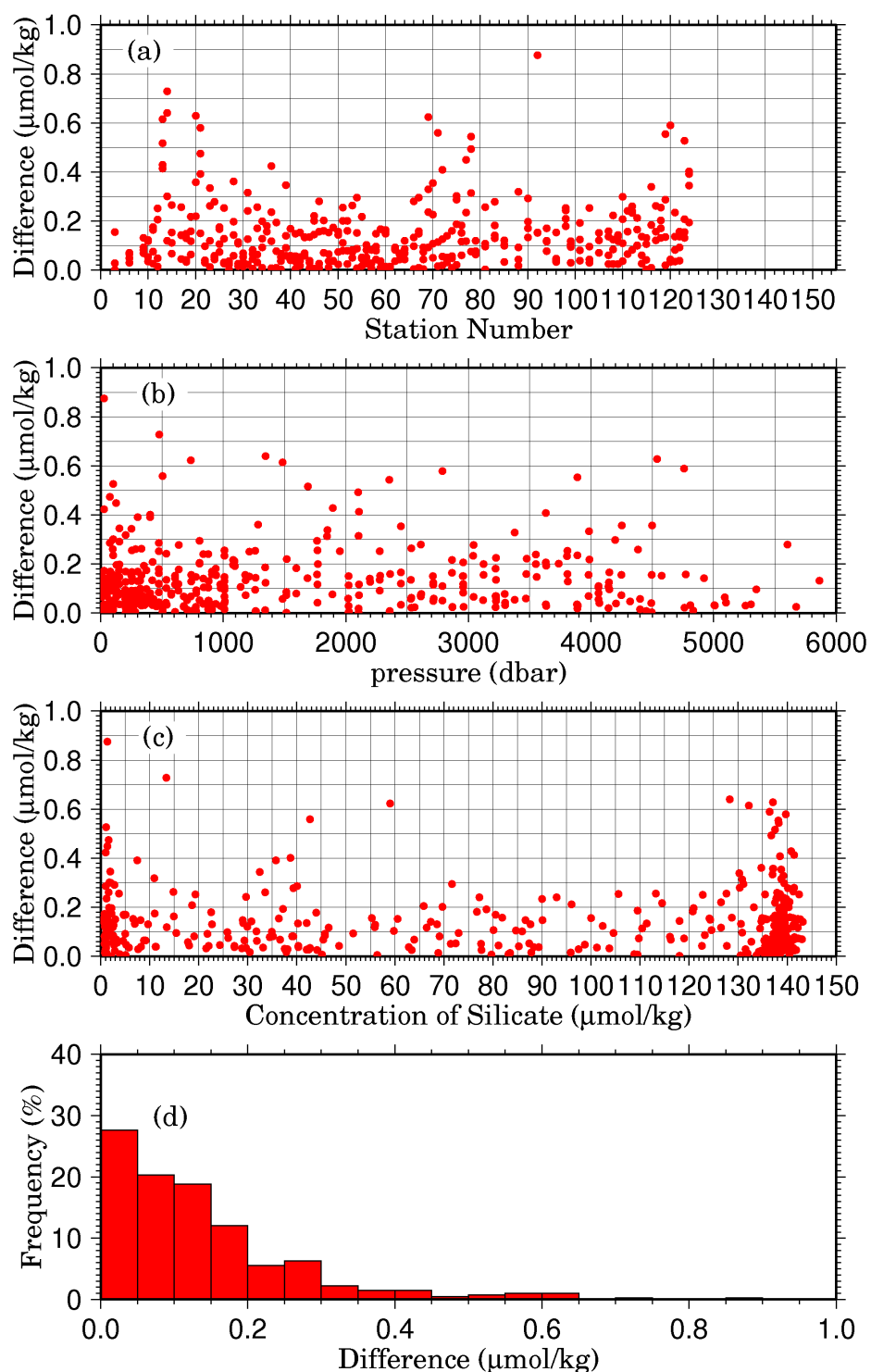
Figure C.4.14. Result of silicate replicate samplings (N=399) during RF10-05 against (a) station number, (b) sampling pressure, (c) concentration and (d) histogram of the result of replicate samplings.

(6.3) Duplicate sample measurement

Duplicate samples were analyzed at every hydrographic station. Total amount of the duplicate sample pairs was 295. Summary of duplicate sample measurements are shown in Table C.4.9, and Figure C.4.15 - C.4.17. During this cruise, the average difference and standard deviation of replicate measurement were 0.040±0.039 μmol/kg for nitrate + nitrite, 0.005±0.004 μmol/kg for phosphate and 0.167±0.163 μmol/kg for silicate, respectively.

Table C.4.9. Average difference of duplicate samples in each run throughout cruise.

Unit: μmol/kg

Nitrate + Nitrite	Phosphate	Silicate
0.040±0.039	0.005±0.004	0.167±0.163

Note: N=293(nitrate + nitrite), N=290(phosphate), N=289(silicate) at flag 2.

RF1005_NO₃ + NO₂ Result of Duplicate Sampling (N=293)
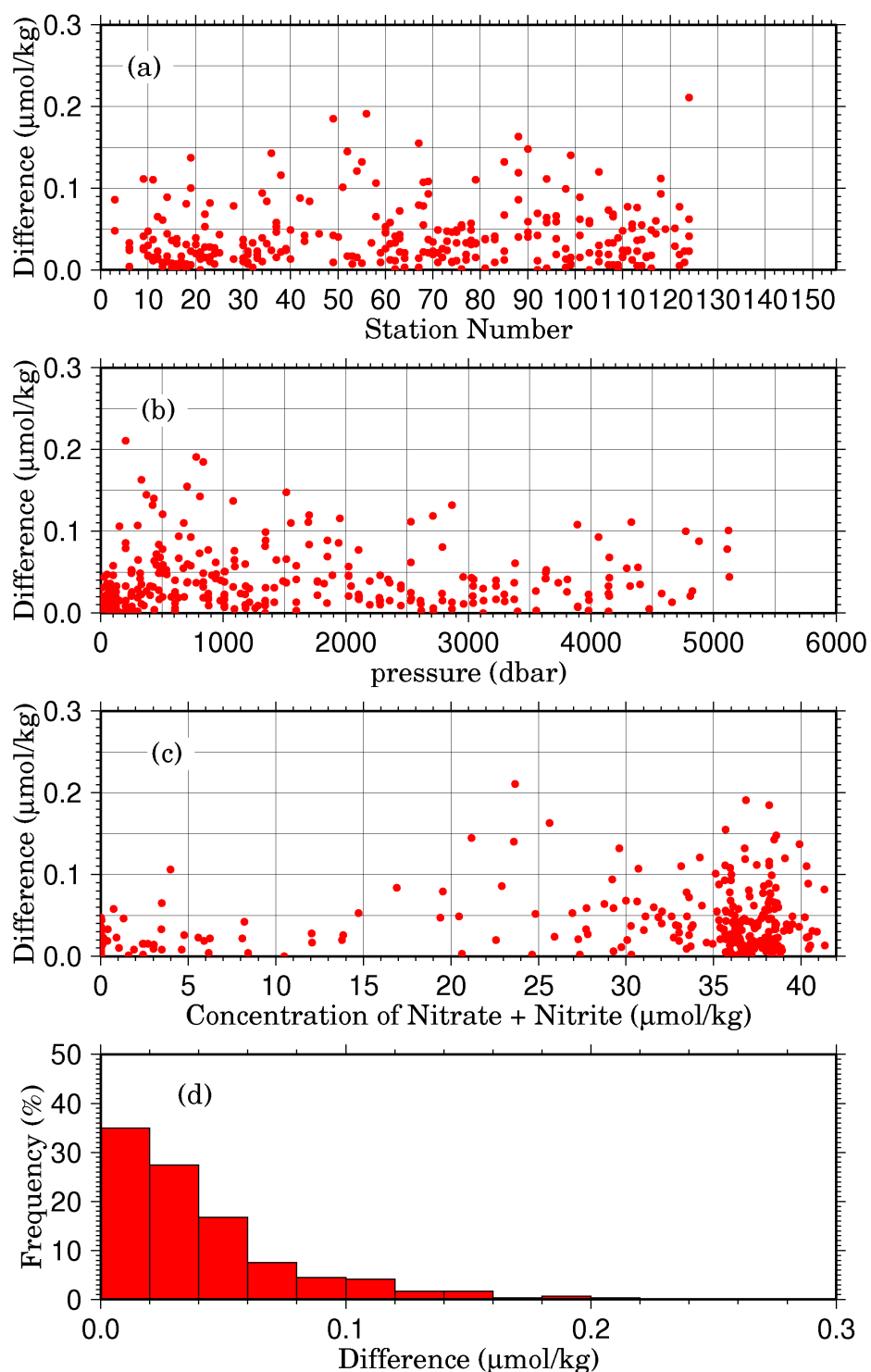
Figure C.4.15. Result of nitrate + nitrite duplicate samplings (N=293) during RF10-05 against (a) station number, (b) sampling pressure, (c) concentration and (d) histogram of the result of duplicate samplings.

RF1005_PO$_4$ Result of Duplicate Sampling (N=290)
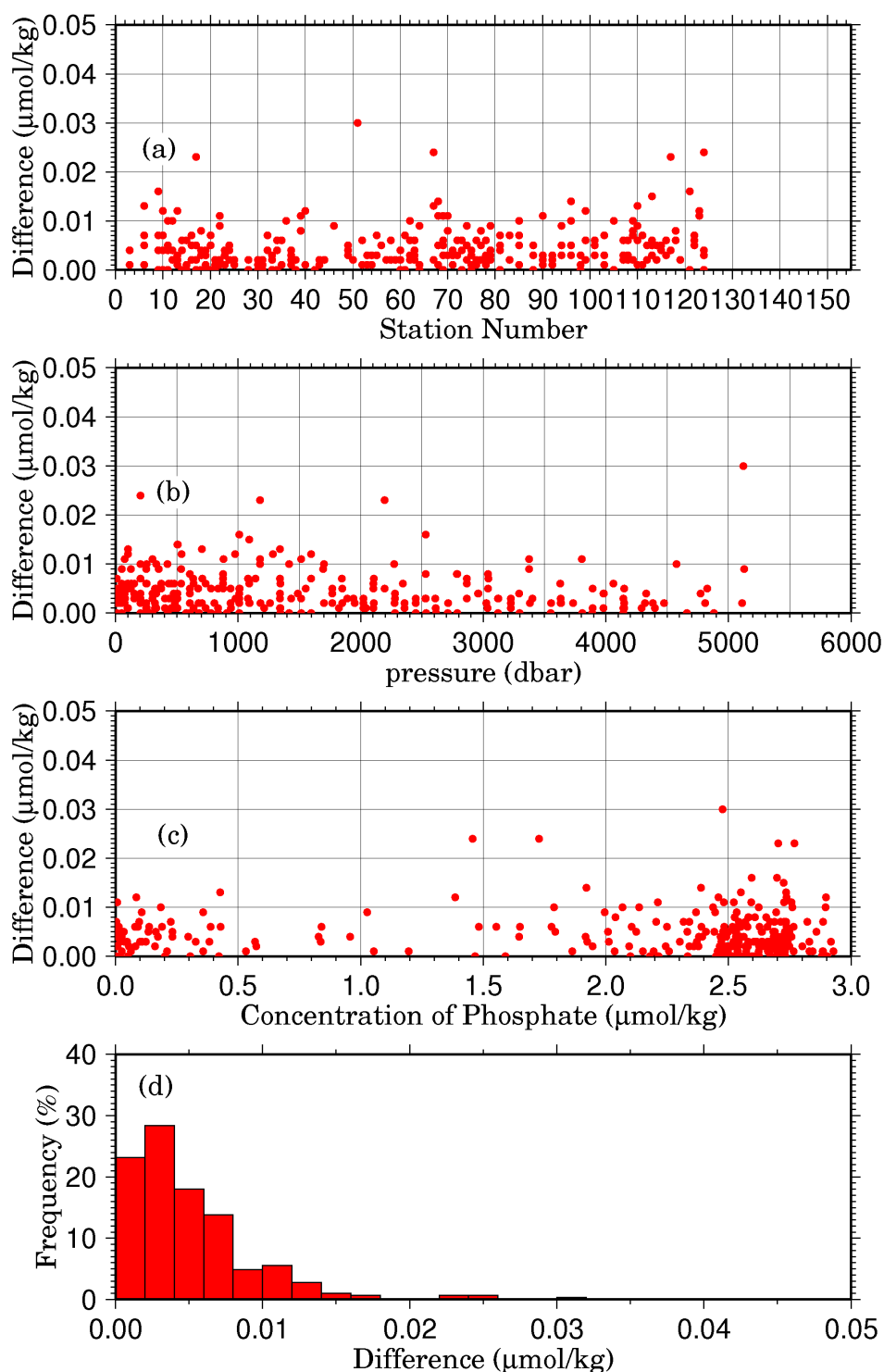
Figure C.4.16. Result of phosphate duplicate samplings (N=290) during RF10-05 against (a) station number, (b) sampling pressure, (c) concentration and (d) histogram of the result of duplicate samplings.

RF1005_SiO$_2$ Result of Duplicate Sampling (N=289)

Figure C.4.17. Result of silicate duplicate samplings (N=289) during RF10-05 against (a) station number, (b) sampling pressure, (c) concentration and (d) histogram of the result of duplicate samplings.

(7) Uncertainty

(7.1) Uncertainty associated with concentration level: U_c

The 44 sets of RMNS were analyzed during the cruise to make empirical equations to estimate uncertainty of concentrations of seawater samples throughout cruise. The average value and CV for each RMNS level were calculated, graphed, and a curve fit determined. The empirical equation (7.1) is an example of the curve fit between nutrients concentration C_x and the uncertainty at each concentration level.

Uncertainty for parameter $X(\%) = a + b(1/C_x) + c(1/C_x)^2$ -- (7.1)

Where C_x is concentration of sample for parameter X.

Empirical equations, eqs. (7.2), (7.3) and (7.4) were used to estimate uncertainty of measurement of nitrate + nitrite, phosphate and silicate during this cruise. The equations are based on analysis of 44 sets of RMNS lots BA, AX, BE and AZ. Figures C.4.18–C.4.20 show graphic presentations of eqs. (7.2) - (7.4).

Nitrate + Nitrite Concentration C_n in μmol/kg:

Uncertainty of measurement of nitrate (%) =

$$0.252 + 2.6214 \times (1/C_n) + 0.030 \times (1/C_n)^2 \qquad \text{-- (7.2)}$$

Where C_n is nitrate concentration of sample.

Phosphate Concentration C_p in μmol/kg:

Uncertainty of measurement of phosphate (%) =

$$0.1588 + 0.4470 \times (1/C_p) + 0.0009 \times (1/C_p)^2 \qquad \text{-- (7.3)}$$

Where C_p is phosphate concentration of sample.

Silicate Concentration C_s in μmol/kg:

Uncertainty of measurement of silicate (%) =

$$-0.092 + 43.838 \times (1/C_s) - 51.669 \times (1/C_s)^2 \qquad \text{-- (7.4)}$$

Where C_s is silicate concentration of sample.
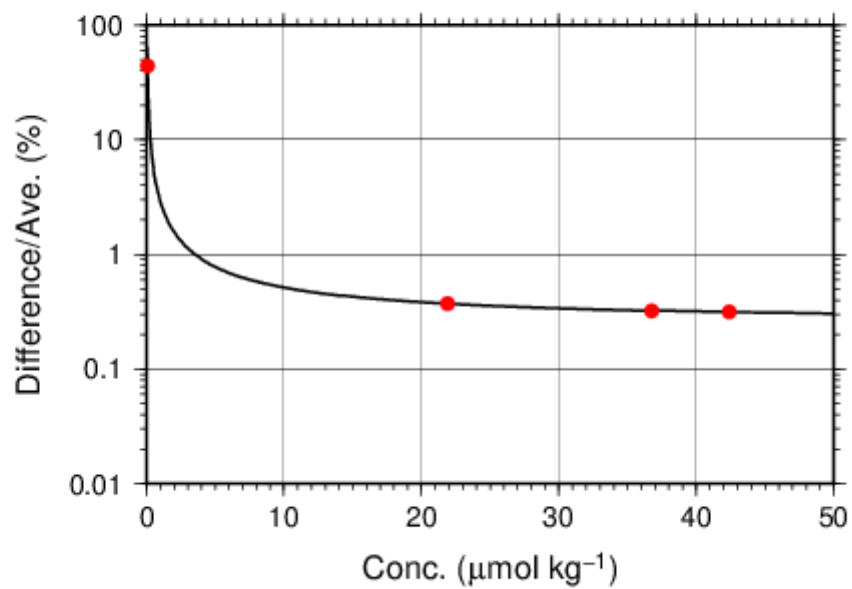
Figure C.4.18. Uncertainty of nitrate + nitrite concentration level.
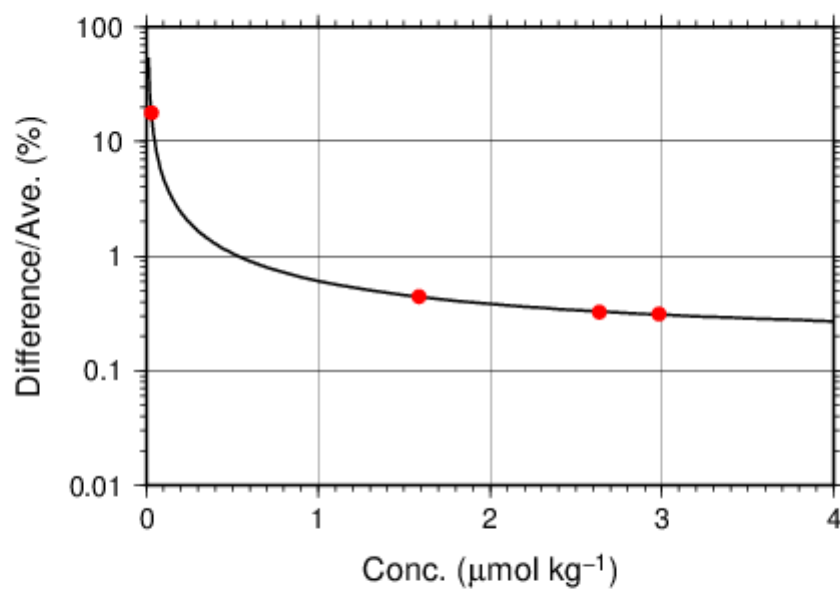
Figure C.4.19. Uncertainty of phosphate concentration level.
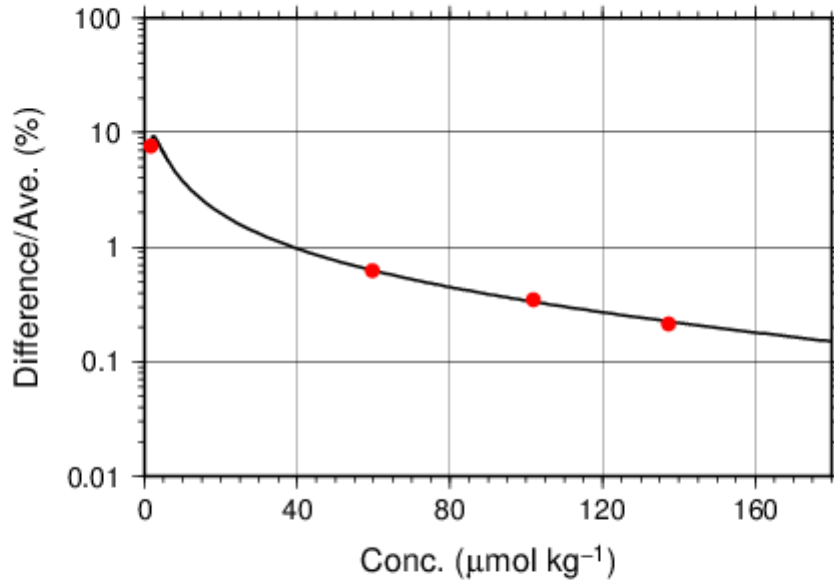
Figure C.4.20. Uncertainty of silicate concentration level.

(7.2) Uncertainty of analysis between runs: U_s

Uncertainty of analysis between runs (U_s) was estimated from relative standard deviation of RMNS throughout cruise as shown in subsection (5.3).

(7.3) Uncertainty of analysis in a run: U_a

Uncertainty of analysis (U_a) was estimated from relative standard deviation of precision throughout cruise as shown in subsection (6.1).

(7.4) Conclusive uncertainty of nutrient measurements of samples: U

To determine the conclusive uncertainty of nutrient measurements of samples, we use two functions depending on U_a value acquired at each run as follows:

When U_a was small and measurement was well-controlled condition, the conclusive uncertainty of nutrient measurements of samples, U, might be as below:

$$U = U_c. \hspace{3cm} \text{-- (7.5)}$$

When U_a was relative large and the measurement might have some problems, the conclusive uncertainty of nutrient measurements of samples, U, can be expanded as below:

$$U = \sqrt{U_c^2 + U_a^2}. \hspace{3cm} \text{-- (7.6)}$$

(8) Problems/improvements occurred and solutions

During the cruise, low-frequency noise (ca. 6 seconds per cycle) in the all channel output of AA III. So moving average was applied to all the raw data.

At Stn.16 (Lat. 30°39.21'N / Long. 136°59.69'E, RF3664), the silicate output of quality control samples and sensitivity compensation sample had exceeded the maximum value of the instrument setting. It was impossible to process silicate data for the station properly, so we neglect it. Pump tubes were replaced after the analysis.

Due to a problem on Phosphate data at Stn.36 (Lat. 20°59.83'N / Long. 136°58.21'E, RF3684), we had done another analytical run for the station. To reduce the analysis time, we omitted the C-2 and C-3 standard on these run, and processed the data as described below.

1. For each phosphate standard measurement in every run except for Stn.36, calculate the difference dC_x between the concentration (C_{x2}) based on quadratic calibration equation and the concentration (C_{x1}) based on linear calibration equation.

2. Calculate mean and standard deviation of dC_x at each level (C-1, C-2, C-3 and C-4) and reject the data for individual run if any of dC_x at each level exceeds the range of mean±standard deviation.

3. The correction equation (8.1) is calculated by the regression analysis using all QCed pair of dC_x and C_{x1}.

$$dC_x(C_{x1}) = a + bC_{x1} + cC_{x1}^2 \quad\quad -- (8.1)$$

4. For phosphate of Stn.36, calculate tentative sample concentrations C_{t1} based on linear calibration equation in each run.

5. The sample concentration C is obtained from equation (8.2) using C_{t1} and eq. (8.1).

$$C = C_{t1} + dC_x(C_{t1}) \quad\quad -- (8.2)$$

The correction term dC_x represents non-linearity of standard calibration. The correction for phosphate at Stn.36 was smaller than 0.003 μmol/kg.

(9) Results

(9.1) Comparison at cross-stations during this cruise

Cross-stations during this cruise were two stations. The one was located at 2°N/142°E, another was located 7°N/137°E. At stations of Stn.83 (RF3731) and Stn.104 (RF3755), hydrocast sampling for nutrients (nitrate, nitrite, phosphate, silicate) were conducted two times at interval of about five days. Each nutrients parameter profiles of the two hydrocasts agreed well within the range of uncertainty when correcting it by using RMNS. At stations of Stn.67 (RF3715), Stn.68 (RF3716) and Stn.124 (RF3772), hydrocast sampling for nutrients were conducted three times. Interval between the first and the second was about a week, interval between the second and the third was about two weeks. Each nutrients parameter profiles of the three hydrocasts agreed well within the range of uncertainty when correcting it by using RMNS. These profiles are shown in Figure C.4.21 - C.4.23.
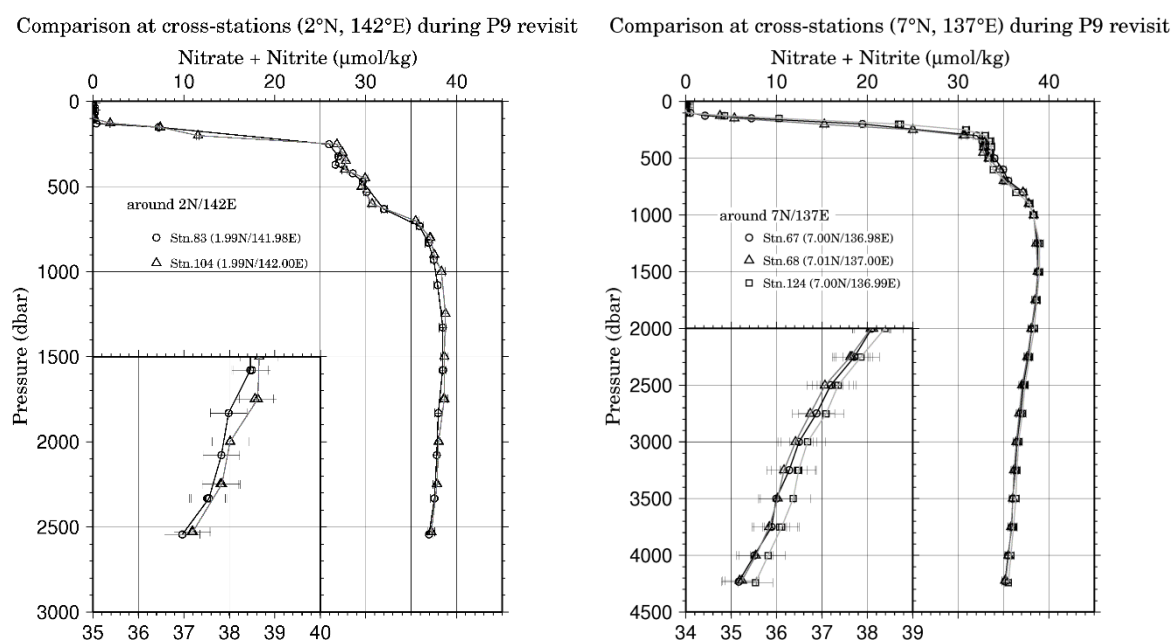
Figure C.4.21. Comparison of nitrate +nitrite profiles between the first hydrocast (circle) and the second one (triangle) at the cross-stations of 2°N/142°E (left), and the first hydrocast (circle), the second one (triangle) and the third one (square) at the cross-stations of 7˚N/137˚E (right).
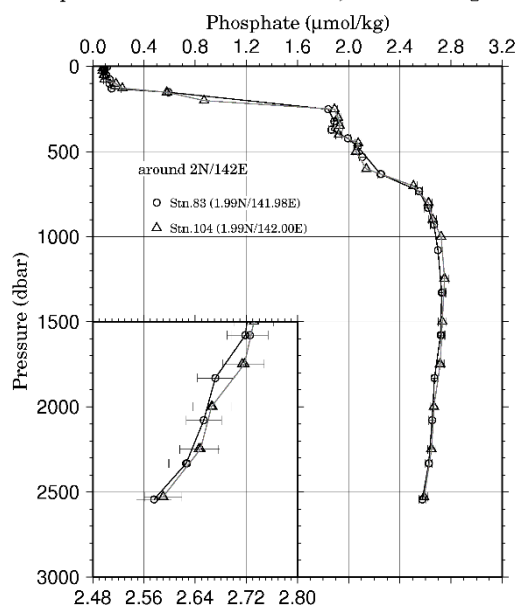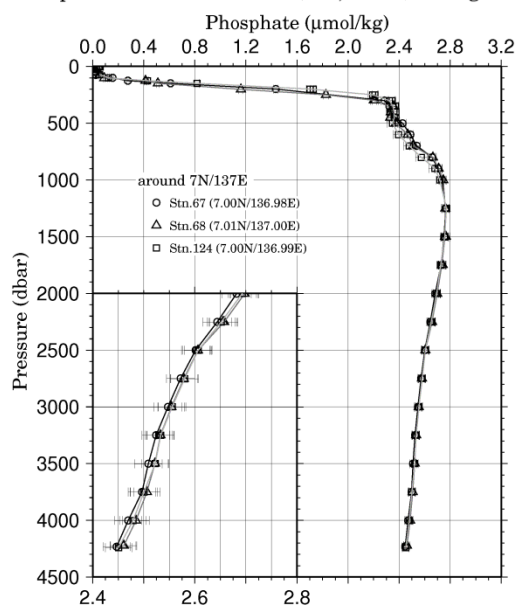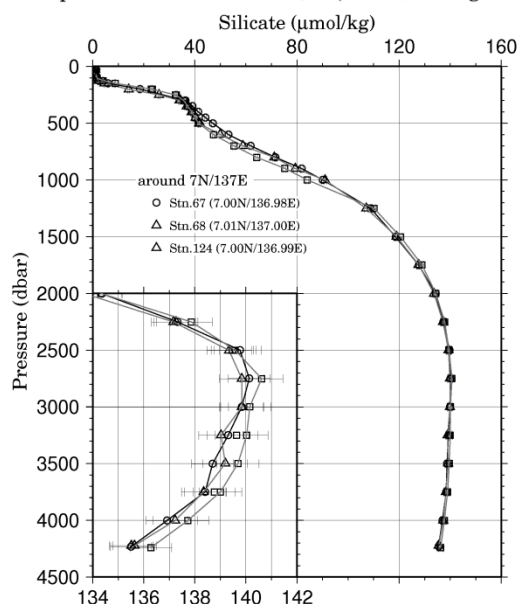
Figure C.4.22. Comparison of phosphate profiles between the first hydrocast (circle) and the second one (triangle) at the cross-stations of 2°N/142°E (left), and the first hydrocast (circle), the second one (triangle) and the third one (square) at the cross-stations of 7°N/137°E (right).
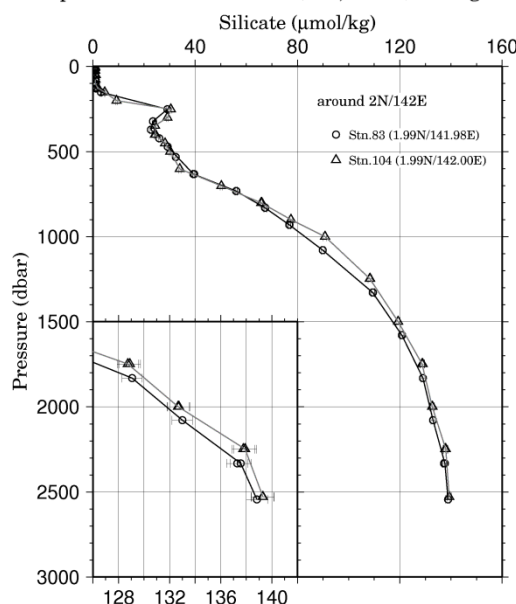
Figure C.4.23. Comparison of silicate profiles between the first hydrocast (circle)and the second one (triangle) at the cross-stations of 2°N/142°E (left), and the first hydrocast (circle), the second one (triangle) and the third one (square) at the cross-stations of 7°N/137°E (right).

(9.2) Comparison at cross-stations of WHP-P2 section in 2004 and WHP-P9 in 1994

We compared our nutrients data with gridded data of WHP-P2 at a cross point around 30°N/137°E. WHP-P2 line was observed two times, the repeat cruise was observed in 2004 by *R/V Melville* belonged to Scripps Institution of Oceanography (SIO). WHP-P9 line was observed in 1994 by JMA. These data may have inter-cruise differences because they did not measure the RMNS in their cruise. Summary of compared these data profiles shown in Figure C.4.24 - C.4.26.
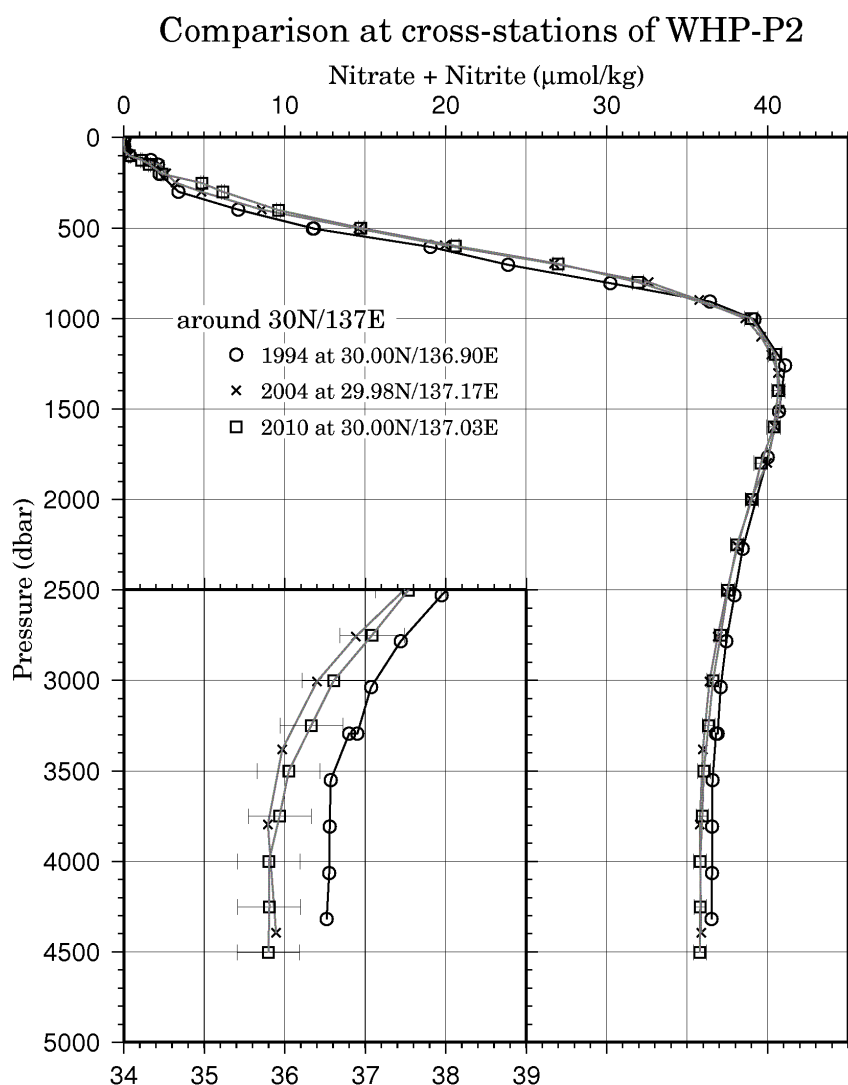
Figure C.4.24. Comparison of nitrate + nitrite profiles at cross-station of WHP-P2. Circle, plus, square show the WHP-P9 in 1994 by JMA, WHP-P2 in 2004 by SIO and WHP-P9 revisit in 2010 by JMA, respectively.
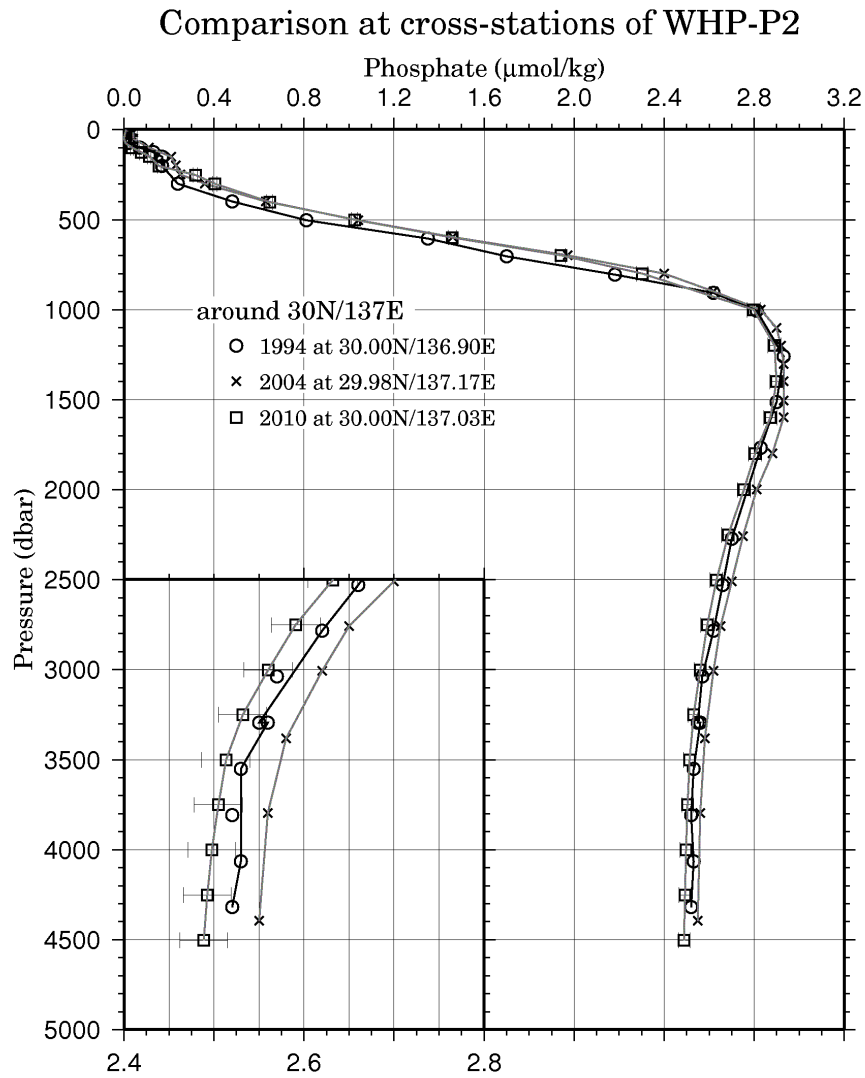
Figure C.4.25. Comparison of phosphate profiles at cross-station of WHP-P2. Circle, plus, square show the WHP-P9 in 1994 by JMA, WHP-P2 in 2004 by SIO and WHP-P9 revisit in 2010 by JMA, respectively.
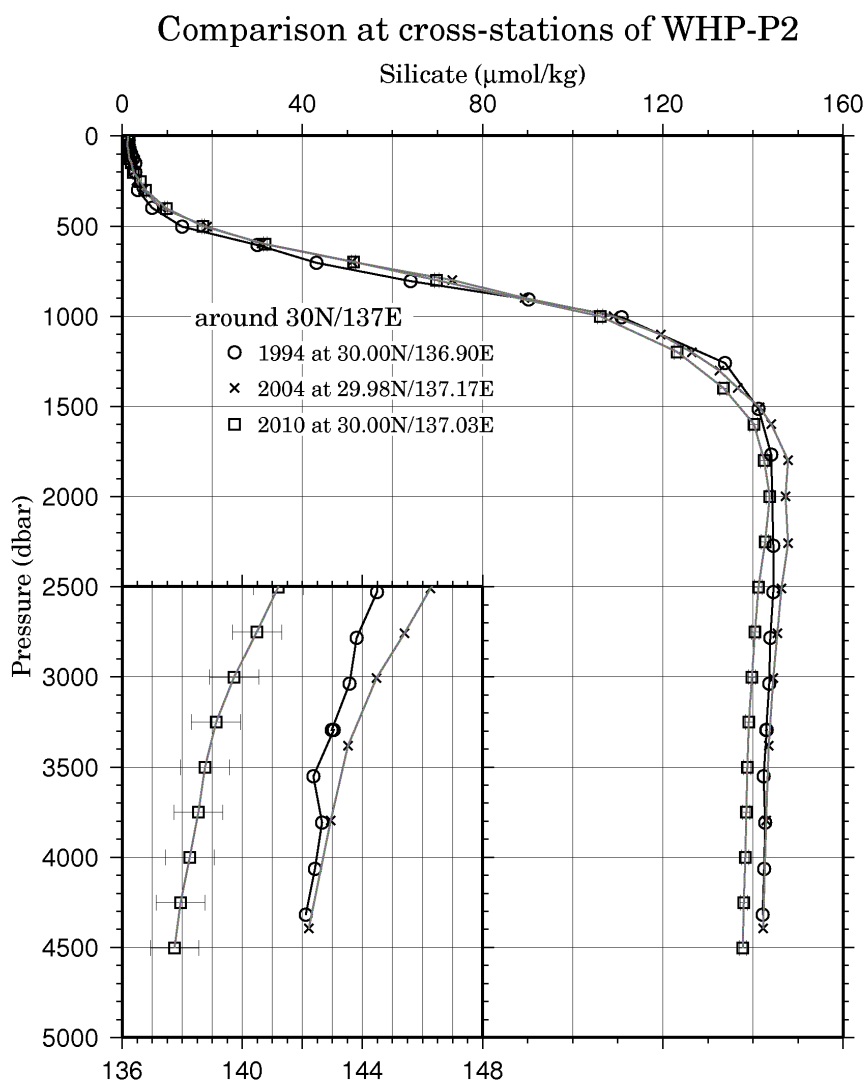
Figure C.4.26. Comparison of silicate profiles at cross-station of WHP-P2. Circle, plus, square show the WHP-P9 in 1994 by JMA, WHP-P2 in 2004 by SIO and WHP-P9 revisit in 2010 by JMA, respectively.

(9.3) Comparison at cross-stations of WHP-P3 section in 1985, 2005/06 and WHP-P9 in 1994

We compared our nutrients data with gridded data of WHP-P3 at a cross point around 24°N/137°E. WHP-P3 line was observed two times, the first was observed in 1985 by *R/V Thomas G. Thompson* belonged to SIO and the repeat cruise was observed in 2005/06 by *R/V Mirai* belonged to Japan Agency for Marine-Earth Science and Technology (JAMSTEC, 2007). WHP-P9 line was observed in 1994 by JMA. Our nutrients data at P9 revisit and JAMSTEC data in 2005/06 are comparable directly through the RMNS. However, SIO data in 1985 and JMA data in 1994 may have inter-cruise differences because they did not measure the RMNS in their cruise. Summary of compared these data profiles shown in Figure C.4.27 - C.4.29.

Note: Silicate data of WHP-P3 revisit (JAMSTEC, 2007) is corrected by a scale factor provided by M. Aoyama, PI of nutrients of the cruise (personal communication).

Comparison at cross-stations of WHP-P3
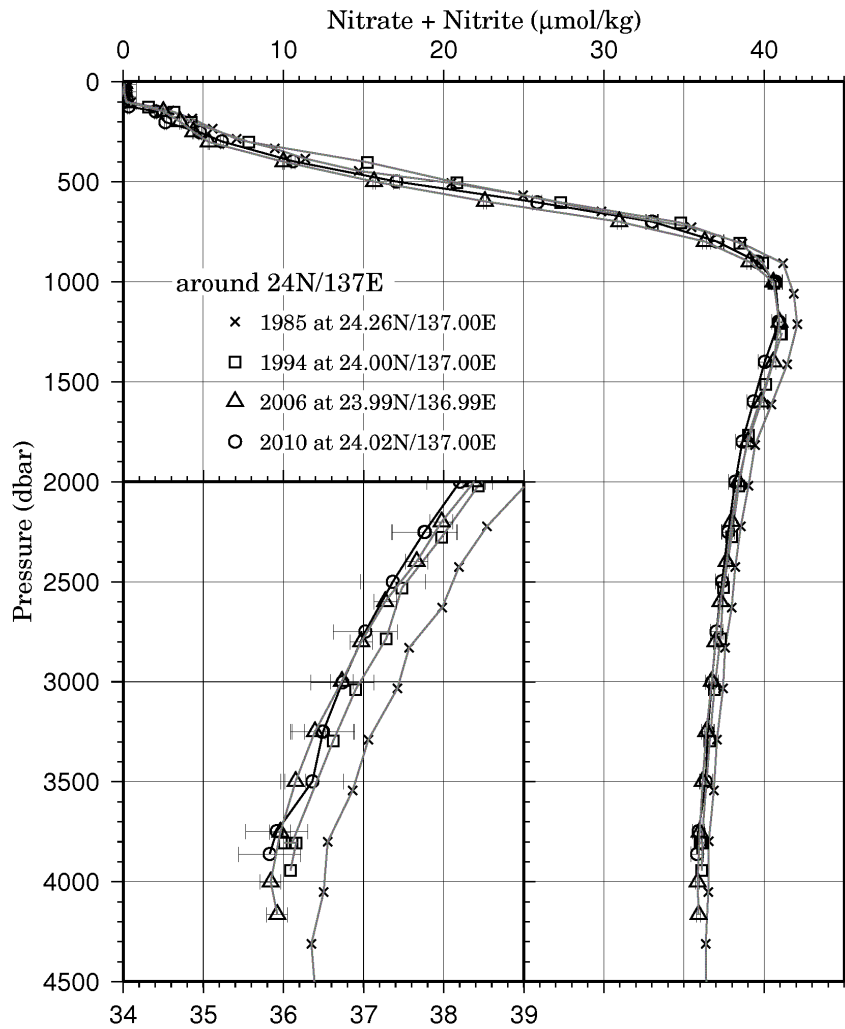
Figure C.4.27. Comparison of nitrate + nitrite profiles at cross-station of WHP-P3. Plus, square, triangle, circle show the WHP-P3 in 1985 by SIO, WHP-P9 in 1994 by JMA, WHP-P3 in 2005/06 by JAMSTEC and WHP-P9 revisit in 2010 by JMA, respectively.
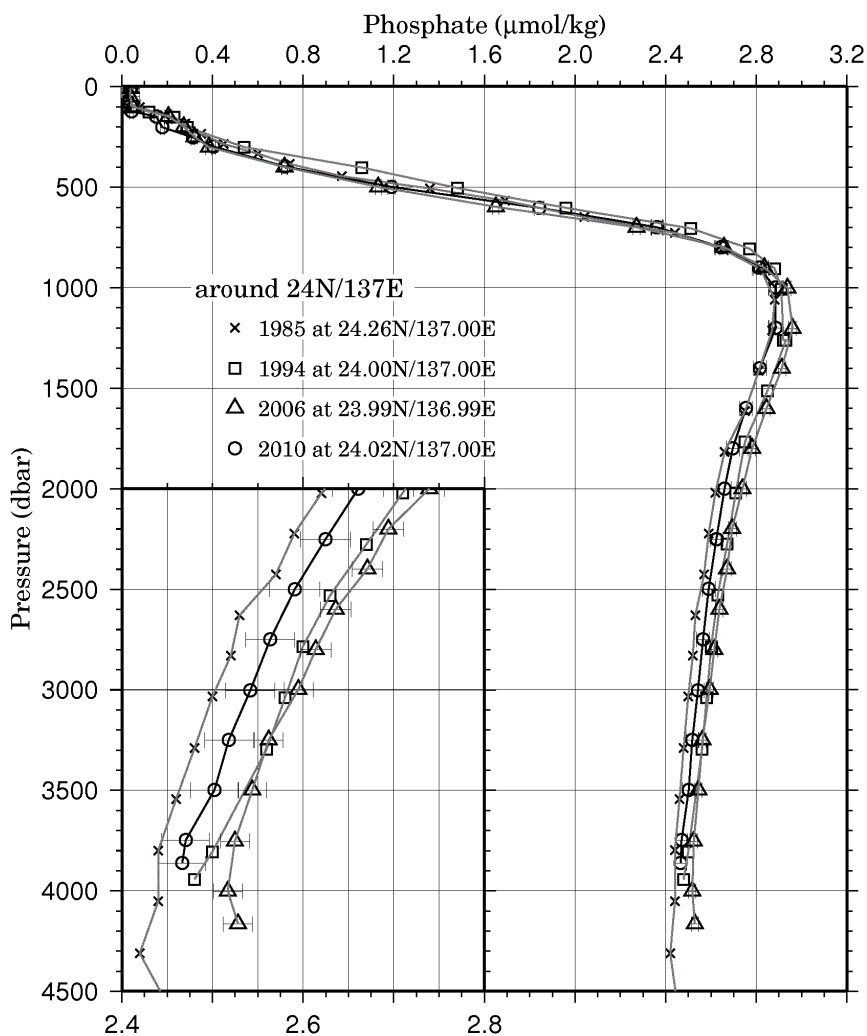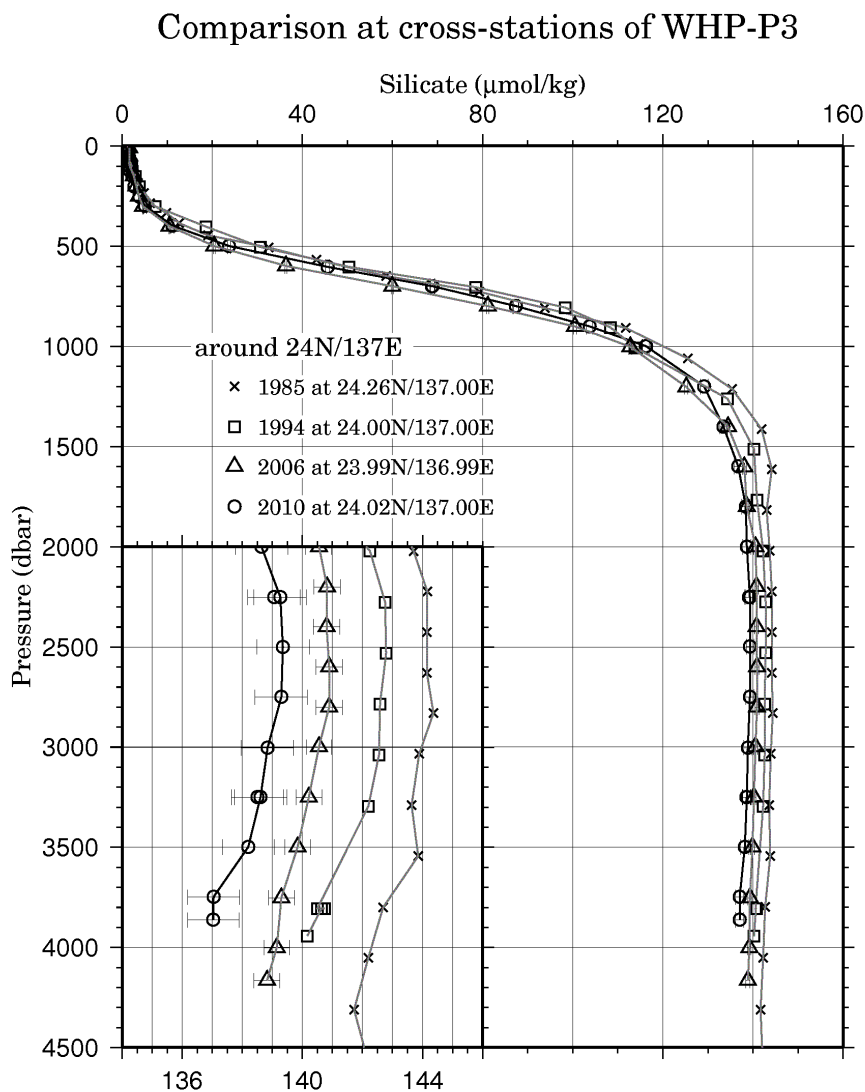
Comparison at cross-stations of WHP-P3

Figure C.4.28. Comparison of phosphate profiles at cross-station of WHP-P3. Plus, square, triangle, circle show the WHP-P3 in 1985 by SIO, WHP-P9 in 1994 by JMA, WHP-P3 in 2005/06 by JAMSTEC and WHP-P9 revisit in 2010 by JMA, respectively.

Comparison at cross-stations of WHP-P3

Silicate (μmol/kg)

Figure C.4.29. Comparison of silicate profiles at cross-station of WHP-P3. Plus, square, triangle, circle show the WHP-P3 in 1985 by SIO, WHP-P9 in 1994 by JMA, WHP-P3 in 2005/06 by JAMSTEC and WHP-P9 revisit in 2010 by JMA, respectively. Data of WHP-P3 revisit (JAMSTEC, 2007) is corrected by a scale factor provided by M. Aoyama, PI of nutrients of the cruise (personal communication).

(9.4) Comparison at cross-stations of WHP-P4 section in 1989, and WHP-P9 in 1994

We compared our nutrients data with gridded data of WHP-P4 at cross point around 9°N/137°E. WHP-P4 line was observed in 1989 by *R/V Moan Wave* belonged to University of Hawaii (UH). WHP-P9 line was observed 1994 by JMA. These data may have inter-cruise differences because they did not measure the RMNS in their cruise. Summary of compared these data profiles shown in Figure C.4.30 - C.4.32.
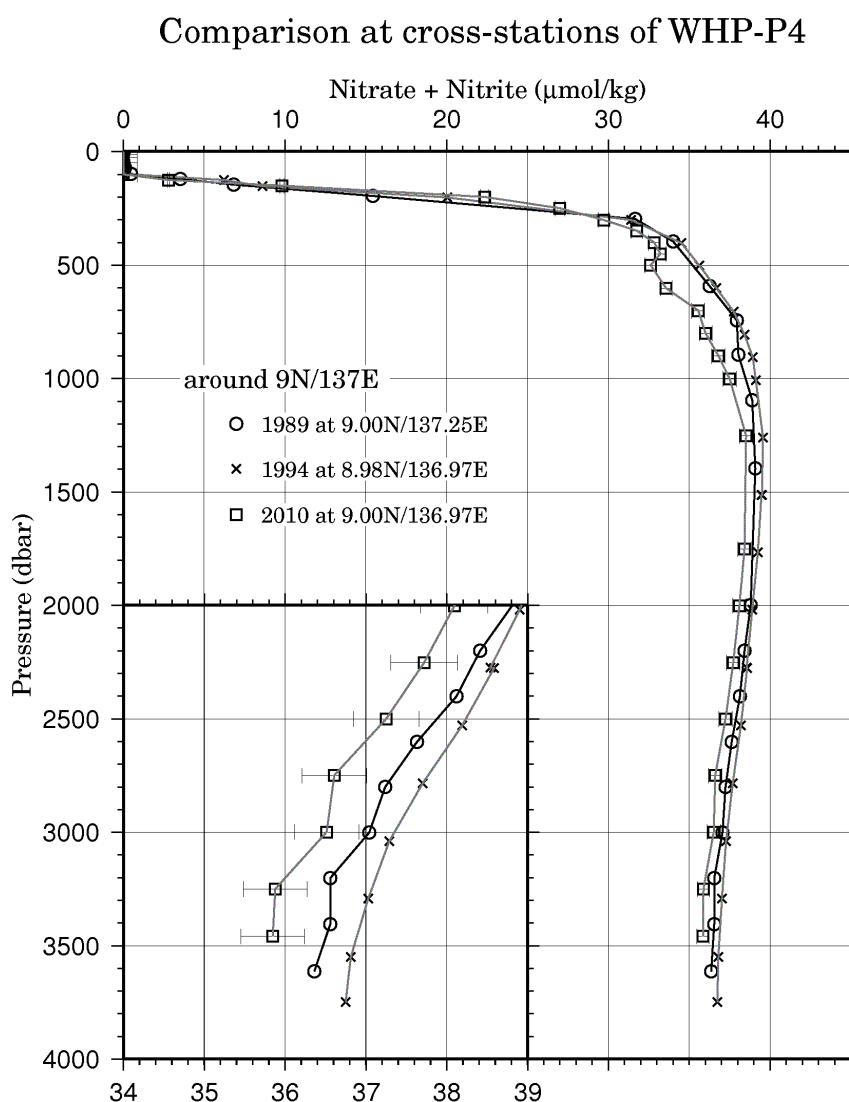

Figure C.4.30. Comparison of nitrate + nitrite profiles at cross-station of WHP-P4. Circle, plus, square show the WHP-P4 in 1989 by UH, WHP-P9 in 1994 by JMA and WHP-P9 revisit in 2010 by JMA, respectively.

Comparison at cross-stations of WHP-P4

Phosphate (μmol/kg)

around 9N/137E

○ 1989 at 9.00N/137.25E

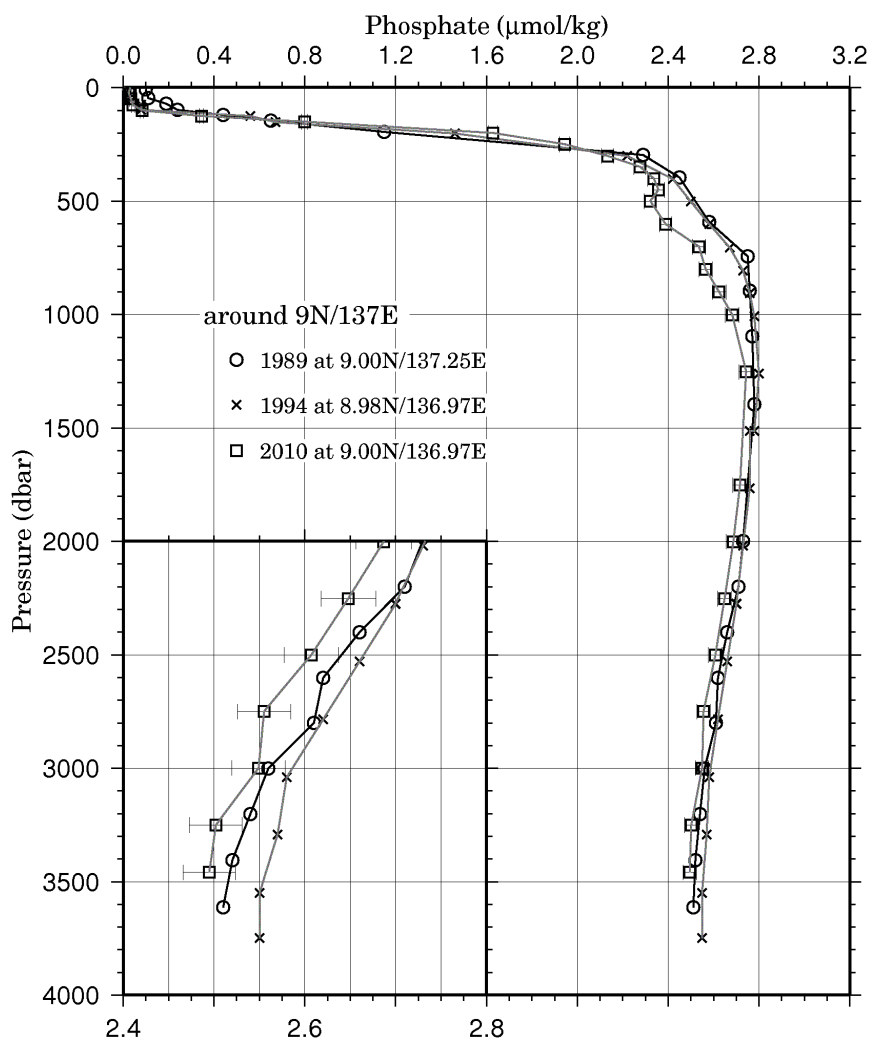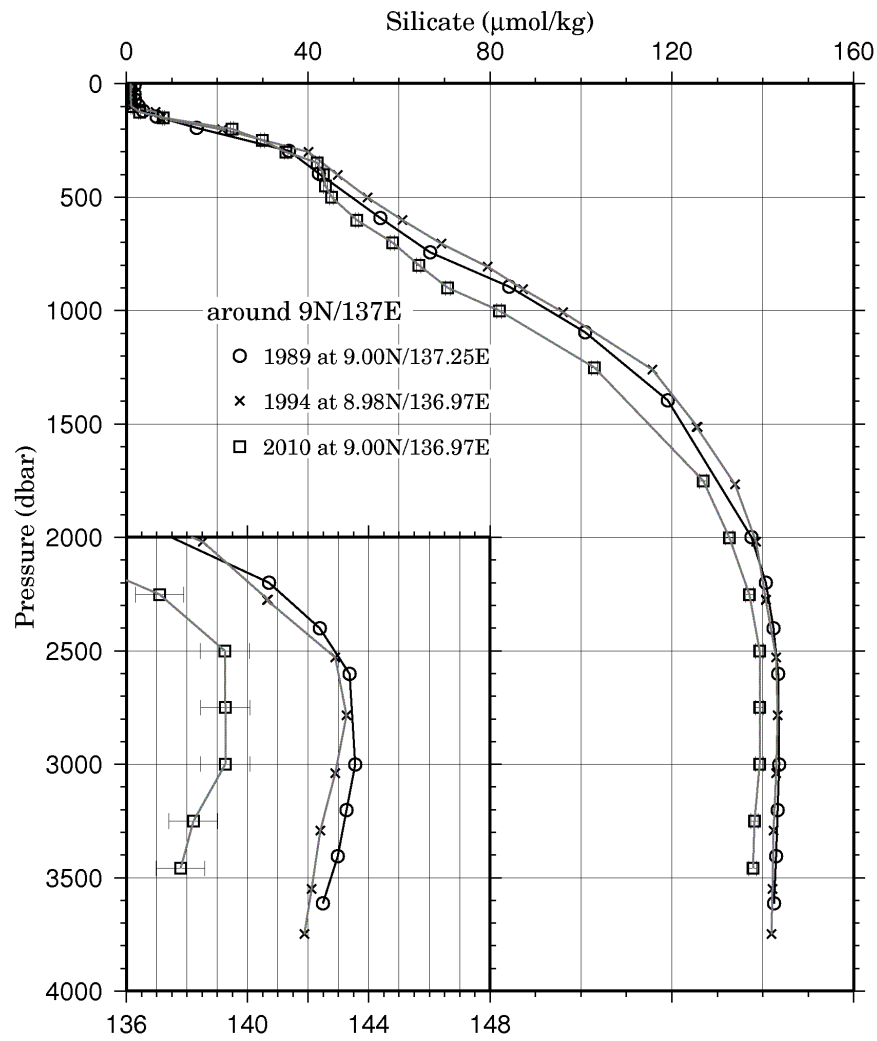× 1994 at 8.98N/136.97E

□ 2010 at 9.00N/136.97E

Figure C.4.31. Comparison of phosphate profiles at cross-station of WHP-P4. Circle, plus, square show the WHP-P4 in 1989 by UH, WHP-P9 in 1994 by JMA and WHP-P9 revisit in 2010 by JMA, respectively.

Comparison at cross-stations of WHP-P4

Silicate (μmol/kg)

Figure C.4.32. Comparison of silicate profiles at cross-station of WHP-P4. Circle, plus, square show the WHP-P4 in 1989 by UH, WHP-P9 in 1994 by JMA and WHP-P9 revisit in 2010 by JMA, respectively.

(10) Update of silicate data

May 27, 2018

For the silicate standard, we used "Silicon standard solution traceable to SRM from NIST SiO2 in NaOH 0.5 mol/l 1000 mg/L Si CertiPUR" provided by Merck with lot number HC814662. The silicate concentration is certified by NIST-SRM3150 as 999 mg/L with the expanded uncertainty of ± 5 mg/L (k=2). However, based on comparison with the solutions of lot HC074650 used in following cruise RF10-07, we assigned correction factor for the lot HC814662 as 0.975 to ensure internal comparability among our cruises in the future. This correction factor between the lots of HC814662 and HC074650 is consistent with that assigned by JAMSTEC (Uchida et al., 2015). Therefore, we updated silicate data to be multiplied by the factor 0.975.

References

Aoyama, M., S. Becker, K. Sato and D. Schuller (2009), Plan of use of RMNS during the CLIVAR P6 revisited cruise by R/V Melville. (unpublished manuscript).

Aoyama, M., A. G. Dickson, D. J. Hydes, A. Murata, J. R. Oh, P. Roose and E. Malcom. S. Woodward (2010), Comparability of nutrients in the world's ocean, *INSS international workshop 10-12 Feb. 2009, Paris*

Armstrong, F. A. J., C. R. Stearns and J. D. H. Strickland (1967), The measurement of upwelling and subsequent biological processes by means of the Technicon TM Autoanalyzer TM and associated equipment, *Deep-Sea Res., 14(3), 381–389.*

Grasshoff, K., Ehrhardt, M., Kremling K. et al. (1983), Methods of seawater analysis. 2nd rev, *Weinheim: Verlag Chemie, Germany, West.*

JAMSTEC (2007), WHP P3 REVISIT DATA BOOK, WHP P03 REVISIT in 2005.

Murphy, J., and Riley, J.P. (1962), Analytica chimica *Acta 27, 31-36.*

Uchida, H., K. Katsumata, and T. Doi (2015): WHP P14S, S04I REVISIT IN 2012 DATA BOOK (http://www.godac.jamstec.go.jp/catalog/data/doc_catalog/media/ 2012_WHP_P14S_S04I_all.pdf).

5. Total Dissolved Inorganic Carbon (DIC) and Total Alkalinity (TA)

13 December 2013

(1) Personnel

Shinji MASUDA (GEMD/JMA)

Kazutaka ENYO (GEMD/JMA)

Naohiro KOSUGI (MRI/JMA)

(2) Overview

The concentration of total dissolved inorganic carbon (DIC) and total alkalinity (TA) were determined simultaneously from a single bottle of seawater sample by using two sets of custom-made DIC/TA analyzer manufactured by Nippon ANS Co. Ltd. (apparatus-A and apparatus-B). DIC was determined by coulometric analysis (*Johnson et al.*, 1985, 1987) using an automated CO_2 extraction unit and a coulometer (2009 model, Nippon ANS Co. Ltd.). TA was determined by one-step volumetric addition of hydrochloric acid (HCl) followed by the spectrophotometric analysis of pH with the sulfonephthalein indicator dye bromocresol green (*Breland and Byrne*, 1993) using an automated titration system equipped with CCD image sensor spectrophotometers (Hamamatsu, TA-CCD-A).

At each station, the precision of analysis was monitored using the Certified Reference Material (CRM) for DIC and TA (batches 93, 99 and 101) supplied by Dr. Andrew G. Dickson in Scripps Institution of Oceanography and a non-certified working reference material we have prepared from a surface seawater taken in the western North Pacific. A reference gas of 1.5% CO_2 in air (Japan Fine Products) was also routinely measured to monitor the integrity of the coulometric cell assembly. However, it was found after the cruise that the elevated pressure in the head-space of coulometric cathode cell due to the insufficient venting capacity for carrier N_2 stream had been making the DIC measurements less precise. It was also found that its effect was in part empirically corrected for by using the data of ambient pressure. We therefore standardized the DIC measurements with the analytical results of CRMs after pressure corrections and their certified DIC concentrations. Concentration of hydrochloric acid (HCl) in the titrant for TA

analysis was also monitored by the analytical result of CRMs and their certified TA values. The overall precision of measurements as estimated from the replicate measurements of CRMs during the course of cruise were 3.2 μmol kg^{-1} for DIC and 1.4 μmol kg^{-1} for TA.

(3) Samplings

Measurements of DIC and TA in the full water column were made at a total of 53 stations (Leg 1: 31, Leg 2: 22) (Figure C.5.1). Intervals of sampling stations are 1° in latitude in open ocean zone and 15' to 40' in offshore regions near Japan and near Papua New Guinea.
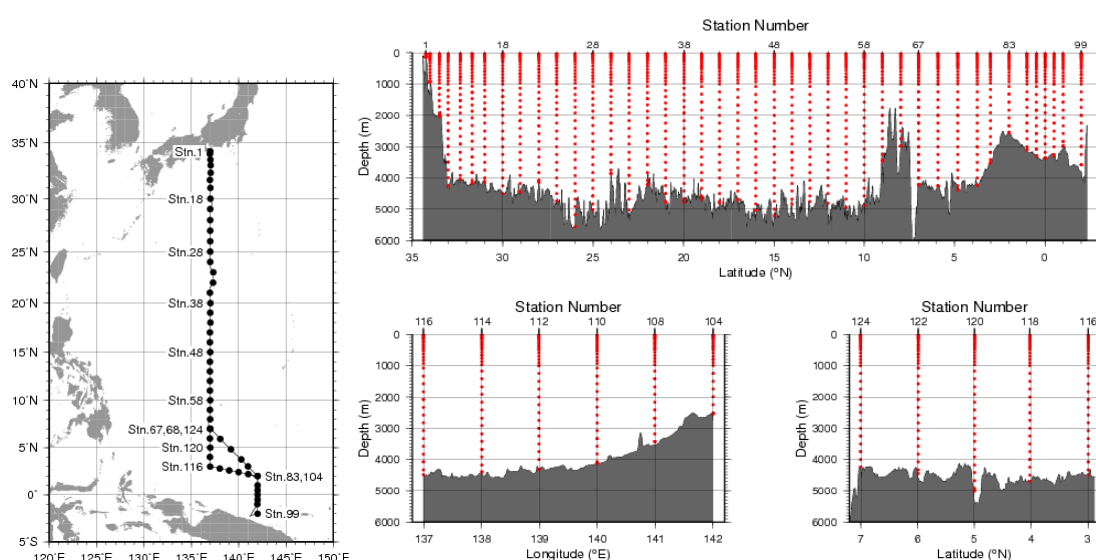

Figure C.5.1. Station locations (left panel) and sampling layers of DIC and TA (middle and right panels)

Samples for the measurements of DIC and TA were drawn according to the procedures outlined by *Dickson et al.* (2007) from 10-L Niskin bottles into clean 300 cm^3 Schott Duran® borosilicate glass bottles using silicone tubing. To minimize CO_2 exchange with the ambient air, samples for DIC/TA were drawn next to those for CFCs and dissolved oxygen. Samples of near-surface seawater were collected from the underway seawater supply from the sea-chest (approx. 5 m).

Total of 176 pairs of replicate samples from the same Niskin bottle and total of 152 pairs of duplicate samples from different Niskin bottles tripped at the same depth were drawn for quality assurance of measurements.

Schott Duran® glass bottles were filled smoothly from the bottom after overflowing double a volume while taking care of not entraining any bubbles.

After creating 2 cm³ of headspace by removing sample to allow thermal expansion, the sample bottles were sealed with ground glass stoppers lubricated with Apiezon® grease (L). Until Stn.15, 0.2 cm³ of saturated mercury (II) chloride solution was added to the samples as a preservative. After Stn.18, no mercury (II) chloride was added and measurements of DIC and TA were started immediately after samplings. Samples were immersed in a thermo stated water bath (25.0 °C) for approx. 1 hour prior to analysis.

All the samples with the preservative were corrected to compensate dilution multiplied by 0.2/300 cm³/cm³ as a dilution factor to each concentration.

(4) Dissolved Inorganic Carbon (DIC)

(4-1) Instrumentation and procedures

The unit for DIC measurement in the coupled DIC/TA analyzer consists of a coulometer with a quartz coulometric titration cell (8 cm outer diameter), a CO_2 extraction unit and a reference gas injection unit. The CO_2 extraction unit includes a sample pipette (approx. 15 cm³) and a CO_2 extraction chamber that is connected to a bottle of 10% v/v phosphoric acid and a carrier N_2 gas supply, two thermoelectric cooling units and so on. The coulometric titration cell and the sample pipette are water-jacketed and are connected to a thermo stated (25 °C) water bath. The automated procedures of DIC analysis in seawater were as follows:

(a) Approximately 2 cm³ of 10% v/v phosphoric acid was injected to an "extraction chamber", i.e., a glass tube (approx. 20 mm outer diameter. and 20 cm in length) with a course glass frit placed near the bottom. Purified N_2 (Japan Fine Products, G1 grade >99.99995%) was then allowed to flow through the extraction chamber for 2 minutes to purge CO_2 and other volatile acids dissolved in the phosphoric acid.

(b) A portion of sample seawater was delivered from the sample bottle into the sample pipette of CO_2 extraction unit by pressurizing the headspace in the sample bottle. After temperature of the pipette was recorded, the sample seawater was transferred into the extraction chamber and mixed with phosphoric acid to convert all carbonate species to CO_2 (aq).

(c) The acidified sample seawater was then stripped of CO_2 with a stream of purified N_2 (130 cm^3 min^{-1}) for 10 minutes. After being dehumidified in a series of two thermoelectric cooling unit (2 °C), the evolved CO_2 in the N_2 stream was introduced into the carbon cathode solution (UIC Inc.) in the coulometric titration cell where it reacts rapidly and quantitatively with 2-aminoethanol to form N-(2-hydroxyethyl)carbamic acid. This strong acid is immediately titrated with hydroxide ion (OH$^-$) generated by the electrolysis of water on Pt electrode in the cathode.

Total amount of CO_2 evolved from the acidified sample seawater is thus measured by integrating the total charge required to generate OH$^-$ to neutralize the N-(2-hydroxyethyl)-carbamic acid. The end-point of titration is determined spectrophotometrically with the indicator dye thymolphthalein as the point of 30.0% transmittance of light at approx. 610 nm.

The entire sequence takes about 13 minutes for a sample. Once every 6 samples, additional 5 minutes are allowed for titration to evaluate the "background count level" of the coulometer.

Cathode and anode solutions of the coulometer were renewed at the beginning of DIC measurements at each station. After conditioning of the solutions, the amount of CO_2 in 1.5% CO_2 in air taken in an electro polished stainless-steel flask (approx. 60 cm^3) was measured in order to monitor the integrity of the coulometric cell assembly. A bottle of CRM (batches 93, 99 and 101) was measured at each run of solutions. A working reference material (SSW-P) prepared from western North Pacific surface water was also measured at the beginning, in the middle, and at the end of measurements at a station.

(4-2) Calculation of DIC

Concentration of DIC (C_T) in moles per kilogram of seawater (mol kg^{-1}) was calculated from equation (1):

$$C_T = N_S / (c \cdot V_S \cdot \rho_S),\tag{1}$$

where N_S is the net counts of coulometer, c is the coulometer calibration factor, *i.e.*, the counts of coulometer per mole of carbon, V_S is the sample volume (volume of pipette), and ρ_S is the

density of seawater that is calculated from the salinity of sample and its temperature in the pipette.

Net counts of coulometer, N_S, is the counts for sample at 10 minutes after starting CO_2 extraction/titration (N_{10}) subtracted by background count level N_B per 10 minute, $i.e.,$

$$N_S = N_{10} - N_B. \tag{2}$$

Background count levels were measured once every six sample measurements. We evaluated this using equation (3) from the increase of coulometer count from 10 minutes (N_{10}) to 15 minutes (N_{15}) after starting CO_2 extraction/titration when CO_2 in sample seawater is expected to have been completely evolved.

$$N_B = (N_{15} - N_{10}) \cdot 10 / (15 - 10) \tag{3}$$

In this cruise, N_B values were averaged for measurements in each run of coulometric cathode and anode solutions.

A problem in DIC measurement in this cruise was that the coulometer counts for 1.5% CO_2 in air, CRM and the working reference material were not as stable as we have expected before the cruise. For example, in the laboratory on land, coefficient of variation (C.V.) for N_S of SSW measurements was usually less than 0.08% after N_S was corrected for the changes in the density of SSW, but was 0.17% (411.46 ± 0.69 µgC; $N = 48$) for apparatus A and 0.19% (411.78 ± 0.78 µgC; $N = 66$) for apparatus B. After the cruise, it was found that the headspace in the cathode cell have been pressurized by the stream of N_2 due to its insufficient venting capacity, and this had been making the coulometer count less stable. It was also found that the change in the coulometer count due to the headspace-pressurizing can be in part empirically corrected for by the change in the ambient pressure (P) as:

$$N_S' = N_S / \{1 - 0.5 \cdot (1 - P/1013.25\text{hPa})\} \tag{4}$$

We used the value of N_S', instead of N_S, for the calculation of DIC concentration using equation (1). The decreasing trend of N_S was decreased by using the value N_S' (Figure C.5.2).
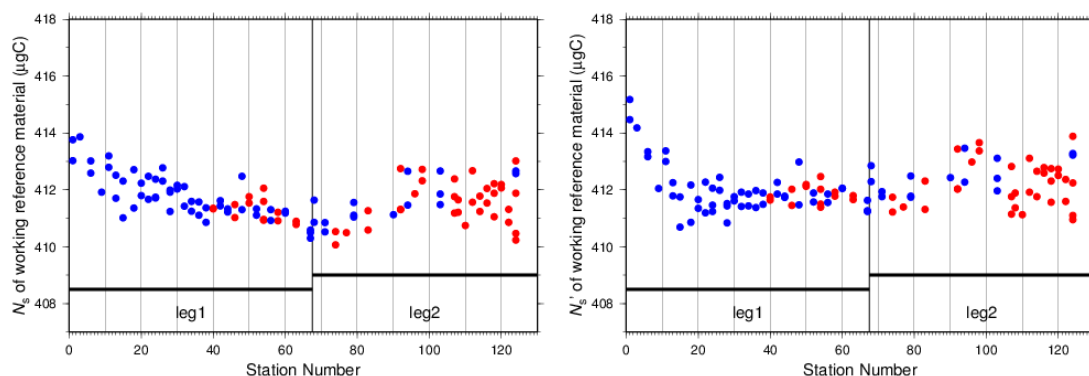
Figure C.5.2. Coulometer counts N_S for SSW (left panel) and the counts corrected for the changes in ambient pressure, N_S' (right panel). The colour of plots denotes the apparatus-A (red) and apparatus-B (blue), respectively.

(4-3) Results of DIC measurements of CRM

The value of $c \cdot V$s was determined for each DIC measurement of CRM (Batch 93, 99 and 101) from equation (5):

$$c \cdot Vs = N_S' / (C_{T, CRM} \cdot \rho_{25}), \tag{5}$$

where $C_{T, CRM}$ denotes the certified DIC concentration of CRM. The results are shown in Figure C.5.3. Values of $c \cdot V$s were averaged over the same leg for each apparatus, except at station 1 where measures were made using the apparatus-B, and used for the calculations of DIC in sample seawaters (Table C.5.1).

Standard deviation of the differences in the analytical DIC concentration of CRM calculated with the averaged $c \cdot V$s was ± 1.5 µmol kg^{-1} ($N = 25$) (Figure C.5.4a), and the repeatability as estimated from the absolute difference in the replicate analyses of CRM was ± 2.8 µmol kg^{-1} (Figure C.5.4b). The precision thus evaluated from the measurement of CRM was ± 3.2 ($= (1.5^2 + 2.8^2)^{1/2}$) µmol kg^{-1}.

Standard deviation of the DIC concentration of working reference material (SSW-P) was ± 3.4 µmol kg^{-1} ($N = 113$) (Figure C.5.5). It is consistent with repeatability of DIC measurements as evaluated from the measurements of the CRMs.
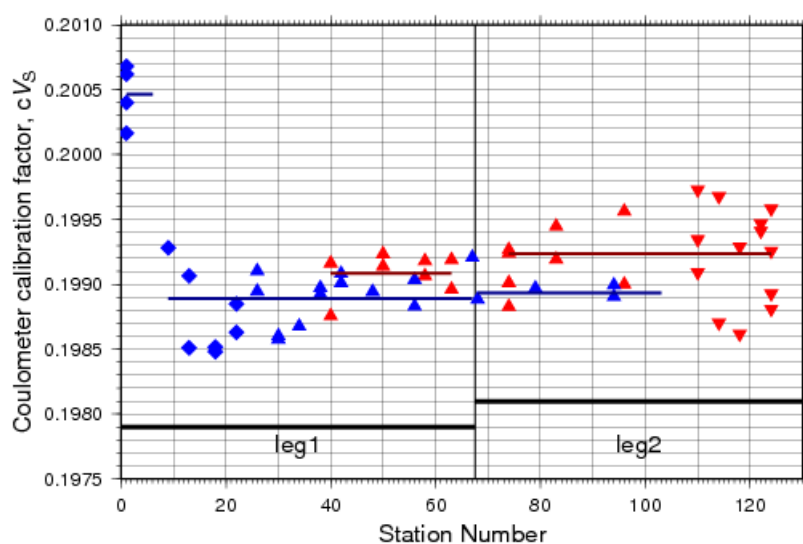
Figure C.5.3. Calibration factor $c \cdot V$s of the coulometeric systems determined from the measurements of CRM batch 93 (diamond), batch 99 (triangle) and batch 101 (inverted triangle) for apparatus A (red) and apparatus B (blue). Horizontal lines show the averages of $c \cdot V$s used for the calculation of DIC concentration in seawater samples (Table C.5.1).

Table C.5.1.   Summary of calibration factor, $c \cdot V$s.

Apparatus	Leg	Mean ± sd.
A	1	0.19909 ± 0.00010
A	2	0.19924 ± 0.00021
B	1[*1]	0.20047 ± 0.00006
B	1[*2]	0.19887 ± 0.00022
B	2	0.19894 ± 0.00005

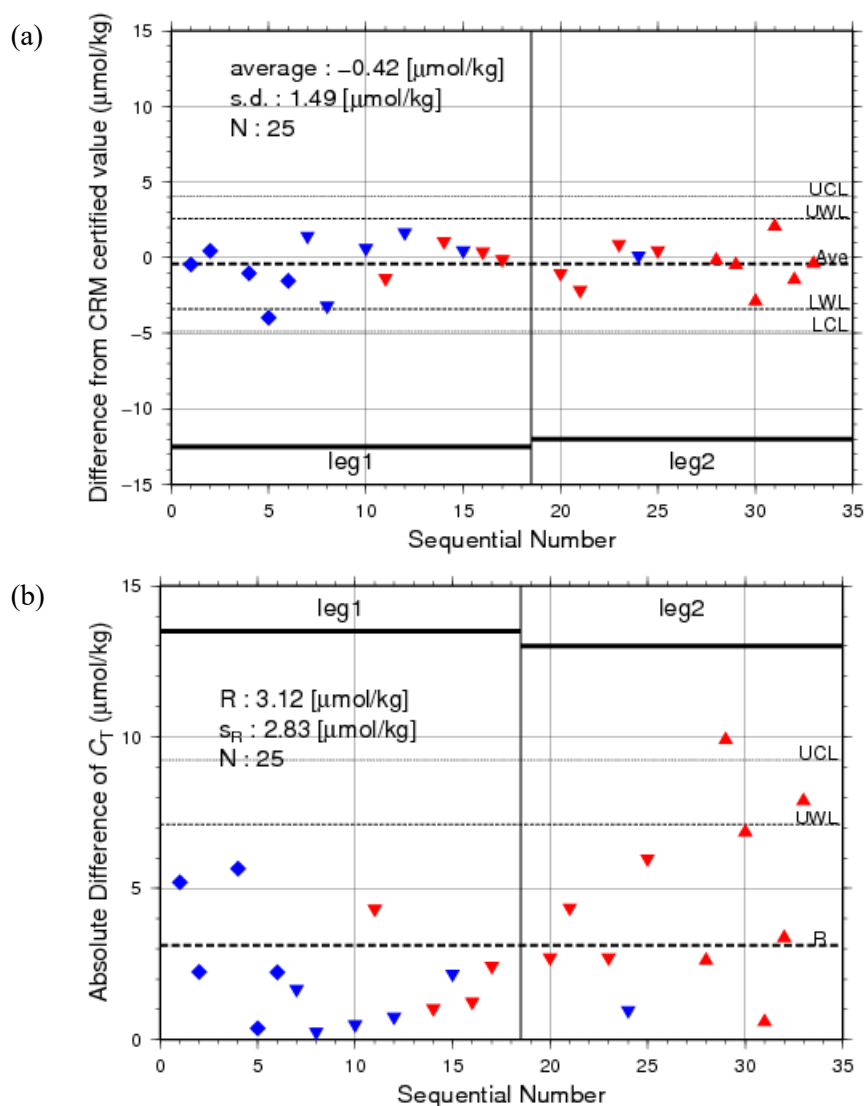[*1] For station Stn.1. [*2] For station Stn.9 and later.

Figure C.5.4. (a) Differences in the measured DIC concentration from the certified value and (b) the absolute differences in replicate DIC measurements (R-chart) of CRM batches 93 (diamond), 99 (triangle) and 101 (inverted triangle) for apparatus-A (red) and apparatus-B (blue). Control limits in (a) were defined from the average (m) and the standard deviation (sd) of the differences; UCL = m + 3 sd, UWL = m + 2 sd, LCL = m – 3 sd, and LWL = m – 2 sd. UCL and UWL in (b) were defined from mean difference (R) as 3.167 R and 2.512 R, respectively (*Dickson et al.*, 2007).
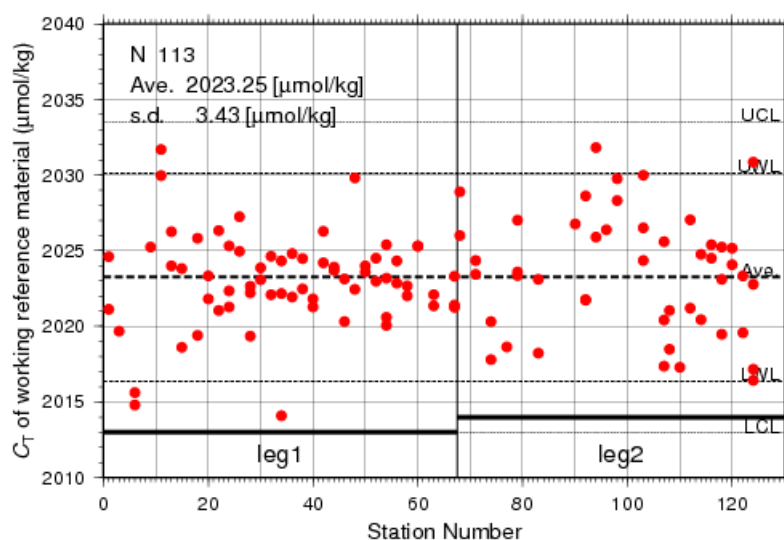
Figure C.5.5 Results of the measurements of working reference materials (SSW-P).

(5) Total Alkalinity

(5-1) Instrumentation and procedures

TA is measured by one-step volumetric addition of hydrochloric acid (HCl) to a known amount of sample seawater with prompt spectrophotometric measurement of excess acid using the sulfonephthalein indicator bromocresol green (BCG) (*Breland and Byrne*, 1993). The unit for TA measurements in the coupled DIC/TA analyzer consists of sample treatment unit (Nippon ANS) with a calibrated sample pipette and an open titration cell that are water-jacketed and connected to a thermo stated (25 °C) water bath, an auto syringe (PSD/8, Hamilton) connected to a bottle (Schott Duran®, 1 dm³) of titrant stored at 25 °C, and a double-beam spectrophotometric system with two CCD image sensor spectrometers (C10083CAH, Hamamatsu Photonics) combined with a high power Xenon lamp (HPX-2000, Ocean Optics). The mixture of 0.05N HCl and 40 µmol dm⁻³ BCG in 0.65M NaCl solution was used as titrant to automatically titrate the sample as follows:

(a) A portion of sample seawater was delivered into the sample pipette (approx. 42 cm³) after the other portion is delivered into the DIC unit for a DIC measurement. After the temperature of pipette was recorded, the sample was transferred into a cylindrical quartz cell (4 cm o. d.).

(b) An absorption spectrum of sample seawater in the visible light domain was then measured, and the absorbances at wavelengths of 444 nm, 509 nm, 616 nm and 730 nm as well as the temperature in the cell were recorded.

(c) The titrant that includes 0.05N HCl was added to the sample seawater by using the auto syringe so that pH of sample seawater becomes in the range between 3.85 and 4.05 after the next step (d).

(d) While the acidified sample was being stirred, the evolved CO_2 was purged with the stream of purified N_2 bubbled into the sample at approx. 100 cm^3 min^{-1} for 5 minutes.

(e) After leaving the bubbled acidified sample still for 1 minute, the absorbance of bromocresol green in the sample was measured in the same way as described in (b), and pH of the acidified seawater was precisely determined spectrophotometrically.

A typical titration including rinse, fill and discharge takes about 13 minutes.

The data of absorbance (A) and temperature (T) were processed to calculate the concentration of excess acid:

$$pH_T = -\log_{10}([H^+]_T/\text{mol kg-seawater}^{-1})$$

$$= 4.2699 + 0.02578 \cdot (35 - S) + \log\{(R_{25} - 0.00131)/(2.3148 - 0.1299 \cdot R_{25})\}$$

$$- \log(1 - 0.001005 \cdot S) \tag{6}$$

$$R_{25} = R_T \cdot \{1 + 0.00907 \cdot (25 - (T/{}^\circ C))\} \tag{7}$$

$$R_T = \left(A^{SA}_{616} - A^{S}_{616} - A^{SA}_{730} + A^{S}_{730}\right) / \left(A^{SA}_{444} - A^{S}_{444} - A^{SA}_{730} + A^{S}_{730}\right) \tag{8}$$

S is salinity of sample in PSS-78 that was measured separately. A^{S}_{λ} and A^{SA}_{λ} denotes absorbance of seawater and acidified seawater, respectively, at wavelength λ nm.

The concentration of excess acid $[H^+]_T$ determined is then combined with the volume of sample seawater (V_S / dm^{-3}), the volume of titrant (V_A / dm^{-3}) added to the sample, and molarity of hydrochloric acid (M_A / mol dm^{-3}) in the titrant to calculate total alkalinity (A_T) in the unit of mol kg-sewater^{-1}:

$$A_T = (-[H^+]_T \cdot (V_S + V_A) \cdot \rho_{SA} + M_A \cdot V_A) / (V_S \cdot \rho_S) \tag{9}$$

ρ_S and ρ_{SA} denotes the density of seawater sample before and after the addition of titrant, respectively. Here we assumed that ρ_{SA} is equal to ρ_S, since the density of titrant has been adjusted to that of seawater by adding sodium chloride and the volume of titrant (approx. 2.5

cm^3) is no more than approx. 6% of seawater sample.

(5-2) Volume of sample seawater, V_S

The volumes of sample seawater, V_S, *i.e.*, the volume of pipette in the TA measurement unit of DIC/TA analyzer, was calibrated gravimetrically and summarized in Table C. 5.2.

Table C.5.2 Summary of sample volumes of seawater V_S for TA measurements.

Apparatus	Leg	Volume (ml)
A	1-2	42.050
B	1	43.354
B	2	41.967

(5-3) Preparation of titrant (0.05N HCl)

76 g of sodium chloride (NaCl) (Wako Pure Chemical Industries, Ltd.) and 0.12 g of bromocresol green (BCG) (Acros Organics) were dissolved in 200 cm^3 of 0.5 mol dm^{-3} HCl solution (Wako Pure Chemical Industries, Ltd.). The solution was diluted with deionised water to a final volume of 2 dm^3 at 25 °C. The concentration of HCl, NaCl and BCG was 0.05 mol dm^{-3}, 0.65 mol dm^{-3} and 40 μmol dm^{-3}, respectively. Sodium chloride was added to make the density and the ionic strength of the solution close to those of seawater.

(5-4) Results of TA measurements of CRMs.

Measurements of TA for CRMs (batch 93, 99 and 101) were made and the apparent molarity of hydrochloric acid (M_A / mol dm^{-3}) in the titrant was determined from equation (10):

$$M_A = (A_{T,\,CRM} \cdot V_S \cdot \rho_S + [H^+]_T \cdot V_S \cdot \rho_{SA}) / V_A \qquad (10)$$

The analytical results of M_A was averaged for each bottle of titrant unless the drift of molarity was clearly seen (Figure C.5.6), and was used to calculate the TA in sample seawaters.

Standard deviation of the differences in the analytical results of TA for CRMs calculated with

the averaged M_A was ±0.8 μmol kg^{-1} (N=27) (Figure C.5.7a). The repeatability as estimated from the absolute difference in the replicate analyses of CRMs was ±1.2 μmol kg^{-1} (Figure C.5.7b). The precision thus evaluated from the measurement of CRM was ±1.4 μmol kg^{-1}. Standard deviation of TA of working reference material (SSW-P) was ±3.2 μmol kg^{-1} (N=114) (Figure C.5.8).
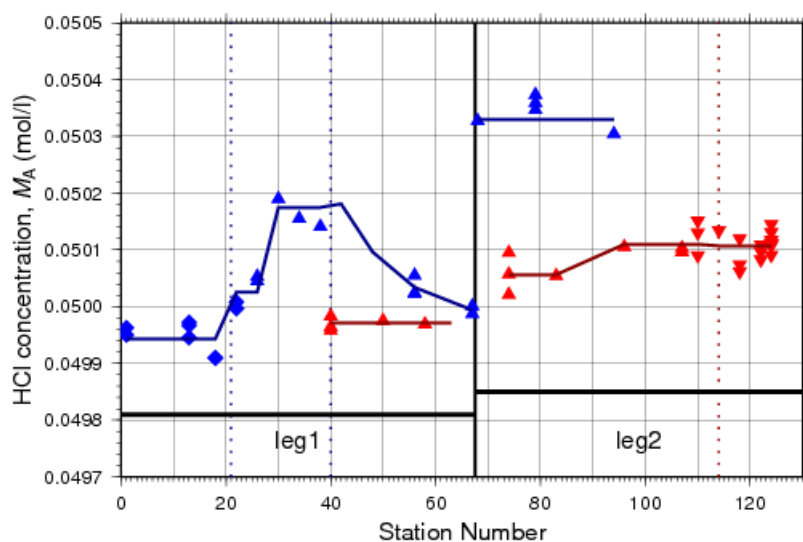

Figure C.5.6. Concentration of acid in HCl solution. The notations of the plots were same as those in Figure C.5.4. Line indicates the mean of each bottle of HCl solution. The lot of HCl solution was switched at the stations indicated as vertical dotted lines.
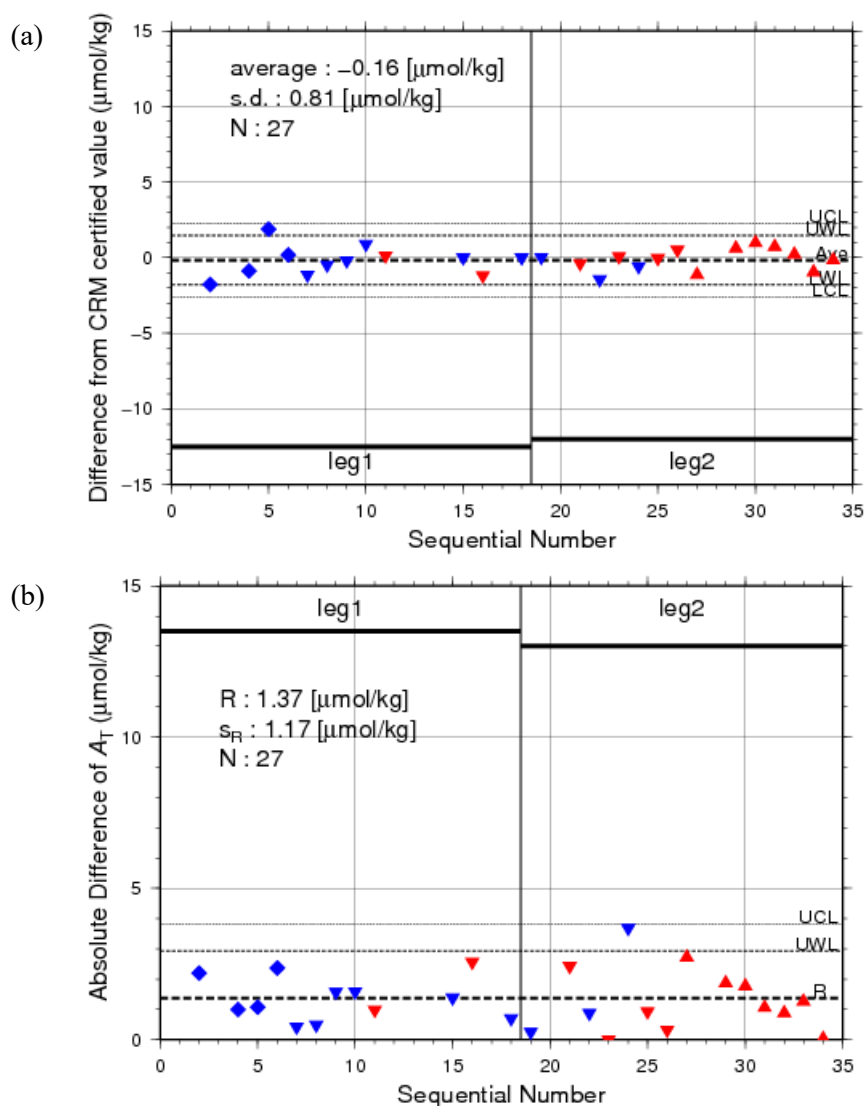
Figure C.5.7. (a) Differences in the measured TA from the certified values and (b) the absolute differences in replicate DIC measurements (R-chart) of CRM batches 93 (diamond), 99 (triangle) and 101 (inverted triangle) for apparatus-A (red) and apparatus-B (blue). Control limits and warning limits were defined in the same way as in Figure C.5.4.
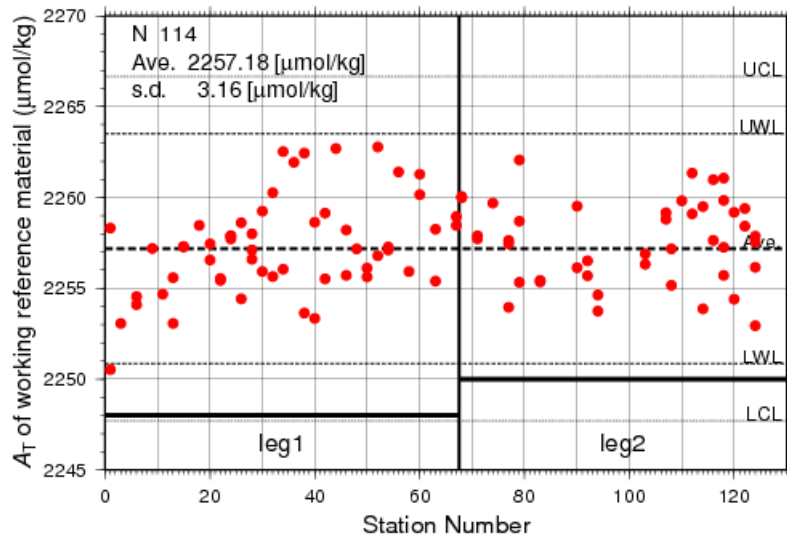
Figure C.5.8. Results of TA of working reference material (SSW-P).

(6) Assignment of quality flag

Quality code was assigned for each of DIC and TA measurements according to the WHP quality code definitions for water sample measurements (*Swift and Diggs*, 2008, *Swift*, 2010). Summary of assigned quality flags is shown in Table C.5.3. Data from replicate samples were averaged and flagged 6 if both flags have been assigned 2. If either of flags has been assigned 3 or 4, younger flag was selected.

TA data of samples collected at stations and layers listed in Table C.5.4 were assigned questionable (QF=3). A possible reason for these questionable data was insufficient rinsing of the optical titration cell after a previous measurement due to the malfunction of peristaltic pump to supply rinsing water to the cell.

Table C.5.3. Summary of assigned quality flags.

Flag	Definition	DIC	TA
2	Good	1874	1824
3	Questionable	118	155
4	Bad (Faulty)	20	36
5	Not reported	3	0
6	Replicate measurements	144[*]	152[*]
	Total number of samples	2015[*]	2015[*]

*Samples of flag 6 are counted as flag 2.

Table C.5.4. Questionable measurements of TA.

Station	Depth
Stn.9	Deeper than or equal to 500 m
Stn.11	Shallower than or equal to 1130 m
Stn.26	Deeper than or equal to 1330 m
Stn.28	Shallower than or equal to 100 m
Stn.40	Shallower than or equal to 730 m

(7) Results of replicate and duplicate sample measurements

Total of 176 pairs of replicate samples, drawn from a same Niskin bottle, were collected at every stations for DIC and TA measurements. The average of difference in acceptable pairs of measurements was 1.8 μmol kg^{-1} for DIC (N=144) and 1.9 μmol kg^{-1} for TA (N=152).   Total of 152 pairs of duplicate samples, drawn from a different Niskin bottle tripped at the same depth, were also collected at every stations for DIC and TA measurements. The average of difference in acceptable pairs of measurements was 2.0 μmol kg^{-1} for DIC (N=137) and 1.7 μmol kg^{-1} for TA (N=133).

Summary of replicates are shown in Figures C.5.9 and C.5.10 and in Table C.5.5. Summary of duplicates are shown in Table C.5.6. The average and standard deviation were calculated using

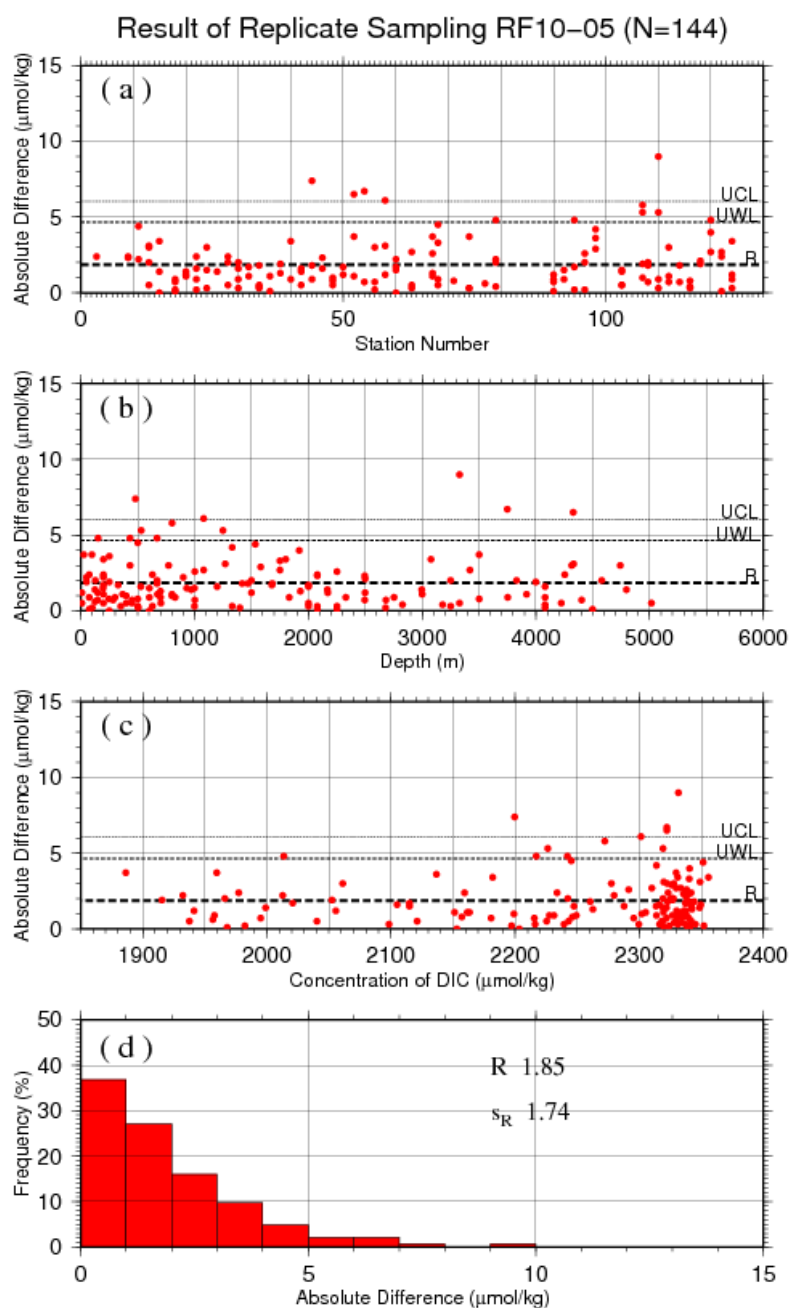a procedure described in SOP23 in *Dickson et al.* (2007).

Figure C.5.9. Absolute differences in DIC between measurements of replicate samples (*N*=144) during the cruise RF10-05 against (a) station number, (b) sampling depth, and (c) concentration of DIC. The histogram of absolute difference is shown in (d).
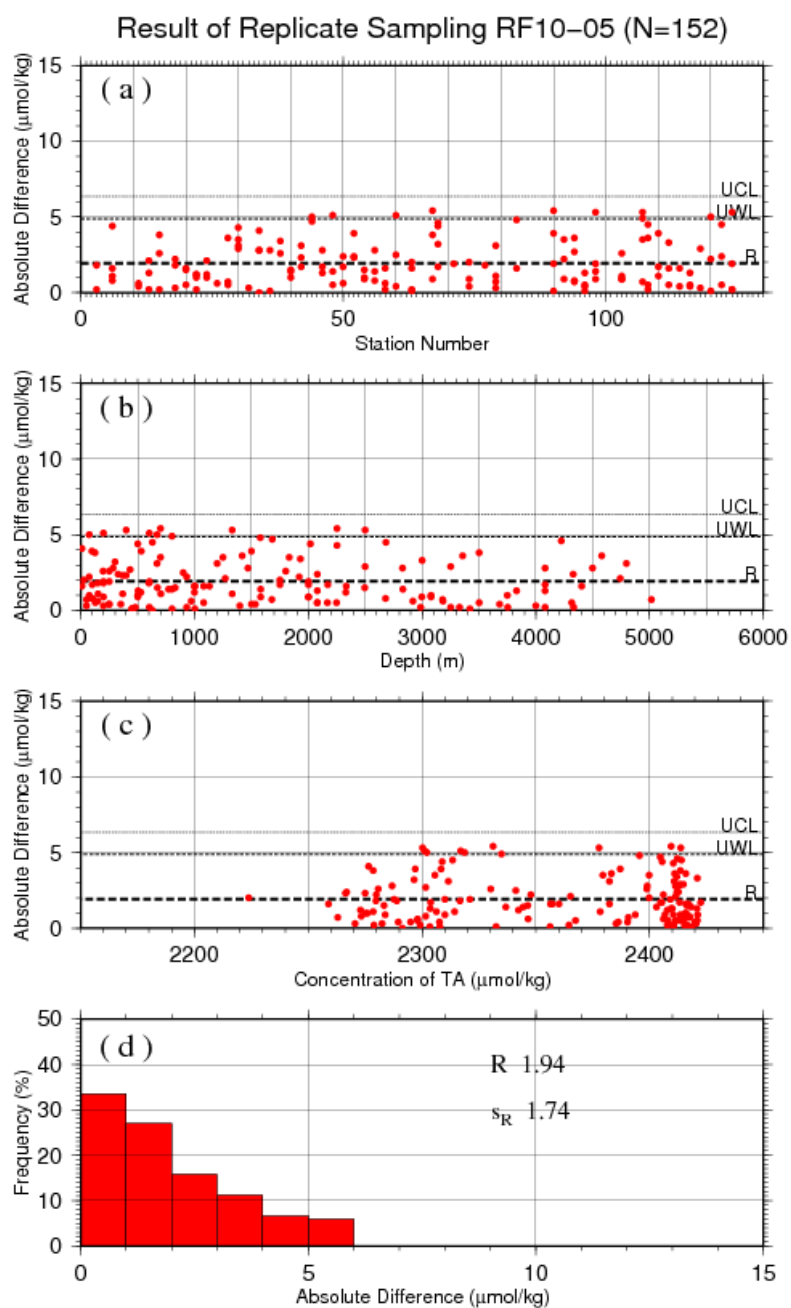
Figure C.5.10. Same as Figure C.5.9 but for TA.

Table C.5.5 Summary for the measurements of replicate samples.

	DIC (μmol/kg)	TA (μmol/kg)
Total number of good measurement pairs	144	152
Average of absolute difference	1.8	1.9
Standard deviation of measurements	1.7	1.7

Table C.5.6. Summary for the measurements of duplicate samples.

	DIC (μmol/kg)	TA (μmol/kg)
Total number of good measurement pairs	137	133
Average of absolute difference	2.0	1.7
Standard deviation of duplicate sampling	1.7	1.6

(8) Comparisons at cross-over stations within this cruise

There were two cross-over stations that were occupied multiple times within this cruise. The one was located at 7˚N, 137˚E. This station was occupied three times; station 67 (RF3715) on July 23, station 68 (RF3716) on August 2, and station 124 (RF3772) on August 16. The other was located at 2˚N, 142˚E. This station was occupied twice; station 83 (RF3731) on August 6 and station 104 (RF3755) on August 11. Vertical profiles of DIC and TA at these stations are shown in Figures C.5.11 and C.5.12.
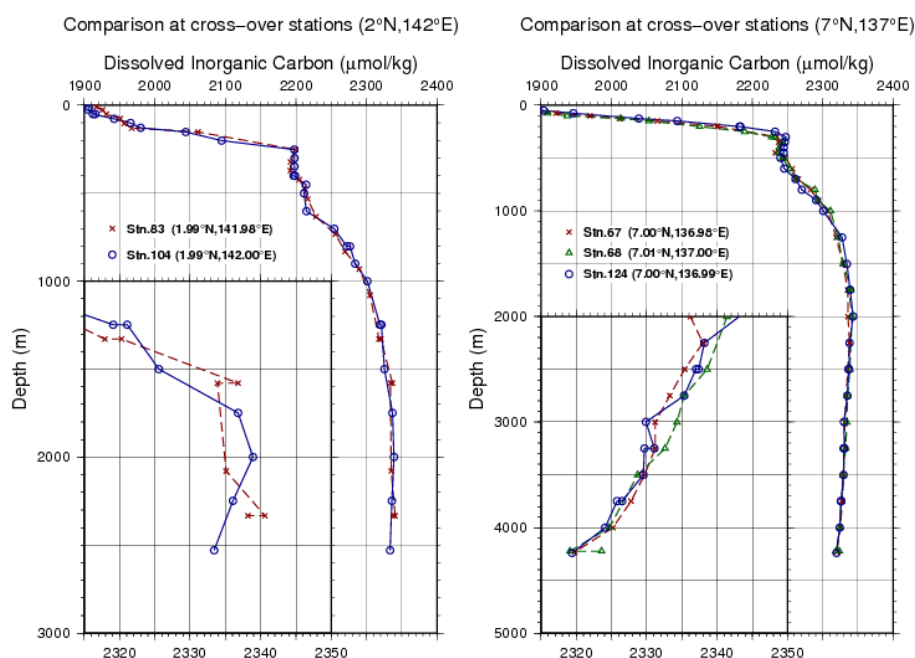

Figure C.5.11. Vertical profiles of DIC at the cross-over stations at 2˚N, 142˚E (left panel: station 83 on August 6 (cross) and station 104 on August 11 (circle)) and at 7˚N, 137˚E (right panel: station 67 (cross) on July 23, station 68 (triangle) on August 2, and station 124 (RF3772) on August 16 (circle)).
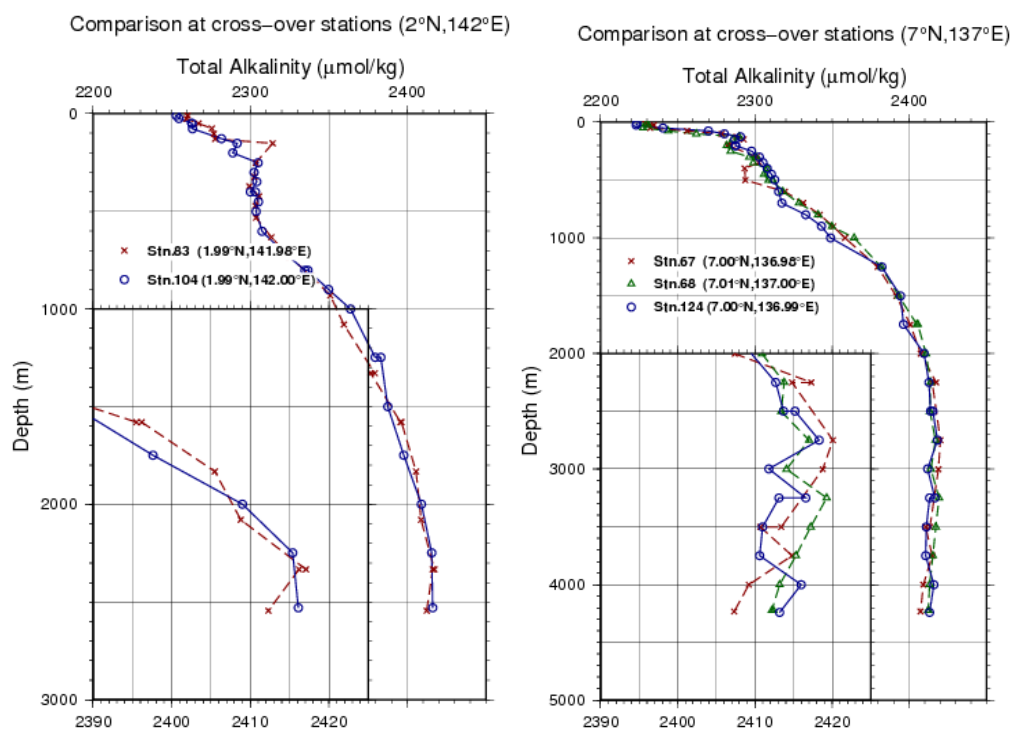
Figure C.5.12. Same as Figure C.5.11 but for TA.

(9) Comparisons at cross-over stations with other WHP and its revisit cruises

The WHP section P9 has been observed in 1994 (*Kaneko et al.*, 1998). Section P9 intersects section P2 at 30˚N, 137˚E and section P3 at 24˚N, 137˚E. DIC and TA in section P2 have been observed twice in the past; first by the cruise 49K6KY9401_1 of *R/V Kaiyo-Maru* in 1994 and second by the cruise 318M200406 of *R/V Melville* in 2004, and those in section P3 has been observed by the cruise 49NZ20051127 of *R/V Mirai* in 2005/2006. Summary of the comparisons of vertical profiles at cross-over stations are shown in Figure C.5.13 and C.5.14.
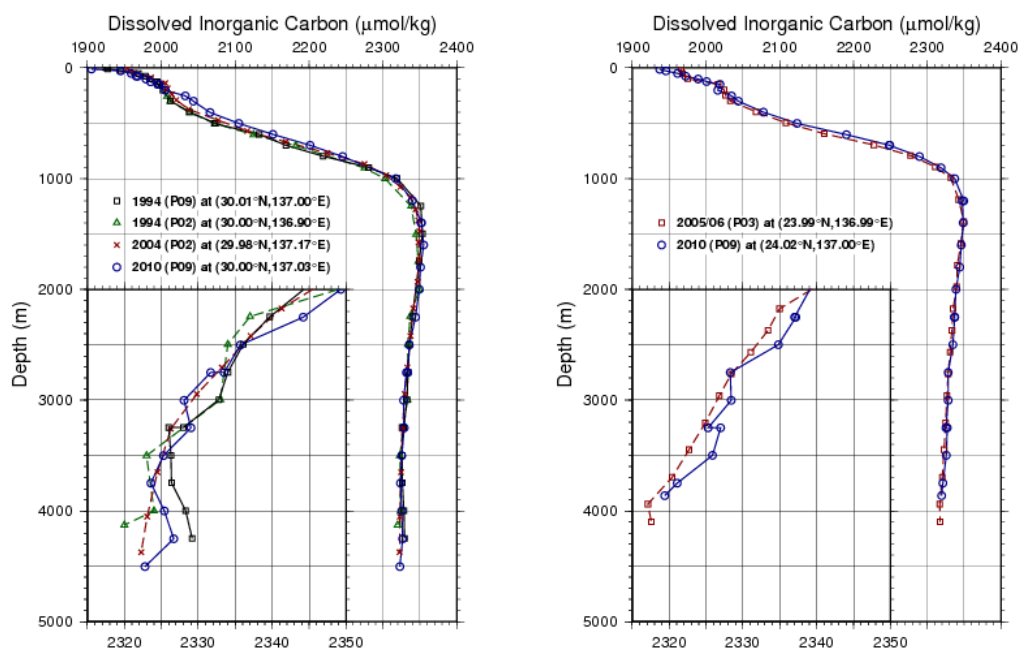
Figure C.5.13. Vertical profiles of DIC with WHP P2 (left panel: P9 at 1994 (square), P2 at 1994 (triangle), P2 at 2004 (cross) and P9 at 2010 (circle)) and WHP P3 (right panel: P3 at 2005/06 (square) and P9 at 2010 (circle)) at cross-over stations.
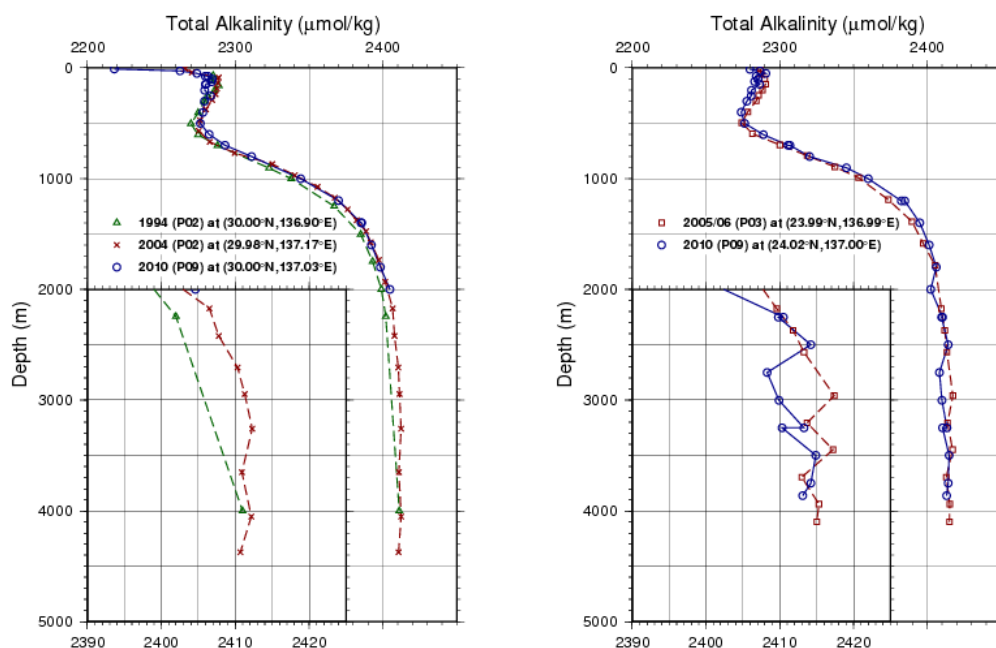

Figure C.5.14. Same as Figure C.5.13 but for TA.

References

Breland II, J. A. and R. H. Byrne (1993): Spectrophotometric procedures for determination of sea water alkalinity using bromocresol green, Deep-Sea Res. I, 470, 629-641.

Dickson, A. G., Sabine, C. L. and Christian, J. R. (Eds.) (2007): Guide to best practices for ocean CO_2 measurements. PICES Special Publication 3, 191 pp.

Johnson, K. M., A. E. King and J. McN. Sieburth (1985): Coulometric TCO_2 analyses for marine studies; an introduction. *Marine Chemistry*, **16**, 61-82.

Johnson, K. M., J. McN. Sieburth, P. J. IeB Williams and L Brändström (1987): Coulometric total carbon dioxide analyses for marine studies: Automation and calibration. *Marine Chemistry*, **21**, 117-133.

Kaneko, I., Y. Takatsuki, H. Kamiya and S. Kawae (1998): Water property and current distributions along the WHP-P9 section (137°-142°E) in the western North Pacific. *J. Geophys. Res.*, **103**, 12959-12984.

Swift, J. H. and S. C. Diggs (2008): A Guide to Submitting CTD/Hydrographic/Tracer Data and Associated Documentation to the CLIVAR and Carbon Hydrographic Data Office (Appendix C: Description of WHP-Exchange Format for CTD/Hydrographic Data)., http://cchdo.ucsd.edu/policies.html.

Swift, J. H. (2010): Reference-quality water sample data: Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.**14**, ICPO Pub. 134, 2010 ver.1*

6. *pH*

13 December 2013

(1) Personnel

Shinji MASUDA (JMA)

Kazutaka ENYO (JMA)

Naohiro KOSUGI (MRI)

(2) Station occupied

A total of 53 stations (Leg 1: 31, Leg 2: 22) were occupied for hydrogen ion index (pH). Station location and sampling layers of pH are shown in Figure C.6.1.
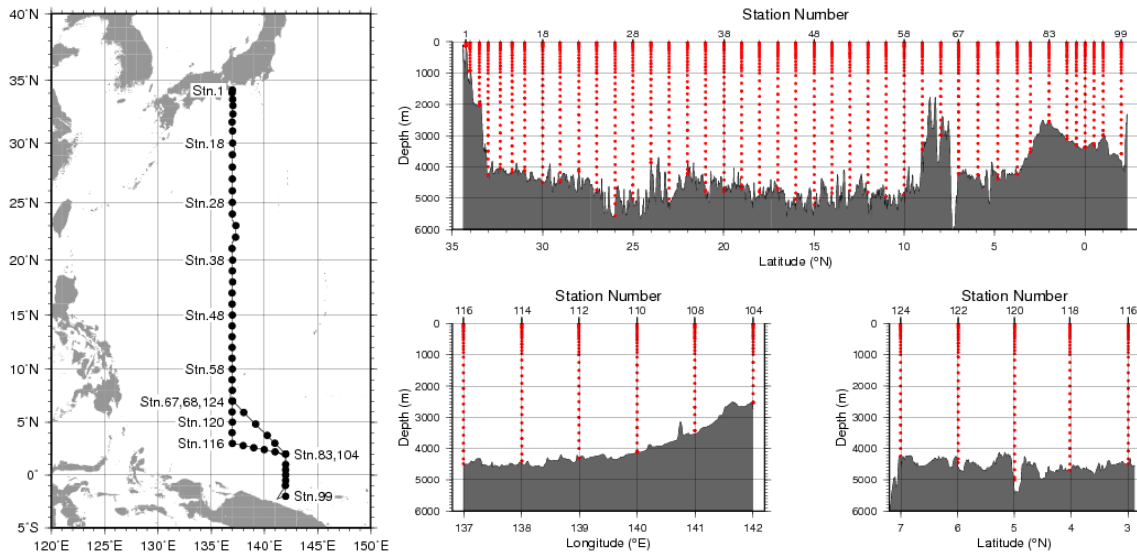
Figure C.6.1. Station location (left panel) and sampling layers of pH (right panels)

(3) Method

(3.1) Principle

The pH analysis was made using spectrometry of indicator dye *m*-cresol purple (*Saito et al.*, 2008; *Clayton and Byrne*, 1993). The pH was reported as the value at temperature of 25°C in "total hydrogen ion scale". In order to state clearly the scale of pH, we mention hereafter as "pH$_T$" that is defined by equation (1),

$$pH_T = -\log_{10}([H^+]_T/C^0) \qquad \text{---(1)}$$

where, $[H^+]_T$ denotes the concentration of hydrogen ion expressed in the total hydrogen ion scale: $[H^+]_T = [H^+]_F\left(1 + [SO_4]_T/K_{HSO_4^-}\right)$, where, $[H^+]_F$ is the concentration of free hydrogen ion, $[SO_4]_T$ is the total concentration of sulphate ion and $K_{HSO_4^-}$ is acid dissociation constant of hydrogen sulphate ion (*Dickson*, 1990). C^0 in equation (1) is the standard value of concentration (1 mole per kilogram of seawater, mol kg^{-1}).

(3.2) pH$_T$ Reagents

- *m*-Cresol purple solution

The air in a borosilicate glass flask (2 dm^3) was replaced by pure nitrogen. 0.67 g of *m*-cresol purple sodium salt (pure water soluble, 199250050, ACROS) was dissolved in 1 kg of deionised water prepared with water purifier "Autopure WR700" (Yamato Scientific Co. Ltd.). Small amount of diluted NaOH (approx. 0.25 mol dm^{-3}) solution was added to regulate the pH (free hydrogen ion scale) of indicator solution to 7.9 ± 0.1. The pH of indicator solution was monitored using glass electrode pH meter.

(3.3) Instruments and procedure

Custom-made pH$_T$ analysers (2009 model; Japan ANS Co., Ltd, Tokyo, Japan) was prepared and operated in the cruise. The analyser comprised of a sample dispensing unit (box **1** in Figure C.6.2), a pre-treatment unit combined with an automated syringe (PSD/8, HAMILTON; box **2** in Figure C.6.2), and two (sample and reference) spectrophotometers (C10083CAH, Hamamatsu Photonics) combined with a high power xenon light source (HPX-2000, Ocean Optics) (box **3** in Figure C.6.2). Whole analyser system was controlled by a personal computer (EX/522PDET3, TOSHIBA) using a custom-made software (Japan ANS Co., Ltd) that runs on an operating system Windows XP^{TM}.

The sample dispensing unit had an auto-sampler (6 ports), which took a seawater from 250 cm^3 borosilicate glass bottles (017030-250, Shibata) to the pre-treatment unit. Spectrophotometric cell (**4** in Figure C.6.2) was made of quartz tube (inner diameter: 4 mm; outer diameter: 6 mm; length: approx. 30 cm) that has figure of "U". This cell was covered with stainless bellows tube

to keep the external surface dry and for total light to reflect in the tube. The temperature of the cell was regulated to $25.0 \pm 0.1°C$ by means of immersing the cell into the thermostat bath, where the both ends of bellows tube located above the water surface of the bath. Spectrophotometer, cell and light source were connected with optical fibre (red lines in Figure C.6.2).
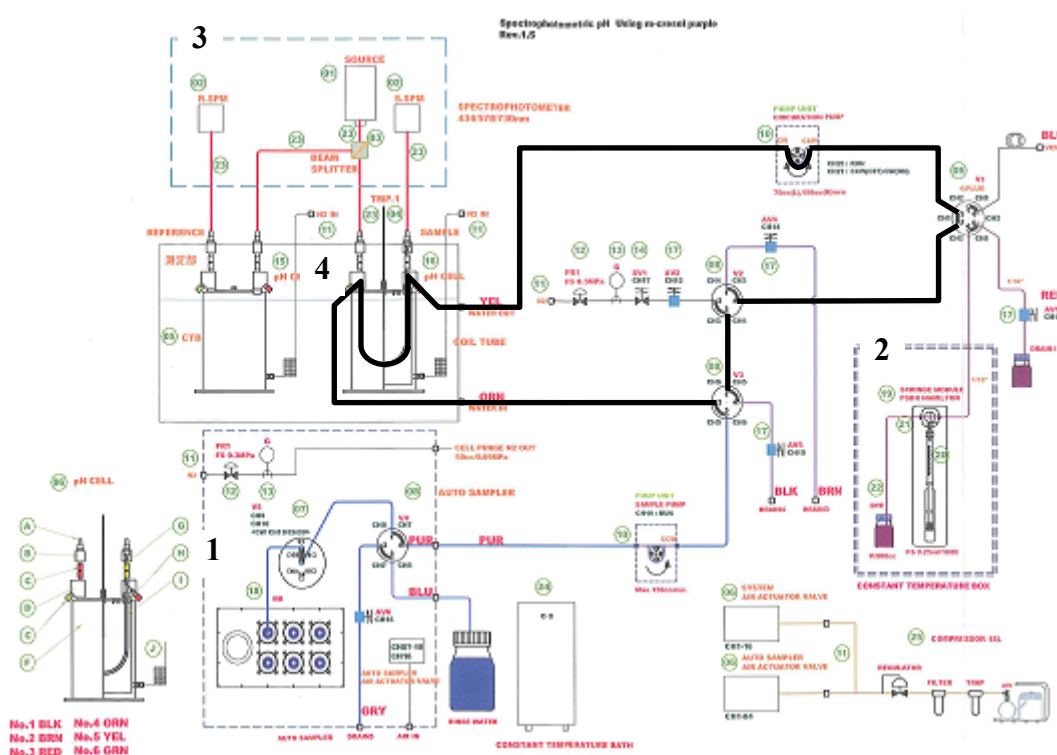
Figure C.6.2. Diagram of pH_T measurement apparatus. **1**: Sample dispensing unit, **2**: automated syringe to inject indicator, **3**: two (sample and reference) spectrophotometers with high power Xe light source and **4**: spectrophotometric cells.

The analysis procedure was as follows:

    a) Seawater was ejected from a sample loop (thick line in Figure C.6.2)

    b) A portion of sample (approx. 30 cm³) was introduced into a sample loop including spectrophotometric cell. The spectrophotometric cell was flushed two times with sample in order to remove air bubbles.

    c) An absorption spectrum of seawater in the visible light range was measured. Absorbance at wavelengths of 434 nm, 488 nm, 578 nm and 730 nm as well as cell temperature were recorded. To eject air bubbles from the cell, the sample was moved four times (approx. 30

cm each in loop tube whose inner diameter was 1/16 inch) and the absorbance was recorded at each stop.

d) 80 μl of indicator *m*-cresol purple solution was injected to the loop.

e) Circulating 2 minutes 40 seconds through the loop tube, seawater sample and indicator dye was mixed together. The final *m*-cresol purple concentration in the sample was approx. 4 μmol dm^{-3}.

f) Absorbance of *m*-cresol purple plus seawater was measured in the same way described above (c).

(4) Seawater Sampling

Samples for pH_T analysis were drawn with the similar way of dissolved inorganic carbon (see chapter C05) from 10-liter Niskin bottles into clean 250 cm^3 borosilicate bottles (Shibata) using silicone rubber tubing on the petcock. To avoid contamination from the air, samples for pH_T were drawn next to the sampling of dissolved inorganic carbon (DIC) and total alkalinity (ALK). Surface sample was collected from continuous flow line pumped from sea-chest. In order to avoid CO_2 exchange with the air, the end of tubing was inserted to the bottom of the bottle, and then the sample was dispensed smoothly into a bottle. Sample of approximately double the volume of bottle was overflowed. The bottle was plugged temporally with a ground glass stopper.

After sampling, 2 cm^3 of seawater was removed from bottle to allow thermal expansion of sample. Until the station RF3663, 0.2 cm^3 of saturated mercury (II) chloride solution was added to prevent change in pH_T caused by biological activity. After the station RF3666, pH_T was analysed immediately after sampling instead of adding mercury chloride solution to the sample seawater.

Bottle was sealed with greased (Apiezon-L) ground glass stopper. Sample bottles were stored at room temperature while awaiting analysis. Sample bottles had been immersed in isothermal bath to keep in 25.0 °C for over 1 hour before analysis.

(5) pH_T measurement

(5.1) Calculation of pH_T from measured absorbance

pH_T was calculated from the measured absorbances based on the following equations (2) – (4).

$$\text{pH}_\text{T} = \text{p}K_2 + \log_{10}([\text{I}^{2-}]/[\text{HI}^-])$$

$$= \text{p}K_2 + \log_{10}\{(R - 0.0069_1)/(2.222_0 - 0.133_1 R)\} \text{ -- (2)}$$

$$R = \left(A_{578}^{\text{SD}} - A_{578}^{\text{S}} - A_{730}^{\text{SD}} + A_{730}^{\text{S}}\right)/\left(A_{434}^{\text{SD}} - A_{434}^{\text{S}} - A_{730}^{\text{SD}} + A_{730}^{\text{S}}\right) \text{ -- (3)}$$

where $\text{p}K_2$ is the acid dissociation constant of *m*-cresol purple, $[\text{I}^{2-}]$ / $[\text{HI}^-]$ is the ratio of *m*-cresol purple base form (I^{2-}) concentration over acid form (HI^-) concentration, which is estimated from absorbance ratio R and the ratios of extinction coefficients (*Clayton and Byrne*, 1993). A_λ^{S} and A_λ^{SD} in equation (3) are absorbances of seawater itself and dye plus seawater, respectively, at wavelength λ (nm). The value of $\text{p}K_2$ ($= -\log_{10}(K_2/k^0)$, $k^0 = 1$ mol / kg) had also been expressed as a function of temperature T (in Kelvin) and salinity S (in psu) by *Clayton and Byrne* (1993), but the calculated value has been subsequently corrected by 0.0047 on the basis of a reported pH_T value accounting for "tris" buffer (*DelValls and Dickson*, 1998):

$$\text{p}K_2 = \text{p}K_2(\text{Clayton \& Byrne}, 1993) + 0.0047$$

$$= 1245.69/T + 3.8322 + 0.00211(35 - S). \text{ --(4)}$$

$$293 \text{ K} \le T \le 303 \text{ K}, 30 \le S \le 37$$

(5.2) pH_T Perturbation caused by addition of dye solution

The injection of m-cresol purple solution affects the pH_T of seawater sample because the acid base equilibrium of the seawater is disrupted by the addition of the dye acid-base pair (*Dickson et al., 2007*). We corrected the R in Equation (2) for the perturbation using empirical method (Equation (5)) in which a second aliquot of dye solution is added to the seawater sample (*Dickson et al., 2007*; *Clayton and Byrne*, 1993).

$R = R_1 - \Delta R,$

$\Delta R = R_2 - R_1 = R_1 - R$ (Assumption), --(5)

where, R_1 and R_2 are the absorbance ratio after the addition of first and second aliquot of dye solution, respectively. The value of ΔR depended on the pH$_T$ of sample. We expressed ΔR as a quadratic function of R_1 based on experimental $R_2 - R_1$ data obtained at this cruise (Figure C.6.3). 6 samples at each station were analysed to obtain $R_2 - R_1$ data, ΔR was expressed as a quadratic function of R_1 and the pH$_T$ was evaluated from $R = R_1 - \Delta R$ using equation (2).
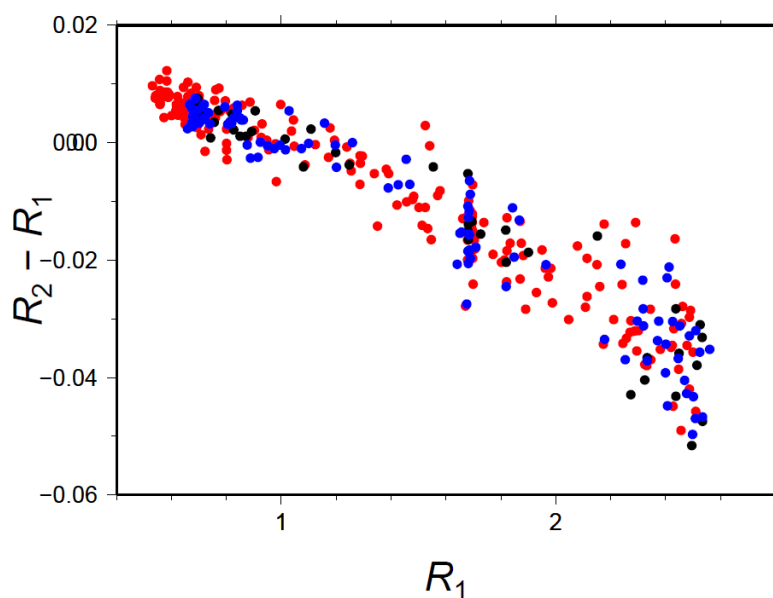

Figure C.6.3. pH$_T$ perturbation caused by the addition of indicator dye solution. The perturbation was expressed as a difference in absorbance ratio between first and second aliquot, $\Delta R = R_2 - R_1$. The colour of plots denotes the station numbers; red: RF3649 - RF3714, black: RF3716 – RF3731, red: RF3742 – 3772. The result of quadratic regression was listed in Table C.6.1.

Table C.6.1. The coefficients of quadratic regression of the pH_T perturbation that was caused by the addition of *m*-cresol purple solution and was expressed as the difference in absorbance ratio *R*. $\Delta R = C_2 \times R_1^2 + C_1 \times R_1 + C_0$

Stations	C_2	C_1	C_0
RF3649 - RF3714	-3.53×10^{-3}	-1.19×10^{-2}	0.0156
RF3716 – RF3731	-7.73×10^{-3}	-3.16×10^{-4}	0.0091
RF3742 – RF3772	-5.27×10^{-3}	-6.98×10^{-3}	0.0125

(6) Quality assurance

(6.1) CRM and in-house standard seawater measurements

To check the repeatability and/or reproducibility of measurements, we analysed two batches (98 and 100) of certified reference materials (CRMs) that were prepared by Dr. A.G. Dickson at Scripps Institute of Oceanography. Three samples were extracted and analysed from a bottle and the difference in initial two data were plotted (R-chart, Figure C.6.4). The upper control limit (UCL), the upper warning limit (UWL) and the standard deviation were estimated using equations described in SOP22 of *Dickson et al.* (2007). The standard deviation estimated from accepted data (less than UCL) was 0.0010 for batch 98 and 0.0013 for batch 100, respectively.
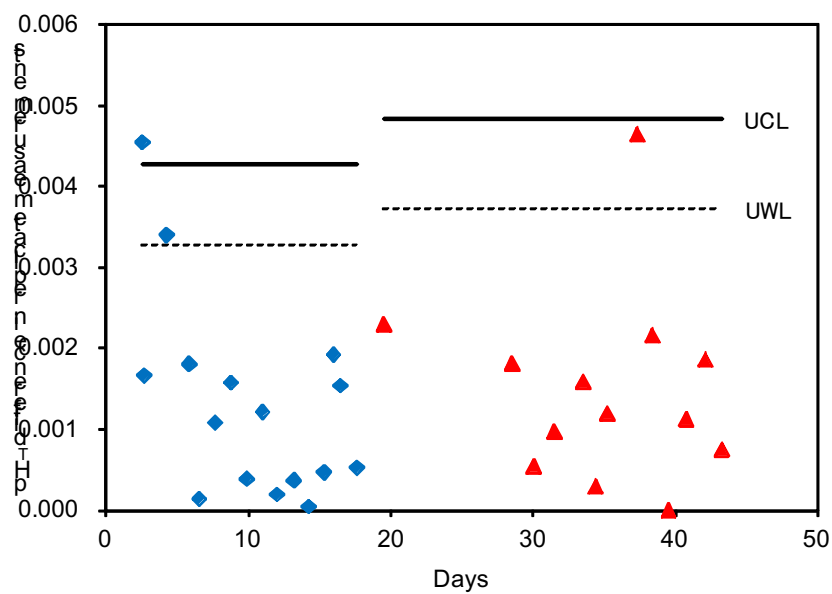
Figure C.6.4. Absolute differences in replicate measurements of pH_T in CRM for each bottle (R-chart). The colour of the plots denotes the batch number; blue: batch 98, red: batch 100.
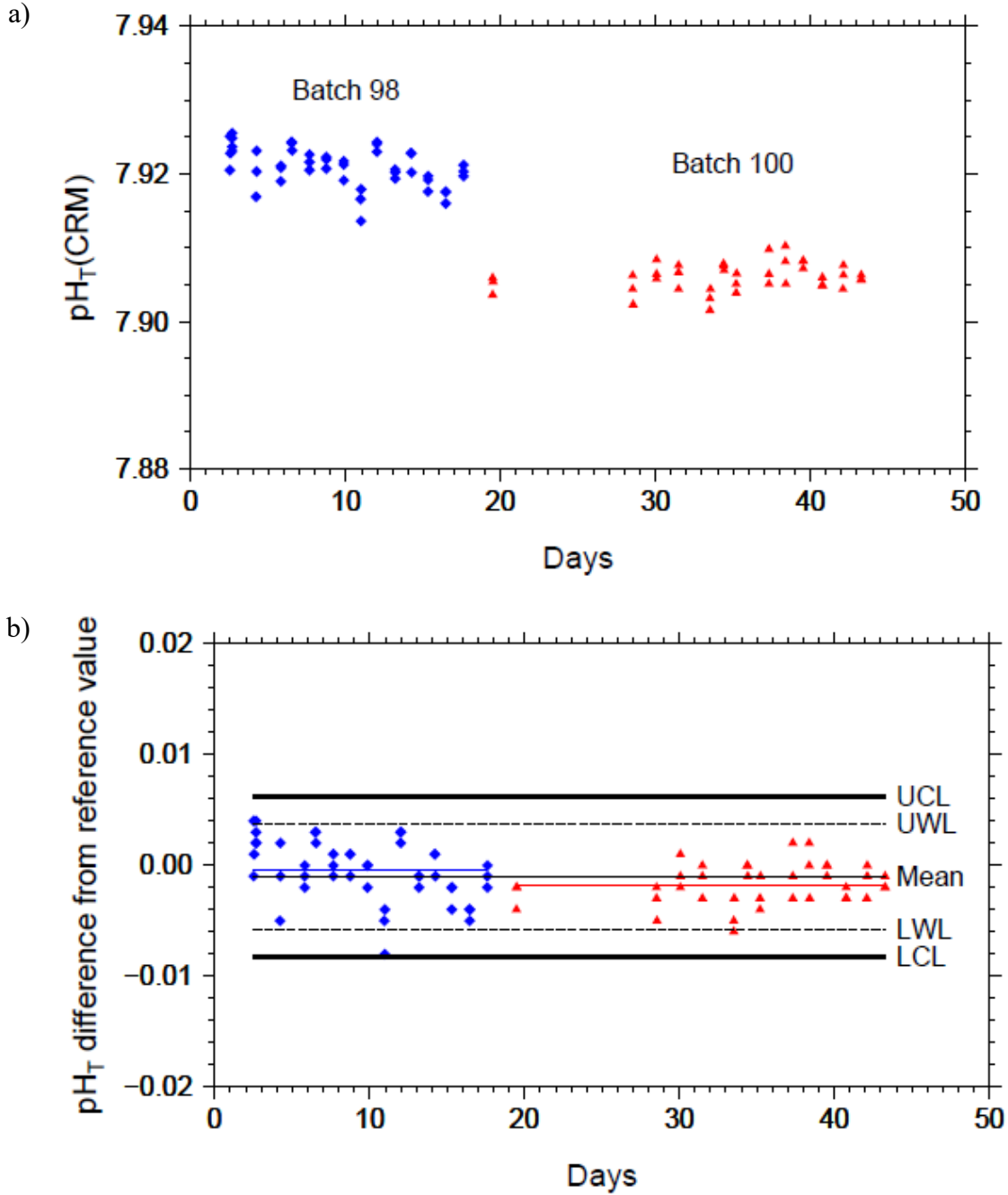
Figure C.6.5. a) Measured pH_T of CRMs, b) Differences in pH_T of CRMs between measured and reference values that was calculated from certified values of DIC and ALK using acid dissociation constants of carbonates described by *Lueker et al.* (2000). The colour of plots denotes the batch of CRM; blue: batch 98, red: batch 100. UCL and LCL are upper and lower control limit, respectively, that is defined as mean ± 3 σ. UWL and LWL are upper and lower warning limit, respectively, that are defined as mean ± 2 σ.

All results of CRM measurements were plotted in Figure C.6.5 a). Measured pH_T was compared

with "reference value" that was calculated from certified values of DIC and ALK using acid dissociation constants of carbonic acid and hydrogen carbonate ion described by *Lueker et al.* (2000). The concentrations of phosphate and silicate were also used for calculation, although the values are not certified. The difference in measured and reference values were plotted in Figure C.6.5 b). The offset of measured value was -0.0010 ± 0.0024 (mean $\pm$ standard deviation, n = 85).

In order to monitor the condition of apparatus, in-house standard seawater (SSW) batch J, which was made using the CRM's manner, was measured. The mean and standard deviation was 7.9392 ± 0.0028 (n = 97) (Figure C.6.6).
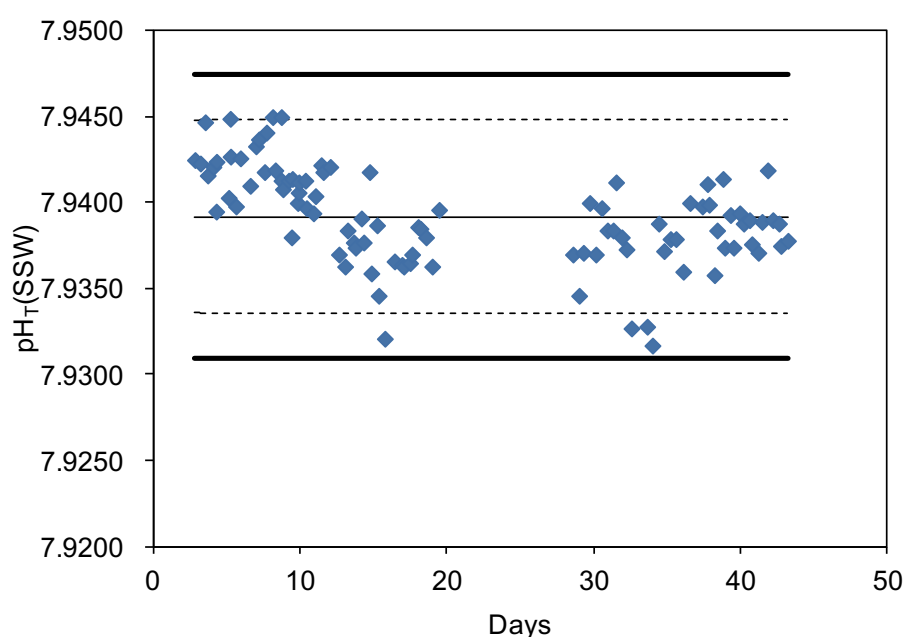
Figure C.6.6. Measured pH_T of in-house SSW.

(6.2) Repeatability of water column samples measurements

To check the repeatability of water column samples measurements, we measured replicate and duplicate samples. At each hydrographic station where sea water samples were drawn, two or more Niskin bottles were closed at the same layer ("Duplicate" sampling) if Niskin bottles on carousel sampler are more than the layers to be sampled at the station. A couple of samples were drawn from each Niskin bottle of 3 layers to obtain 3 "Replicate" samples at each hydrographic station.

Total amounts of the duplicate and replicate sample pairs were 162 and 175, respectively. The control limits and standard deviations were calculated using the method described in SOP22 of *Dickson et al. (2007)*. The average differences and the standard deviations estimated from accepted data are listed in Table C.6.2.

Table C.6.2 Summary of replicate and duplicate samples measurements

	Duplicate	Replicate
Total number of good measurement pairs	152	163
Average of absolute difference	0.0019	0.0021
Standard deviation of measurements	0.0017	0.0018

(6.3) Quality flag assignment

Summary of assigned quality control flags are listed in Table C.6.3. The replicate data were averaged and flagged 6 if both of the flag were 2. If either of the flag was 3 or 4, younger flag was selected.

Table C.6.3 Summary of assigned quality control flags.

Flag	Definition	Number of samples
1	need further correction	1840
3	Questionable	98
4	Bad (Faulty)	21
5	Not reported	3
6	Replicate measurements	163[*]
	Total number of samples	1962[*]

[*] Samples of flag 6 are counted as flag 1

Figure C.6.7. Result of pH$_T$ replicate samplings (n=163) during the cruise RF10-05 versus (a) Station number, (b) Sampling depth, (c) pH$_T$ values and (d) Histogram of the result of replicate samplings. The lines in the panel (a) indicate upper control limit (thick), upper warning limit (dashed) and average of absolute difference (dotted), respectively.
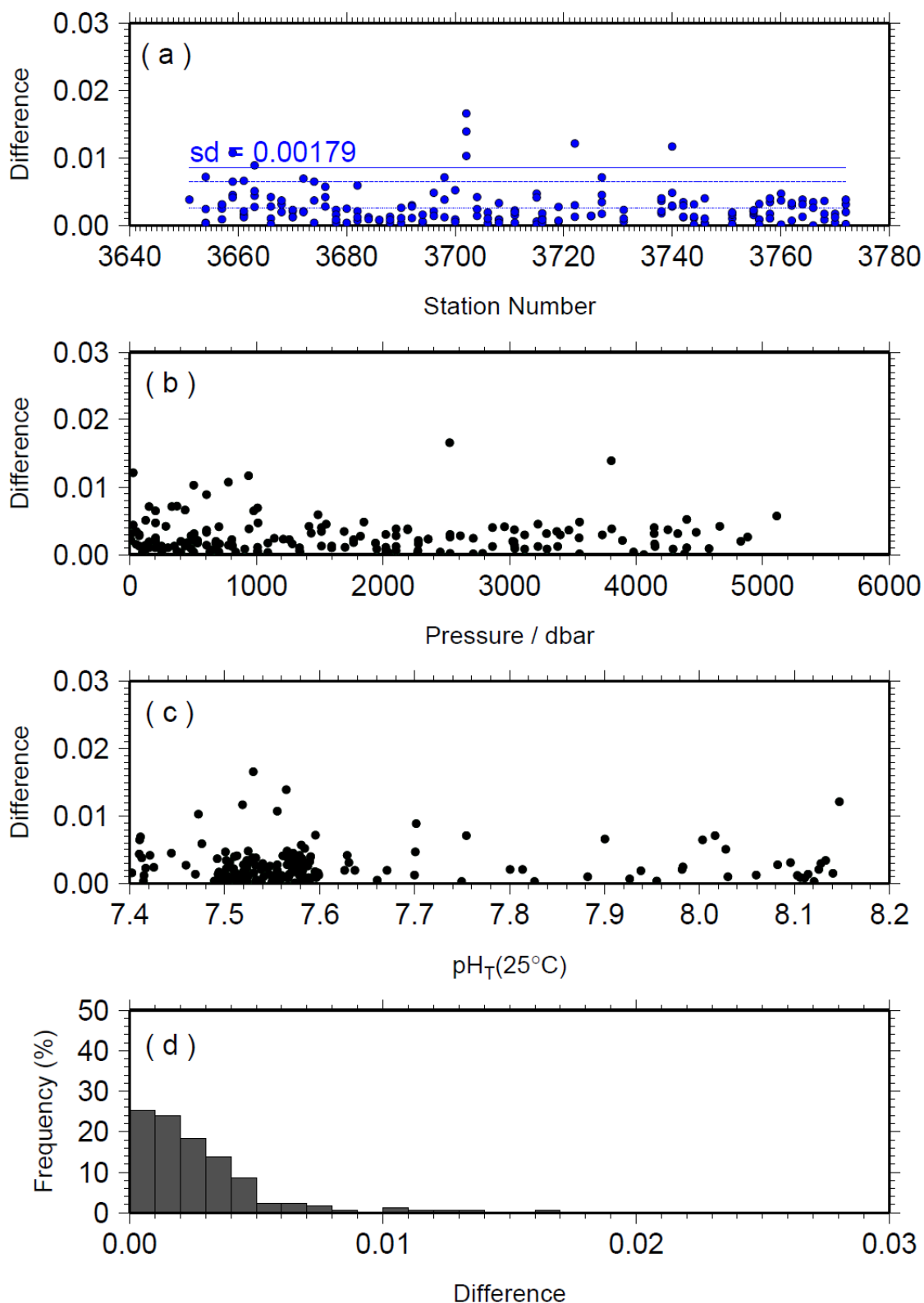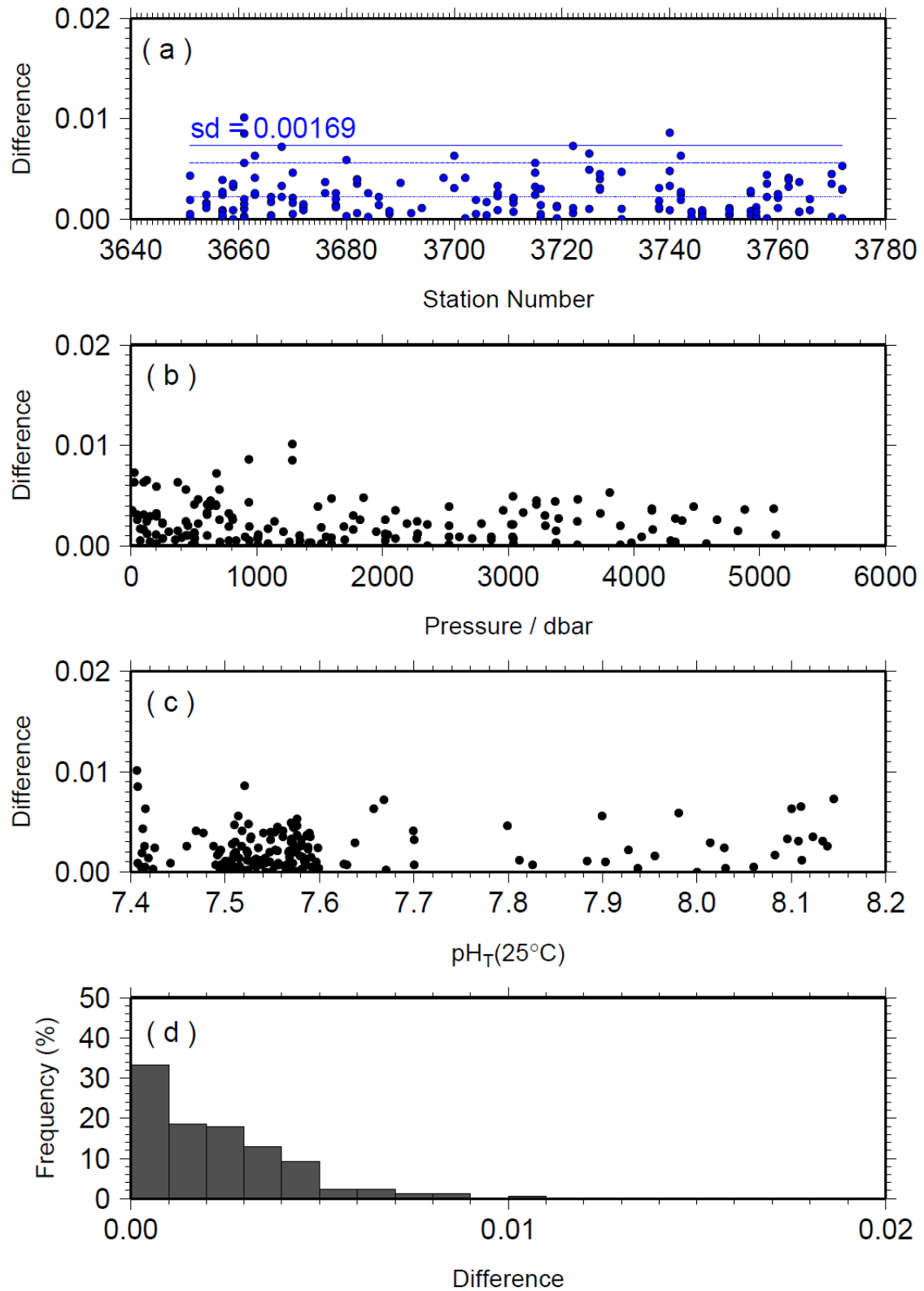
Figure C.6.8. Result of pH$_T$ duplicate samplings (N=152) during the cruise RF10-05 versus (a) Station number, (b) Sampling depth, (c) pH$_T$ values and (d) Histogram of the result of duplicate samplings.

(7) Problems

pH$_T$ data of 1840 samples (Table C.6.3) were assigned as QF.1 because the data could have significant bias due to non- linear response of our spectrophotometer. A method of correction is under consideration.

pH$_T$ data of 98 samples (Table C.6.3) were assigned as questionable data (QF = 3) because the data was sufficiently (approx. 2 σ of measurements) apart from smooth line of vertical profile of a station. The pH$_T$ data for these samples showed different characters from the data of DIC, ALK, dissolved oxygen or nutrients. Possible reason for this problem was a lack of rinsing optical cell after a measurement, because of malfunction of circulation pump of pre-treatment unit. pH$_T$ data of 21 samples (Table C.6.3) were assigned as bad (faulty) data (QF = 4). The absorbance at wavelength 730 nm of these data was anomalously high, which represented air bubbles remained in an optical cell. If all of five absorbance data per a sample measurement was faulty, the data was assigned as bad. pH$_T$ data of 3 samples were not reported (QF = 5) because the samples were lost in the measurement procedure, for example, attaching sample bottles at the wrong position of sampler.

(8) Results

(8.1) Comparison at cross-stations during the cruise

There were two cross-stations during the cruise. The one was located at 2˚N/142˚E, another was located at 7˚N/137˚E. At stations of Stn.83 (RF3731) and Stn.107 (RF3755), hydrocast sampling for pH$_T$ was conducted two times at interval of about five days.

At stations of Stn.67 (RF3715), Stn.68 (RF3716) and Stn.124 (RF3772), hydrocast sampling for pH$_T$ was conducted three times. Interval between the first and the second was about a week, interval between the second and the third was about two weeks.

These profiles are shown in Figure C.6.9.
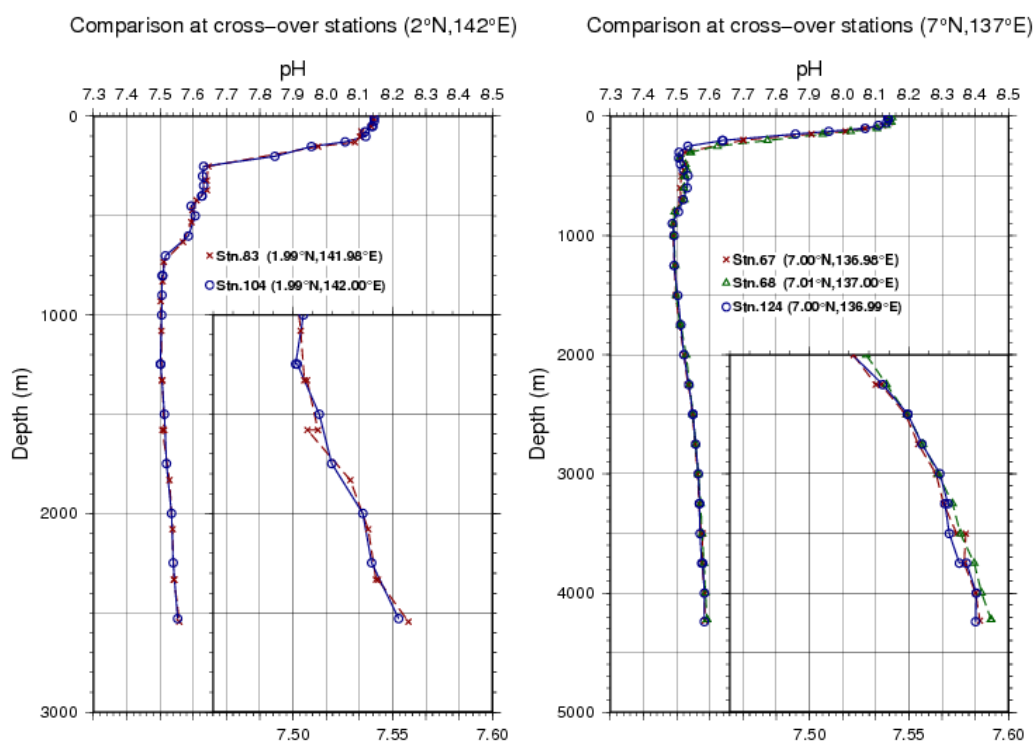
Figure C.6.9. Comparison of pH$_T$ profiles between the first hydrocast (cross) and the second one (circle) at the cross-stations of 2˚N/142˚E (left panel), and between the first hydrocast (cross), the second one (triangle) and the third one (circle) at the cross-stations of 7˚N/137˚E (right panel)

(8.2)   Comparison at cross-stations of WHP-P3 section

We compared our pH$_T$ data and WHP-P3 at a cross point (around 24˚N/137˚E). WHP-P3 line was observed in 2005/06 by R/V Mirai that belonged to Japan Agency for Marine-Earth Science and Technology (JAMSTEC).

Summary of the comparison of these profiles is shown in Figure C.6.10.

Figure C.6.10. Comparison of pH$_T$ profiles at cross-stations of WHP-P3. Circle show this cruise.

References

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

Dickson, A.G. 1990. Standard potential of the reaction: AgCl(s) + 1/2 H2(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO$_4^-$ in synthetic sea water from 273.15 to 318.15 K. *J. Chem. Thermodynamics*, **22**, 113-127.

Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) 2007. Guide to best practices for ocean CO$_2$ measurements. *PICES Special Publication* 3, 191 pp.

Lueker, T.J, A.G. Dickson and C.D. Keeling, 2000. Ocean *p*CO$_2$ calculated from dissolved inorganic carbon, alkalinity, and equations for K_1 and K_2: validation based on laboratory measurements of CO$_2$ in gas and seawater at equilibrium. *Marine Chem.*, **70**, 105-119.

Saito, S., M. Ishii, T. Midorikawa and H.Y. Inoue 2008. Precise Spectrophotometric Measurement of Seawater pH$_T$ with an Automated Apparatus using a Flow Cell in a Closed Circuit. *Technical Reports of Meteorological Research Institute*, **57**, 1-28.

7. Chlorofluorocarbon (CFC-11 and CFC-12)

13 December 2013

(1) Personnel

Kazuki ISHIMARU (GEMD/JMA)

Etsuro ONO (GEMD/JMA)

(2) Station occupied

A total of 27 stations (Leg 1: 15, Leg 2: 12) were occupied for analyses of CFCs (CFC-11 and CFC-12). Station location and sampling layers for CFCs analyses are shown in Figure C.7.1.
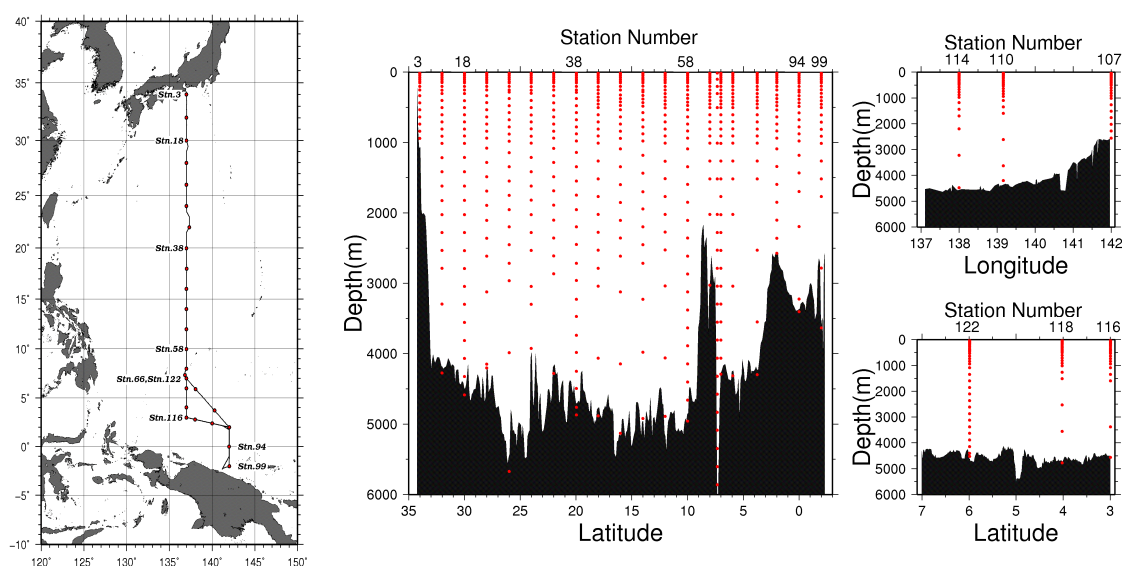
Figure C.7.1. Station location (left panel) and sampling layers of CFCs (right panel).

(3) Sampling

On the casts where water samples were collected for dissolved CFC-11, CFC-12 analysis, these were the first samples drawn from bottles to reduce CFC contamination. To minimize contact with air, the CFC samples were drawn directly through the stopcocks of the 10-liter Niskin bottles into 100 ml precision glass syringes equipped with three-way stopcocks. The syringes were immersed in a holding tank of clean surface seawater with ice before being analyzed.

(4) Instruments and methods

Concentrations of CFC-11 and CFC-12 in seawater and air samples were measured by shipboard gas chromatography (GC) equipped with an electron capture detector (ECD) using techniques described by *Bullister and Weiss* (1988). The flow diagram is shown in Figure C.7.2. For seawater analyses, sample water was transferred from a glass syringe to a fixed volume chamber (volume approximately 40 ml). The contents of the chamber were then injected into a purging chamber made of glass. The dissolved gases in the seawater sample were extracted by passing CFC-free purge gas through the purging chamber for a period of 6 minutes at 75 ml min^{-1}. Water vapour was removed from the sample gas during passage through a 10 cm long, 3/8 inch outer diameter stainless tube packed with the desiccant magnesium perchlorate. The sample gases were concentrated on a cold-trap consisting of a 1/8 inch outer diameter stainless steel tube with a 5 cm section packed with Porasil C (80-100 mesh) and a 5 cm section packed with Porapak T (80-100 mesh). A cooler was used to cool the trap to approximately -35 °C. After 6 minutes of purging, the trap was isolated, and was transferred to the bath heated to approximately 95 °C. The sample gases held in the trap were then injected onto a precolumn (approximately 25 cm of 1/8 inch outer diameter stainless steel tubing packed with 80-100 mesh Porasil C, held at 70 °C) for the initial separation of CFC-12 and CFC-11. The CFCs that had passed from the pre-column entered the main analytical column (approximately 250 cm of 1/8 inch outer diameter stainless steel tubing packed with Porasil C, 80-100 mesh, held at 70 °C) of GC (a Shimadzu GC-8A with ECD).
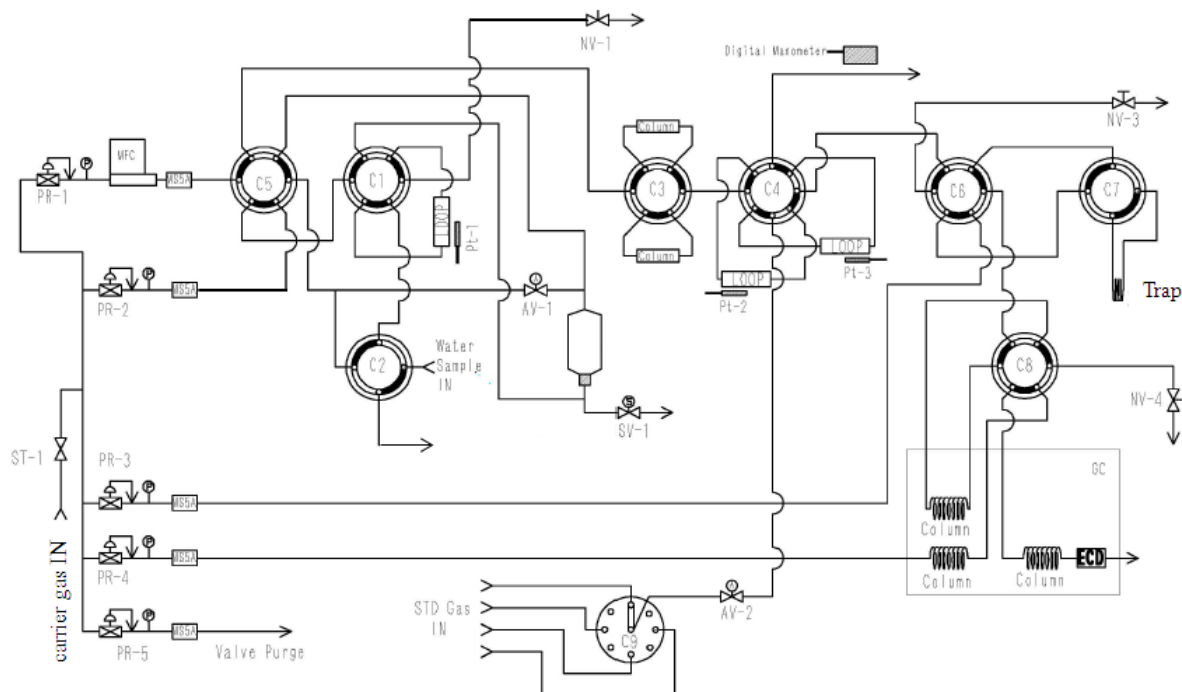
Figure C.7.2. Schematic flow diagram of CFCs analytical system.

The analytical systems were calibrated using a standard gas of known CFC composition after analyses of a station. Gas sample loops of known volume were thoroughly flushed with standard gas and then the standard gas was injected into the system. Concentrations of CFCs standard gas were determined by a gravimetric technique developed by TAIYO NIPPON SANSO Corporation, Japan (Table C.7.1). The temperature and pressure was recorded so that the amount of gas injected could be calculated.

The procedures used to transfer the standard gas to the trap, precolumn, main chromatographic column, and ECD were similar to those used for analyzing water samples. Air samples and blank samples (CFC-free gas) were injected and analyzed in a similar manner with standard gases.

CFC concentrations in seawater and air samples were determined by the multi-point calibration curves made by fitting chromatographic peak areas in a quadratic polynomial. Two sizes of gas sample loops (2 ml and 10 ml) were prepared. Multiple injections of these loops volumes could be made to allow the system to be calibrated over a relatively wide range (from 0 to the

concentration of air sample). The typical analysis time for seawater, air, standard gases or blank samples was approximately10 minutes.

Table C.7.1. Concentrations of standard gases.

Cylinder No.	CFC-11 (pptv)	CFC-12 (pptv)
CPB23436	50.20	49.35
CPB29414	150.2	100.0
CPB30485	349.3	200.0

(5) Results

CFCs concentrations in the air are reported as mole fraction CFC in dry gas, and are typically in the parts per trillion (ppt). Dissolved CFC concentrations in seawater are given in units of picomoles per kilogram seawater (pmol kg^{-1}). Full-range calibration curves (quadratic fitting of chromatographic peak areas for the number of moles of CFCs injected) were made after every station analyses. Figure C.7.3 shows time-series of concentrations determined by self-calibrations among these cylinders. It suggested that the stability of CFCs cylinders was ensured during the cruise.

The repeatability for the standard gas in the fixed volume were 0.98% for CFC-12 and 0.92% for CFC-11 (n = 10). We estimated the detection limit for our analytical system to be 0.05 pmol kg^{-1} for both CFC-11 and CFC-12.
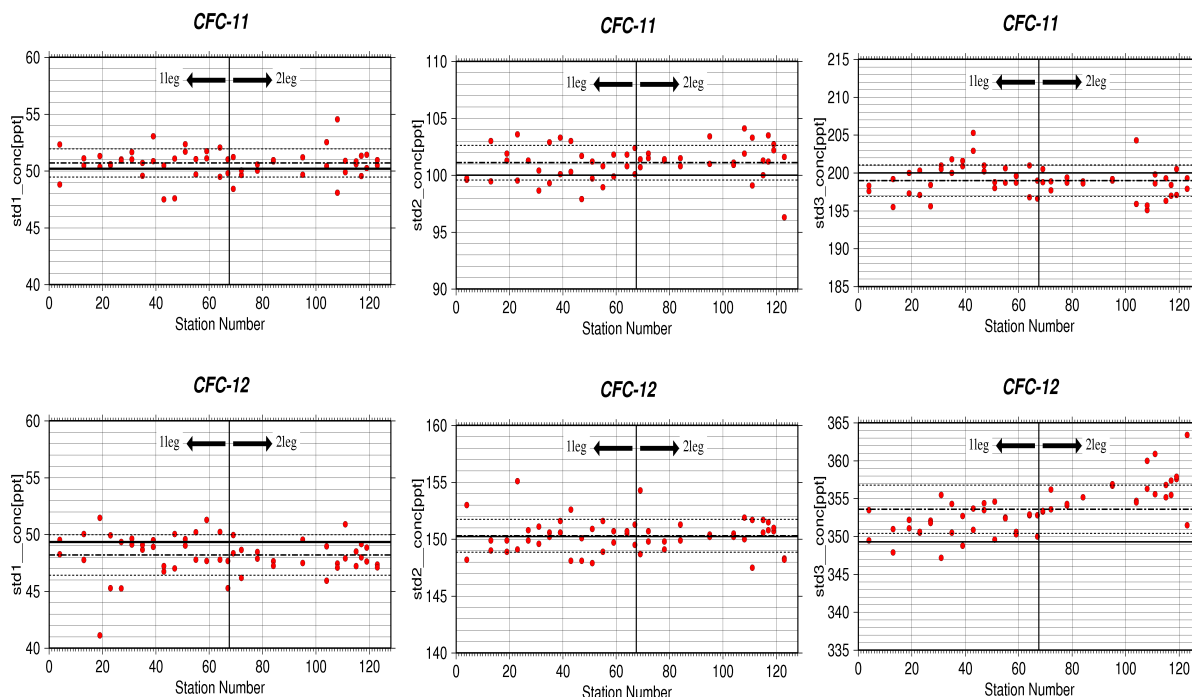
Figure C.7.3. Self-calibration of standard gas cylinder (left panel is CPB23436, centre panel is CPB29414, right panel is CPB30485). CFC-11 (top panel) and CFC-12 (bottom panel). Thick lines denote concentration of standard gases cylinders, which is assigned by gravimetric technique. Dash-dot lines denote average of self-calibration. Dash lines were its standard deviation.

The purging efficiency was estimated periodically by re-purging high concentration surface water samples and measuring this residual signal. At a flow rate of 75 ml min^{-1} for 6 minutes, purging efficiency were >99.9% for CFC-11 and CFC-12. And no correction for this has been applied to the reported water concentration values.

On this expedition, based on the analysis of 37 pairs of replicate for CFC-11 and 36 pairs of replicate for CFC-12, the average of differences between pairs were calculated to be 0.019 pmol kg^{-1} for CFC-11 and 0.020 pmol kg^{-1} for CFC-12 (Figure C.7.3). And, based on the analysis of 23 pairs of duplicate samples for CFC-11 and 20 pairs of duplicate samples for CFC-12, the average of differences between pairs were calculated to be 0.022 pmol kg^{-1} for CFC-11 and 0.022 pmol kg^{-1} for CFC-12 (Figure C.7.4).
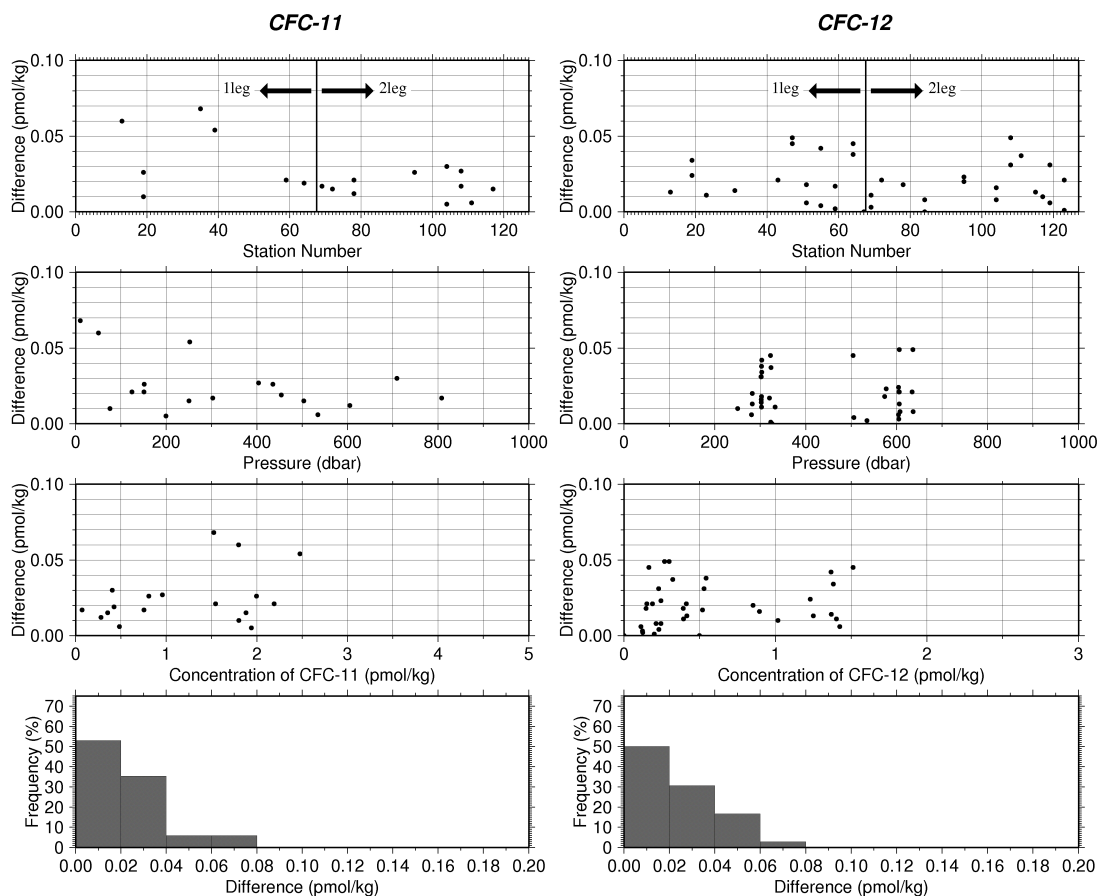
Figure C.7.4. Result of replicate samplings during this cruise versus station number (top panel), sampling depth in dbar (second from the top panel) and concentration of CFCs (second from bottom panel). Bottom panel shows histogram of the result of replicate samplings. Left panel shows CFC-11 and right panel shows CFC-12.
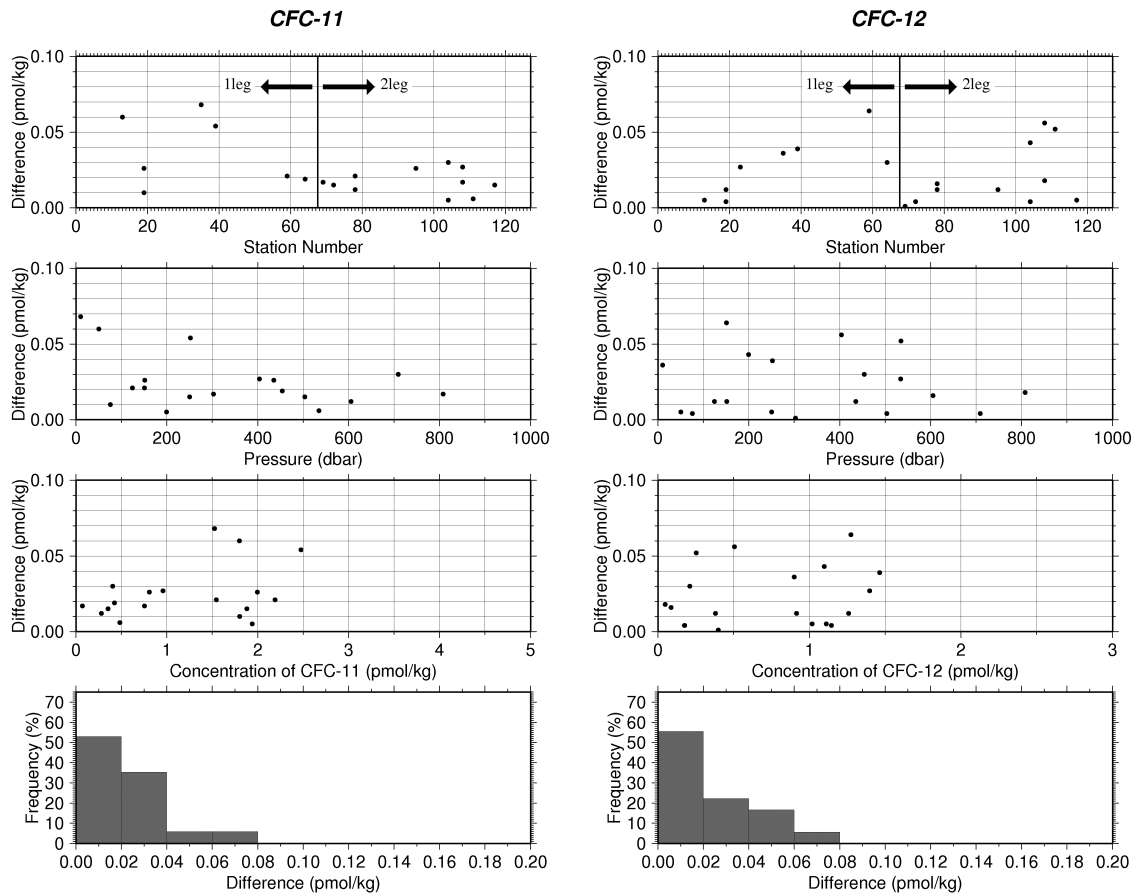
Figure C.7.5. Same as Fig.C.7.3 but for duplicate samplings

Air measurement at each station was useful in order to check CFCs measurements by calculating CFC saturation levels in the surface water. Averages of atmospheric CFC-11 and CFC-12 concentrations were estimated to be 241.7 ± 5.1 ppt and 533.8 ± 7.1 ppt respectively, based on 49 of measurement of air samples (Figure C.7.5).
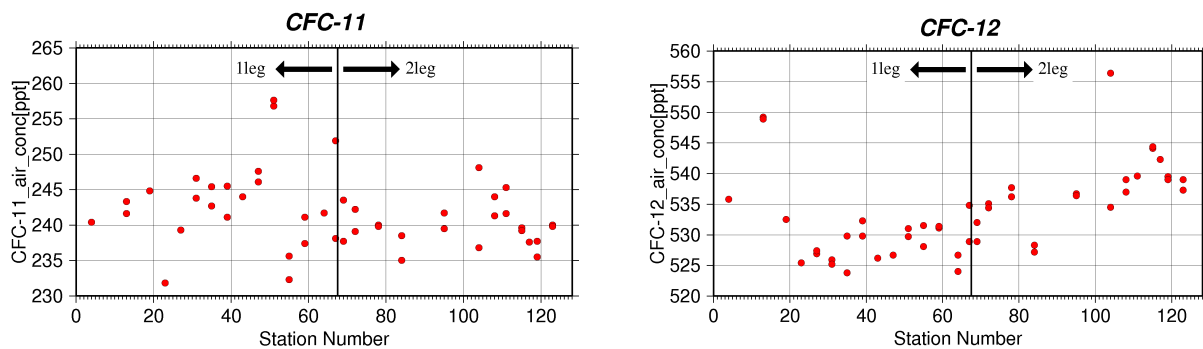
Figure C.7.6. Result of CFCs concentrations in the air versus station number. CFC-11 (left panel) and CFC-12 (right panel).

We drew *p*CFCs property-property plots with the atmospheric CFC history for flagging (Figure C.7.7).

pCFC-11 vs pCFC-12
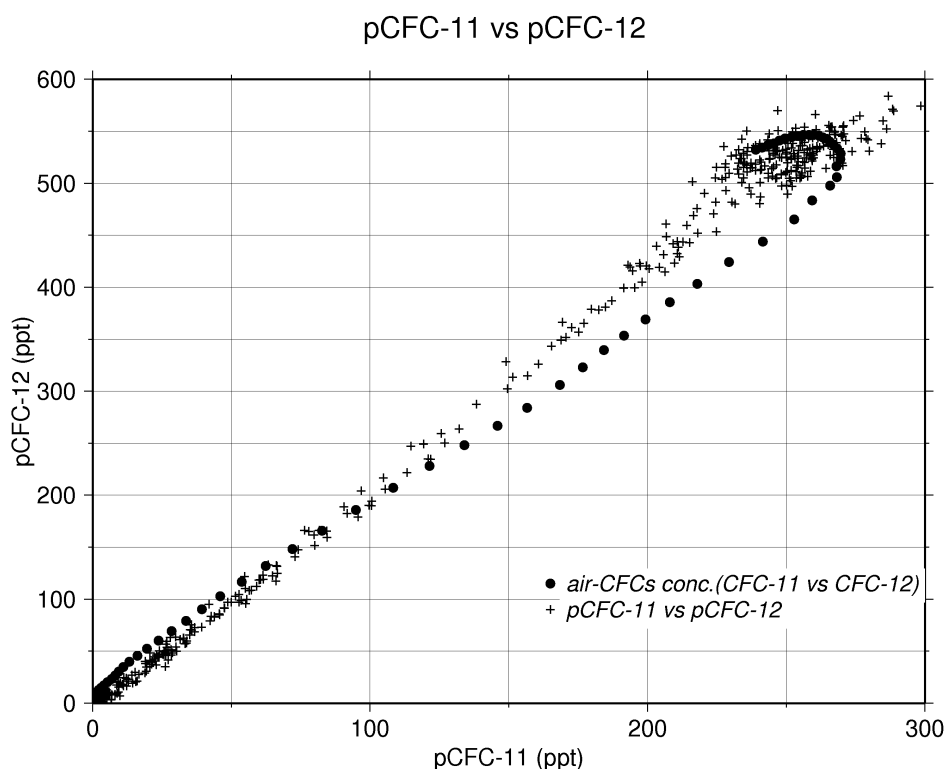
Figure C.7.7. *p*CFCs property-property plots. Plus and circle show *p*CFCs in seawater samples and historical CFCs of air concentration, respectively.

A small number of water samples showed anomalously high CFC concentrations compared with the samples obtained at adjacent layers. These results occurred sporadically during the cruise and were not clearly associated with other features in the water column (e.g., anomalous dissolved oxygen, salinity, or temperature features). This suggests that these samples were probably contaminated with CFCs during the sampling or analysis processes.

Measured concentrations for these anomalous samples are included in the preliminary data, but are given a quality flag values of either 3 (questionable measurement) or 4 (bad measurement). A quality flag of 5 was assigned to the data for samples which were drawn from the Niskin bottle but never analyzed due to a variety of reasons (e.g., leaking stopcock, plunger jammed in syringe barrel). A total of 29 analyses of CFC-11 and 32 analyses of CFC-12 were assigned a quality flag of 3. A total of 47 analyses of CFC-11 and 41 analyses of CFC-12 were assigned a quality flag of 4.

Table C.7.2. Summary of assigned quality control flags

Flag	Definition	CFC-11	CFC-12
2	Good	658	662
3	Questionable	29	32
4	Bad (Faulty)	47	41
5	Not reported	7	7
6	Mean of replicate measurements	35	34
	Total number of samples	776	776

We show the vertical section of CFC-11 and CFC-12 along WHP-P9 line (Figure C.7.8) observed in this work.
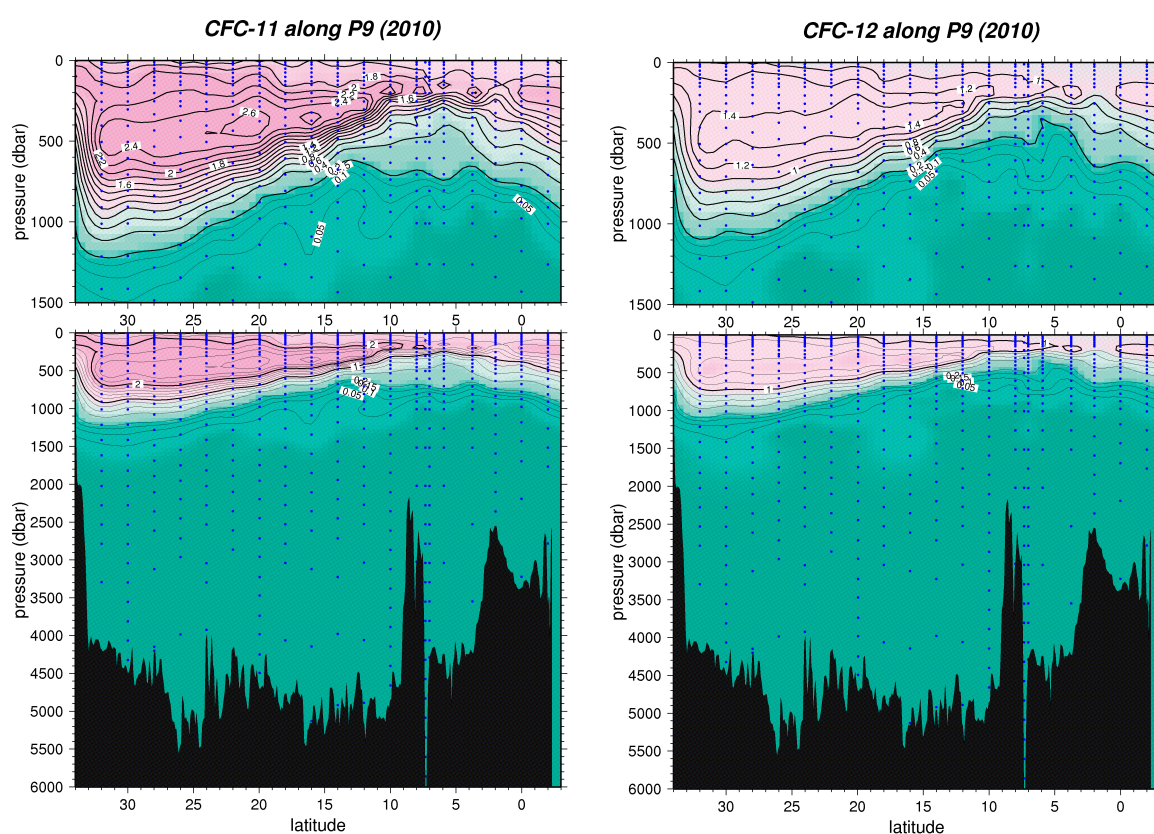
Figure C.7.8. Vertical section of CFC-11 and CFC-12 concentration (in pmol kg^{-1}) along WHP-P9 line observed in this work. Blue dots indicate sampling layer.

Also we show the previous CFC-11 section along WHP-P9 line conducted by JMA in 1994 (Figure C.7.9), and vertical profiles of CFCs at cross-point with WHP-P2 conducted by Scripps Institution of Oceanography (SIO) in 2004 (Figure C.7.10) and WHP-P3 conducted by SIO in 1985 and by Japan Agency for Marine-Earth Science and Technology (JAMSTEC) in 2005/06 (C.7.11). The implication of these results will be discussed elsewhere.
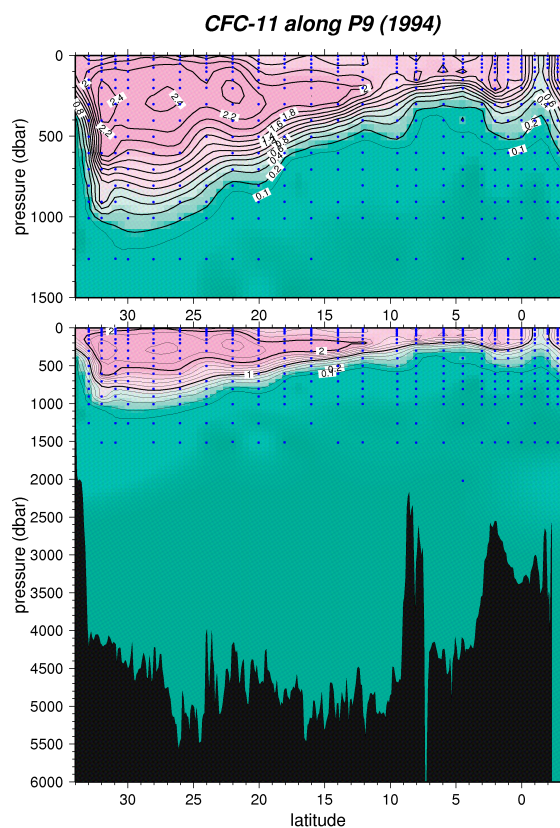
Figure C.7.9. Section of CFC-11 concentration (in pmol kg^{-1}) along WHP-P9 line observed in 1994 by JMA. Blue dots indicate sampling layer.

Comparison at cross-point of WHP-P2 in 2004
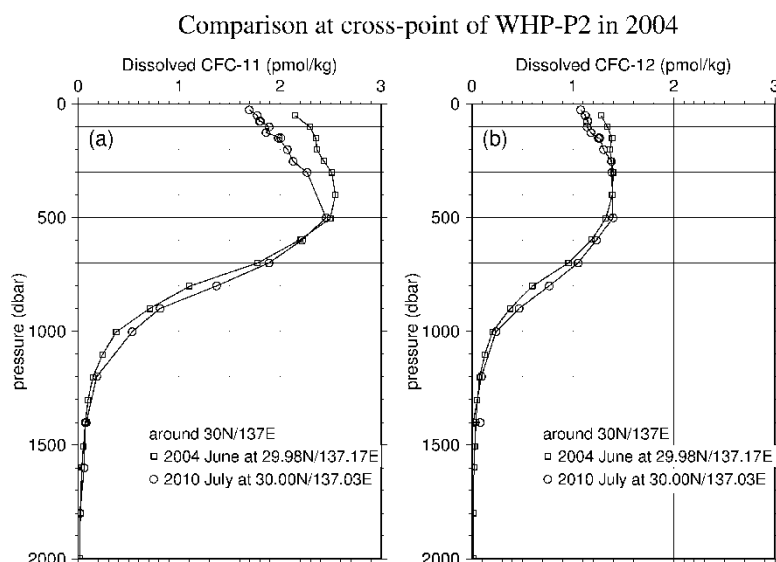
Figure C.7.10. Comparison of dissolved CFCs profiles at cross-point of (a) CFC-11 (left panel) and (b) CFC-12 (right panel). Circle and square show WHP-P9 revisit in 2010 by JMA and WHP-P2 in 2004 by SIO, respectively.

Comparison at cross-point of WHP-P3 in 2005/06
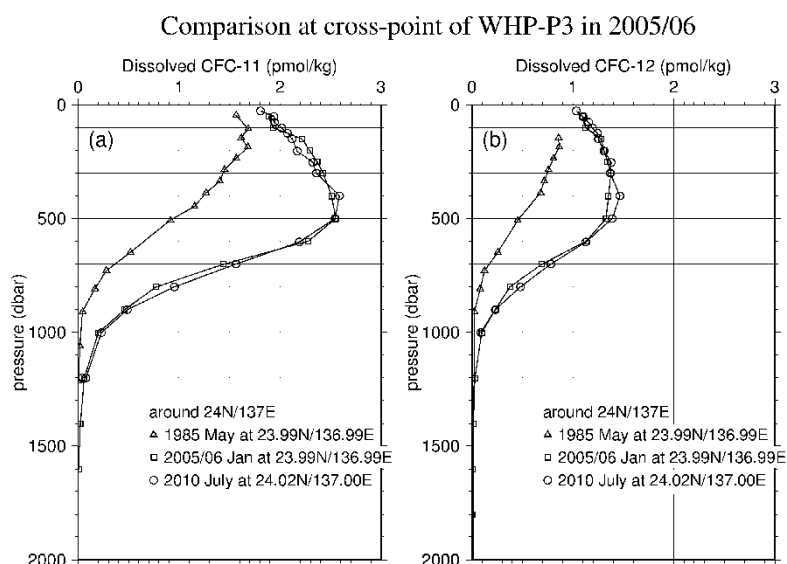
Figure C.7.11. Comparison of dissolved CFCs profiles at cross-point of (a) CFC-11 (left panel) and (b) CFC-12 (right panel). Triangle, square, circle show the WHP-P3 in 1985 by SIO, WHP-P3 in 2005/06 by JAMSTEC and WHP-P9 revisit in 2010 by JMA, respectively.

C7-11

References

Bullister, J.L., and R.F. Weiss (1988): Determination of $CC1_3F$ and $CC1_2F_2$ seawater and air.

Deep-Sea Res., **25**, 839-853.

8. *Phytopigment (chlorophyll-a and phaeopigments)*

13 December 2013

(1) Personnel

Yusuke TAKATANI (GEMD/JMA)

Shinichiro UMEDA (GEMD/JMA)

(2) Station occupied

A total of 50 stations (Leg 1: 29, Leg 2: 21) were occupied for phytopigment. Station location and sampling layers of phytopigment are shown in Figure C.8.1.
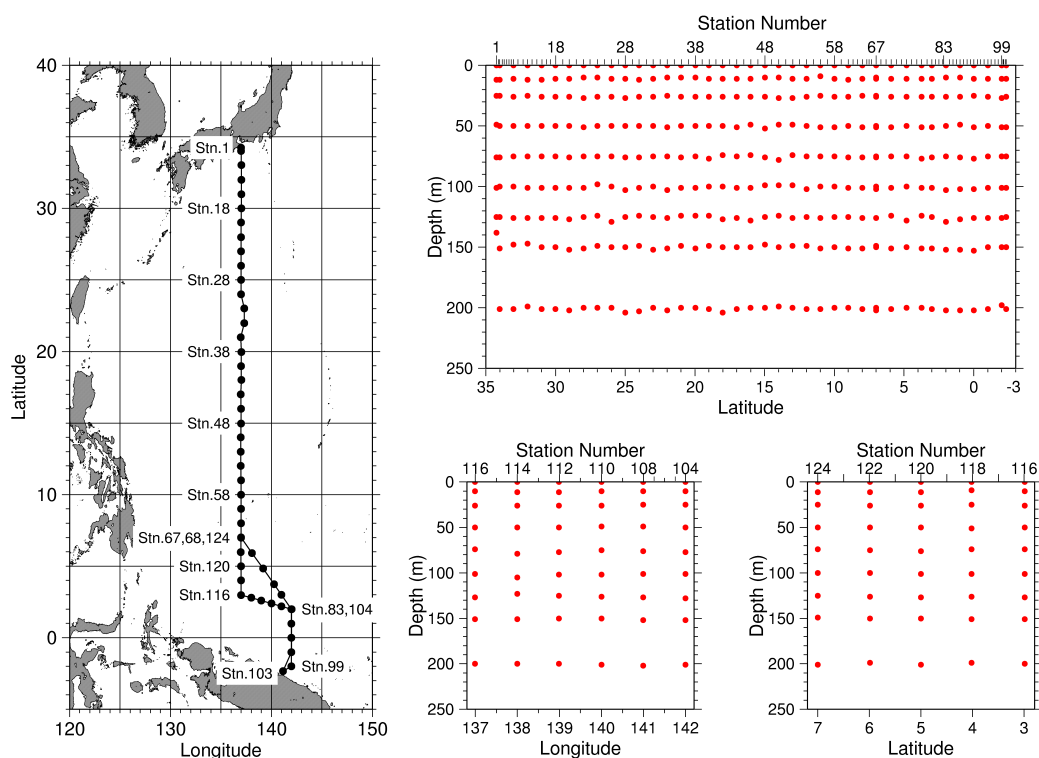
Figure C.8.1. Sation location (left panel) and sampling layers of phytopigment (right panels).

(3) Reagents

N,N-dimethylformamide (DMF)

0.5 N hydrochloric acid (0.5N HCl)

Chlorophyll-*a* standard from *Anacystis nidulans* algae (Lot. BCBB4166) manufactured by

Sigma Chemical Co.

Rhodamine WT manufactured by Turner Designs.

(4)   Instruments

Fluorometer; 10-AU (S/N:6718) manufactured by Turner Designs

Spectrophotometer; UV-1800 (S/N:A114547) manufactured by Shimadzu Co. Ltd.

Glass Fiber Filiter; Whatman GF/F filter (25 mm)

(5)   Standardization

A chlorophyll-*a* standard calibration for fluorometric determination was performed by the method described by *UNESCO* (1994). Before standardization, fluorometer was calibrated by using 100 % DMF and a Rhodamine solution diluted to 1ppm with deionized water. Chlorophyll-*a* standard was dissolved in DMF. The concentration of chlorophyll-*a* solution was determined spectrophotometrically as follows;

$$\text{Chl } \alpha \text{ concentration } (\mu g/ml) = A_{chl}/\text{specific absorption coefficient}$$

where A_{chl} is the difference between absorbance at 663.8 nm and 750 nm. The specific absorption coefficient is 88.74 L/g·cm (*Porra et al.*, 1989). Using this precise chlorophyll-*a* concentration, the linear calibration factor (f_{ph}) and the acidification coefficient (R) were calculated. f_{ph} was calibrated for each cuvette as the slope of the unacidified fluorometric reading vs. chlorophyll-*a* concentration calculated spectrophotometrically. R was calculated by averaging the ratio of the unacidified and acidified readings of pure chlorophyll-*a*. Table C.8.1 shows f_{ph} and R in this cruise.

Table C.8.1. f_{ph} and R determined by the standardization.

Linear calibration factor (f_{ph})	5.13
Acidification coefficient (R)	1.848

(6) Seawater sampling and measurement

Seawater samples were collected from 10-liters Niskin bottle attached the CTD-system and a stainless steel bucket for the surface in 200 ml. The seawater samples were immediately filtered through 25 mm GF/F filter by low vacuum pressure, and the particulate matter was made to adsorb to the filter. The filter was put into the vial containing 9 ml of DMF, then stored to extract phytogigment in the refrigerator for more than 24 hours at –30 deg-C until analysis.

After the extracts were put on the room temperature for at least one hour in the dark, only the extracts except the filter were decanted from the vial to the cuvette. Fluorometer readings for each cuvettes were taken before and after acidification with 1-2 drops 0.5 N HCl. Chlorophyll-*a* (Chl) and phaeopigment (Phaeo) concentration in the sample are calculated using the following equations;

$$\text{Chl (μg/l)} = \frac{F_0 - F_a}{f_{ph} \cdot (R - 1)} \cdot \frac{v}{V}$$

$$\text{Phaeo (μg/l)} = \frac{R \cdot F_0 - F_a}{f_{ph} \cdot (R - 1)} \cdot \frac{v}{V}$$

F_0 = reading before acidification

F_a = reading after acidification

R = acidification coefficient (F_0/F_a) for pure chlorophyll-*a*

f_{ph} = linear calibration factor

v = extraction volume

V = sample volume

(7) Quality control flag assignment

Quality flag values were assigned to phytopigment measurements using the code defined in IOCCP Report No.14 (*Swift*, 2010). Measurement flags of 2 (good), 3 (questionable), and 4 (bad) have been assigned (Table C.8.2).

Table C.8.2. Summary of assigned quality control flags.

Flag	Definition	Chl	Phaeo
2	Good	437	437
3	Questionable	0	0
4	Bad (Faulty)	12	12
Total number		449	449

References

Porra, R. J., W. A. Thompson and P. E. Kriedemann (1989): Determination of accurate coefficients and simultaneous equations for assaying chlorophylls *a* and *b* extracted with four different solvents: verification of the concentration of chlorophyll standards by atomic absotption spectroscopy. *Biochem. Biophy. Acta,* ***975***, 384-394

Swift, J. H. (2010): Reference-quality water sample data: Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.**14**, ICPO Pub. 134, 2010 ver.1*

UNESCO (1994), Protocols for the joint global ocean flux study (JGOFS) core measurements: Measurement of chlorophyll *a* and phaeopigments by fluorometric analysis, *IOC manuals and guides **29**, Chapter 14.*

9. *Lowered Acoustic Doppler Current Profiler*

13 December 2013

(1) Personnel

Tetsuya NAKAMURA (GEMD/JMA)

Yoshikazu HIGASHI (GEMD/JMA)

Tomoyuki KITAMURA (GEMD/JMA)

Takahiro SEGAWA (GEMD/JMA)

Keizo SHUTTA (GEMD/JMA)

Yasuaki BUNGI (GEMD/JMA)

(2) Instrument and measurement

Direct flow measurement from sea surface to the bottom was carried out using a Lowered Acoustic Doppler Current Profiler (LADCP). The instrument used was the RDI Workhorse Monitor 307.2 kHz unit (S/N 13666; Teledyne RD Instruments, USA). The instrument was attached on the CTD frame, orientating downward. The CPU firmware version was 50.36.

One ping raw data were recorded. Settings for the collecting data were as listed in Table C.9.1. A total of 124 operations were made with the CTD observations. The performance of the LADCP was good between Stn.1 (RF3649) and Stn.42 (RF3690). From Stn.43 (RF3691) the echo intensity of beam 4 got weak, and from Stn.50 (RF3698) it might be broken down. From Stn.109 (RF3757), the beam 1 might be also broken down. And besides, data transfer errors often occurred during download process from the LADCP to the PC. So the data processing was performed for 101 stations.

Table C9.1. Setting for the correcting data.

Bin length	8m
Bin number	25
Error Threshold	2000mm/s
Ping interval	1.0sec

(3) Data process and result

Vertical profiles of velocity are obtained by the inversion method (*Visbeck*, 2002). Both the up and down casts are used for the inversion. Since the first bin from LADCP is influenced by the turbulence generated by CTD frame, the weight for the inversion is set to small value of 0.1. The GPS navigation data are used in the calculation of the reference velocities and the bottom-track data are used for the correction of the reference velocities. Shipboard ADCP (SADCP) data averaged for 5 minutes are also included in the calculation. The CTD data are used for the sound speed and depth calculation. IGRF (International Geomagnetic Reference Field) 11th generation data are used for calculating magnetic deviation to correct the direction of velocity. In the processing, we use Matlab routines (version 8b: 5 April 2004) provided by M. Visbeck and G. Krahmann. We set the weight for SADCP data in the calculation to 3.0, so vertical profiles of velocity obtained by the inversion method is similar to SADCP upper 1000 dbar. The uncertainty of velocity observed by SADCP is about 10 cm/s. So we regard the error velocity from LADCP upper 1000 dbar as about 10 cm/s. Figure C.8.1 and C.8.2 show the results of the zonal velocity (eastward is positive) and the meridional velocity (northward is positive), respectively. The major currents in the western Pacific such as the Kuroshio (34°N to 32°N), the Equatorial Under Current (EQ to 3°N), and New Guinea Coastal Under Current (around 2°S) appeared in the figures. Figure C.8.3 shows error velocity estimated by the inversion method. The error velocities are very small (less than 5 cm/s) upper 1000 dbar and adjacent to the bottom from Stn.1 to Stn.42. After Stn.43, the error velocity below 1000 dbar become larger and exceed 50 cm/s at maximum. This is because the echo intensity of beam 4 got weak down after Stn.43.
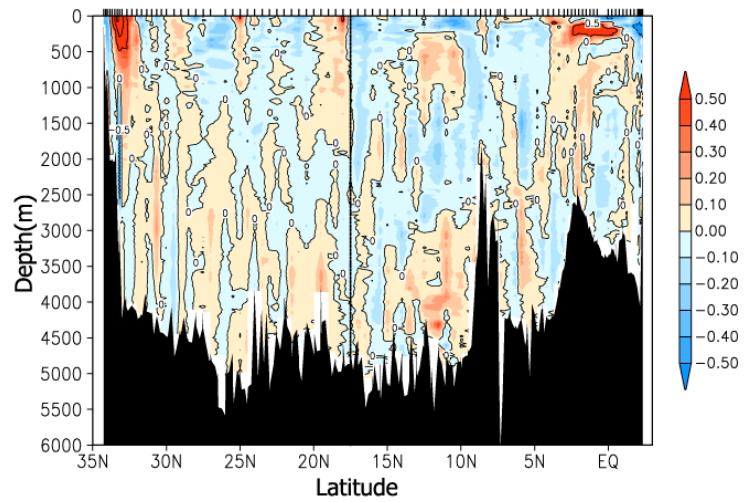
Figure C.9.1. The cross-section of zonal velocity (m/s, eastward is positive). Black line shows the Stn.43. The data south of the Stn.43 is doubtful due to malfunction of the instrument.
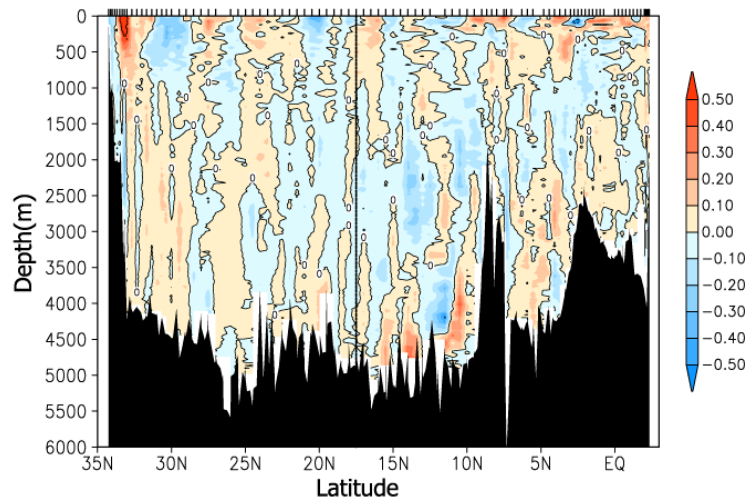
Figure C.9.2 The cross-section of meridional velocity (m/s, northward is positive). Black line shows the Stn.43. Note that southern of Stn.43 is doubtful.
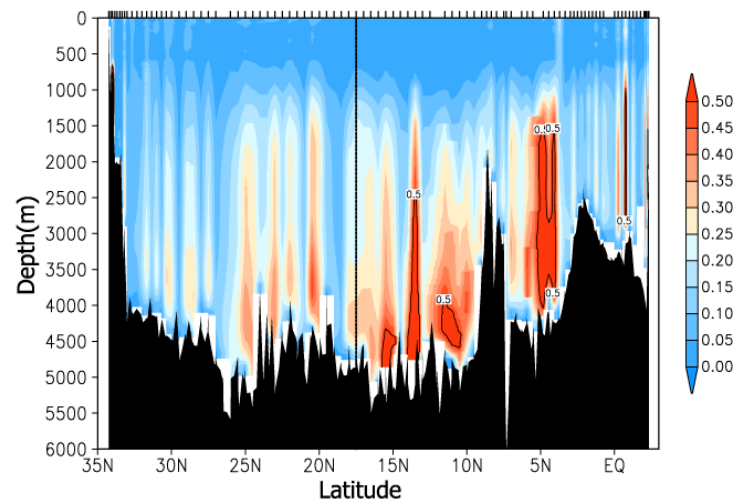
Figure C.9.3. Cross-section of error velocity (m/s) estimated by the inversion method. Black line shows the Stn.43. Note that southern of Stn.43 is doubtful.

Reference

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

References

Akaike, H. (1974): A new look at the statistical model identification. *IEEE Transactions on Automatic Control, **19**:716 – 722.*

Aoyama, M., A. G. Dickson, D. J. Hydes, A. Murata, J. R. Oh, P. Roose and E. Malcom. S. Woodward (2010), Comparability of nutrients in the world's ocean, *INSS international workshop 10-12 Feb. 2009, Paris*.

Aoyama, M., S. Becker, K. Sato and D. Schuller (2009), Plan of use of RMNS during the CLIVAR P6 revisited cruise by R/V Melville. (unpublished manuscript).

Aoyama, M., T. Joyce, T. Kawano and Y. Takatsuki (2003): Standards seawater comparison up to P129. *Deep-sea Research, 1, Vol. **49**, 1103-1114.*

Armstrong, F. A. J., C. R. Stearns and J. D. H. Strickland (1967), The measurement of upwelling and subsequent biological processes by means of the Technicon TM Autoanalyzer TM and associated equipment, *Deep-Sea Res., **14**(3), 381–389.*

Budeus. G., and W. Schneider (1998): In-situ temperature calibration: A remark on instruments and methods. *International WOCE Newsletter, No.**30**, WOCE International Project Office, Southampton, United Kingdom, 16-18.*

Chen, C.-T. and F. J. Millero (1977): Speed of sound in seawater at high pressures. *J. Acoust. Soc. Am. **62(5)**,* 1129-1135.

Cullberson, A.H. (1994), Dissolved oxygen, in *WHPO Pub. **91-1** Rev. 1*, November 1994, Woods Hole, Mass., USA.

Cullberson, A.H., G. Knapp, M.C. Stalcup, R.T. Williams, and F. Zemlyak (1991), A comparison of methods for the determination of dissolved oxygen in seawater, *WHPO Pub. **91-2***, August 1991, Woods Hole, Mass., USA.

DOE (1994), Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water; version 2. A.G. Dickson and C. Goyet (eds), ORNL/CDIAC-74.

Garcìa, H. E., and L. I. Gordon (1992): Oxygen solubility in seawater: Better fitting equations. *Limnol. Oceanogr., 37, 1307-1312*.

Gouretski, V.V. and K. Jancke (2001), Systematic errors as the causes for an apparent deep water property variability: global analysis of the WOCE and historical hydrographic data, *Prog. Oceanogr., **48**, 337-402.*

Grasshoff, K., Ehrhardt, M., Kremling K. et al. (1983), Methods of seawater analysis. 2nd rev, *Weinheim: Verlag Chemie, Germany, West.*

Holm-Hansen, O., and B. Riemann (1978): chlorophyll *a* determination: improvements in methodology. *Oikos, **30**,* 438-447.

Holm-Hansen, O., C. J. Lorenzen, R. W. Holmes and J. D. H. Strickland (1965): Fluorometric determination of chlorophyll. *J. Cons. Perm. Int. Explor. Mer., **30**,* 3-15.

JAMSTEC (2007), WHP P3 REVISIT DATA BOOK, WHP P03 REVISIT in 2005.

JAMSTEC, WHP P03 REVISIT DATA BOOK (2001), edited by T. Kawano and H. Uchida, JAMSTEC.

Johson, G.C., P.E. Robbins, and G.E. Hufford (2001), Systematic adjustments of hydrographic sections for internal consistency, *J. Atomos. Oceanic Technol.*, *18*, 1234-1244.

Joyce, T. M. (1988): On in-situ "calibration" of shipboard ADCPs. *J. Atmos. Oceanic Technol., 6*, 169-172.

Langdon, C. (2010), Determination of dissolved oxygen in seawater by Winkler titration using the amperometric technique, *IOCCP Report No.14, ICPO Pub. 134, 2010 ver.1*.

Larson, N., and A.M. Pedersen (1996): Temperature measurements in flowing water: Viscous heating of sensor tips. *Proc. of the First IGHEM Meeting, Montreal, QC, Canada, International Group for Hydraulic Efficiency Measurement.*
[Available online at http://www.seabird.com/technical_references/viscous.htm]

McTaggart, K. E., G. C. Johnson, M.C.Johnson, F.M.Delahoyde, and J.H.Swift (2010): The GO-SHIP Repeat Hydrography Manual : A Collection of Expert Reports and guidelines. IOCCP Report No *14*, ICPO Publication Series No. 134, version 1, 2010.

Murphy, J., and Riley, J.P. (1962), Analytica chimica *Acta 27, 31-36*.

Murray, C.N., J.P. Riley and T.R.S. Wilson (1968), The solubility of oxygen in Winkler reagents used for the determination of dissolved oxygen, *Deep-Sea Res., 15*, 237-238.

Porra, R. J., W. A. Thompson and P. E. Kriedemann (1989): Determination of accurate coefficients and simultaneous equations for assaying chlorophylls *a* and *b* extracted with four different solvents: verification of the concentration of chlorophyll standards by atomic absotption spectroscopy. *Biochem. Biophy. Acta, 975*, 384-394.

Sea-Bird Electronics (2009): SBE 43 dissolved oxygen (DO) sensor – hysteresis corrections, *Application note no. 64-3, 7 pp.*

Shanno, David F. (1970): Conditioning of quasi-Newton methods for function minimization. *Math. Comput. 24, 647-656. MR 42 #8905.*

Swift, J. H. (2010): Reference-quality water sample data: Notes on acquisition, record keeping, and evaluation. *IOCCP Report No.14, ICPO Pub. 134, 2010 ver.1*.

Uchida, H., K. Ohyama, S. Ozawa, and M. Fukasawa (2007): In-situ calibration of the Sea-Bird 9plus CTD thermometer. *J. Atmos. Oceanic Technol.24, 1961-1967.*

Uchida, H., T. Kawano, I. Kaneko, and M. Fukasawa (2008): In –situ calibration of optode-based oxygen sensors. *J. Atmos. Oceanic Technol., 25, 2271-2281.*

UNESCO (1981): Tenth report of the Joint Panel on Oceanographic Tables and Standards. *UNESCO Tech. Papers in Mar. Sci., 36, 25 pp.*

UNESCO (1994), Protocols for the joint global ocean flux study (JGOFS) core measurements: Measurement of chlorophyll *a* and phaeopigments by fluorometric analysis, *IOC manuals and guides 29, Chapter 14*.

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

Data History

- **File Online Jerry Kappa**

  [p09_49RY20100706_do.pdf (download)](download) #4596a
  Date: 2021-02-25
  Current Status: merged
  Notes

  ```
  Includes new CTD/Hydrography and LADCP sections (dated 2013-12-13)
  ```

- **File Online Jerry Kappa**

  [p09_hy1_20191112.csv (download)](download) #3c110
  Date: 2020-10-15
  Current Status: unprocessed

- **File Online Jerry Kappa**

  [49UP20100706_C_hydrography_20201015.docx (download)](download) #7affd
  Date: 2020-10-15
  Current Status: unprocessed

- **File Submission Daisuke SASANO**

  [49UP20100706_C_hydrography_20201015.docx (download)](download) #7affd
  Date: 2020-10-15
  Current Status: unprocessed
  Notes

  ```
  I submitted "bottle_oxygen_update_20181113.doc" in 2019-11-01, but the
  content has already been included in the previous cruise report.
  Additionally, "silicate_update_20180831.doc" submitted in the same time
  is included in this uploading cruise report. Therefore, please remove
  the unnecessary files "silicate_update_20180831.doc" and
  "bottle_oxygen_update_20181113.doc" from CCHDO database.
  ```

- **File Submission Daisuke SASANO**

  [p09_hy1_20191112.csv (download)](#) #3c110
  Date: 2020-10-15
  Current Status: unprocessed
  Notes

  ```
  I submitted "bottle_oxygen_update_20181113.doc" in 2019-11-01, but the
  content has already been included in the previous cruise report.
  Additionally, "silicate_update_20180831.doc" submitted in the same time
  is included in this uploading cruise report. Therefore, please remove
  the unnecessary files "silicate_update_20180831.doc" and
  "bottle_oxygen_update_20181113.doc" from CCHDO database.
  ```

- **File Online Carolina Berys**

  [49UP20100706.exc.csv (download)](#) #b7448
  Date: 2020-06-25
  Current Status: unprocessed

- **File Submission Robert Key**

  [49UP20100706.exc.csv (download)](#) #b7448
  Date: 2020-06-25
  Current Status: unprocessed
  Notes

  ```
  This is a reformat and new header for the Japanese file p09_hy1.csv
  that you posted with date of 2018-05-12. I calculated NITRAT from
  NO3+NO2 - NITRIT and added the header, but otherwise no changes.
  ```

- **File Merge CCHSIO**

  [20120208_p09_ct1.zip (download)](#) #eb915
  Date: 2020-06-22
  Current Status: merged

- **File Merge CCHSIO**

  [p09_49RY20100706_nc_ctd.zip (download)](download) #f0cad
  Date: 2020-06-22
  Current Status: merged

- **File Merge CCHSIO**

  [p09_49RY20100706_ct1.zip (download)](download) #b0163
  Date: 2020-06-22
  Current Status: merged

- **File Merge CCHSIO**

  [ct1.zip (download)](download) #f18e4
  Date: 2020-06-22
  Current Status: merged

- **update online CTD files CCHSIO**

  Date: 2020-06-22
  Data Type: CTD
  Action: Website Update
  Note:

```
    2010 49RY20100706 processing - CTD/merge -
CTDPRS,CTDTMP,CTDSAL,CTDOXY

2020-06-22

CCHSIO

Submission

filename             submitted by    date        id
-------------------- --------------- ---------- -----
ct1.zip              Toshiya Nakano  2018-05-12 13996
20120208_p09_ct1.zip Toshiya Nakano  2012-02-21  6076

Changes
-------

20120208_p09_ct1.zip
        - older file, did not use.  moved to Data History
```

```
ct1.zip
        - Renamed files to match EXCHANGE standard. Put original file
name in file as a comment.
        - Changed EXPOCODE from 49UP20100706_2 and 49UP20100706_1 to
49RY20100706.  Saved submitted EXPOCODE as comment.
        - Added cruise, units, and citation comments.


Conversion
----------

file                    converted from      software
----------------------- ------------------- -----------------------
49RY20100706_nc_ctd.zip 49RY20100706_ct1.zip hydro 0.8.2-57-g8aa7d7a


Updated Files Manifest
----------------------

file                    stamp
----------------------- --------------
49RY20100706_ct1.zip    20200622CCHSIO
49RY20100706_nc_ctd.zip 20200622CCHSIO

:Updated parameters: CTDPRS,CTDTMP,CTDSAL,CTDOXY

opened in JOA 5.4.0 with no apparent problems:
     49RY20100706_ct1.zip
     49RY20100706_nc_ctd.zip

opened in ODV with no apparent problems:
     49RY20100706_ct1.zip
```

- **File Online Carolina Berys**

  [49UP20100706_P09_nut_RM_measurement.csv (download)](download) #74cd2
  Date: 2020-04-20
  Current Status: unprocessed

- **File Submission Daisuke Sasano**

  [49UP20100706_P09_nut_RM_measurement.csv (download)](download) #74cd2
  Date: 2019-11-01
  Current Status: unprocessed

- **File Online** Carolina Berys

  [ct1.zip (download)](download) #f18e4
  Date: 2018-06-09
  Current Status: merged

- **File Online** Carolina Berys

  [p09_hy1.csv (download)](download) #b8d47
  Date: 2018-06-09
  Current Status: unprocessed

- **File Online** Carolina Berys

  [p09su.txt (download)](download) #2428a
  Date: 2018-06-09
  Current Status: unprocessed

- **File Submission** Toshiya NAKANO

  [p09su.txt (download)](download) #2428a
  Date: 2018-05-12
  Current Status: unprocessed
  Notes

  ```
  CTDO2 and bottle data were updated.
  ```

- **File Submission** Toshiya NAKANO

  [p09_hy1.csv (download)](download) #b8d47
  Date: 2018-05-12
  Current Status: unprocessed
  Notes

  ```
  CTDO2 and bottle data were updated.
  ```

- **File Submission Toshiya NAKANO**

  ct1.zip (download) #f18e4
  Date: 2018-05-12
  Current Status: merged
  Notes

  ```
  CTDO2 and bottle data were updated.
  ```

- **File Online CCHDO System**

  49RY20100706su.txt (download) #a33e6
  Date: 2015-04-23
  Current Status: dataset
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Online CCHDO System**

  p09_49RY20100706trk.jpg (download) #28b8f
  Date: 2015-04-23
  Current Status: merged
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Online CCHDO System**

  p09_49RY20100706do.txt (download) #b6a44
  Date: 2015-04-23
  Current Status: dataset
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Online CCHDO System**

  [p09_49RY20100706do.pdf (download)](download) #4596a
  Date: 2015-04-23
  Current Status: dataset
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Online CCHDO System**

  [p09_49RY20100706trk.gif (download)](download) #332e5
  Date: 2015-04-23
  Current Status: merged
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Online CCHDO System**

  [49RY20100706_nc_ctd.zip (download)](download) #acde2
  Date: 2015-04-23
  Current Status: dataset
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Online CCHDO System**

  [49RY20100706_ct1.zip (download)](download) #6fe61
  Date: 2015-04-23
  Current Status: dataset
  Notes

  ```
  Files migrated to new CCHDO backend, there is not enough information to
  know where this file should go in the timeline.
  ```

- **File Merge Carolina Berys**

  [20120321_p09su.txt (download)](download) #70a67
  Date: 2014-08-28
  Current Status: merged
  Notes

  ```
  SUM
  ```

- **Put SUM file online Geetha Ratnam**

  Date: 2014-08-28
  Data Type: SUM
  Action: Website Update
  Note:

  ```
  =====================================
  P09 2010 49RY20100706 processing - SUM
  =====================================

  2014-08-28

  G Ratnam

  .. contents:: :depth: 2

  Submission
  ==========

  ================== ============== ========== ========= ====
  filename           submitted by   date       data type id
  ================== ============== ========== ========= ====
  20120321_p09su.txt Toshiya Nakano 2012-02-21 SUM       None
  ================== ============== ========== ========= ====

  Process
  =======

  Changes
  -------
  -Put SUM file online.
  20120321_p09su.txt
  ~~~~~~~~~~~~~~~~~~

  .. _merge:

  Merge
  -----

  20120321_p09su.txt
  ```

```
~~~~~~~~~~~~~~~~~~

Directories
===========
:working directory:

/data/co2clivar/pacific/p09/p09_49RY20100706/original/2014.08.28_SUM_GR
:cruise directory:
  /data/co2clivar/pacific/p09/p09_49RY20100706

Updated Files Manifest
======================
================= =====
file              stamp
================= =====
49RY20100706su.txt
================= =====
```

- **Available under 'Files as received' CCHDO Staff**

  Date: 2014-02-14
  Data Type: CrsRpt/BTL
  Action: Website Update
  Note:

  ```
  The following files are now available online under 'Files as received',
  unprocessed by the CCHDO.

  C_hydrographic_20131213.doc
  Table_of_contents_20131213.doc
  B_underway_20131213.doc
  20131213_p09_hy1.csv
  ```

- **File Submission Toshiya NAKANO**

  20131213_p09_hy1.csv (download) #e7da7
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Bottle file
  ```

- **File Submission** Toshiya NAKANO

  [20131213_p09_hy1.csv (download)](#) #e7da7
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Expocode: 49UP20100706
  Ship: Ryofu Maru
  Woce Line: P09
  Note: None
  ```

- **File Submission** Toshiya NAKANO

  [Table_of_contents_20131213.doc (download)](#) #441c4
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Cruise documentation
  ```

- **File Submission** Toshiya NAKANO

  [Table_of_contents_20131213.doc (download)](#) #441c4
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Expocode: 49UP20100706
  Ship: Ryofu Maru
  Woce Line: P09
  Note: None
  ```

- **File Submission** Toshiya NAKANO

  [C_hydrographic_20131213.doc (download)](#) #5fa00
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Cruise documentation
  ```

- **File Submission** Toshiya NAKANO

  [C_hydrographic_20131213.doc (download)](#) #5fa00
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Expocode: 49UP20100706
  Ship: Ryofu Maru
  Woce Line: P09
  Note: None
  ```

- **File Submission** Toshiya NAKANO

  [B_underway_20131213.doc (download)](#) #dcaa4
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Cruise documentation
  ```

- **File Submission** Toshiya NAKANO

  [B_underway_20131213.doc (download)](#) #dcaa4
  Date: 2013-12-12
  Current Status: unprocessed
  Notes

  ```
  Expocode: 49UP20100706
  Ship: Ryofu Maru
  Woce Line: P09
  Note: None
  ```

- **to go online** Toshiya Nakano

  Date: 2013-12-12
  Data Type: BTL/CrsRpt
  Action: Submitted

- **ExpoCode changed Matt Shen**

  Date: 2013-12-10
  Data Type: ExpoCode
  Action: Website Update
  Note:

  ```
  ======================
  49RY20100706 processing
  ======================

  2013-12-10

  M Shen

  .. contents:: :depth: 2

  Process
  =======

  ExpoCode changed from 49UP20100706 to 49RY20100706. 49UP20100706 added
  as an alias for the cruise.
  Directories
  ===========
  :working directory:

  /data/co2clivar/pacific/p09/./original/2013.12.10_expocode_correction_M
  YS
  :cruise directory:
    /data/co2clivar/pacific/p09/p09_49UP20100706

  Updated Files Manifest
  ======================
  ```

- **to go online Toshiya Nakano**

  Date: 2013-12-05
  Data Type: CrsRpt
  Action: Submitted

- **to go online Toshiya Nakano**

  Date: 2013-12-05
  Data Type: CTD
  Action: Submitted

- **to go online** Toshiya Nakano

  Date: 2013-12-05
  Data Type: BTL
  Action: Submitted

- **Available under 'Files as received'** Carolina Berys

  Date: 2012-04-17
  Data Type: BTL/SUM
  Action: Website Updated
  Note:

  ```
  File 20120321_p09_hy1.csv containing bottle file update, submitted by
  Toshiya Nakano on 2012-03-21, available under 'Files as received',
  unprocessed by CCHDO.

  File 20120321_p09su.txt containing SUM file update, submitted by
  Toshiya Nakano on 2012-03-21, available under 'Files as received',
  unprocessed by CCHDO.
  ```


- **File Submission** Nakano, Toshiya

  [20120321_p09su.txt (download)](download) #70a67
  Date: 2012-03-21
  Current Status: merged
  Notes

  ```
  Expocode: 49RY20100706
  Ship: Ryofu Maru
  Woce Line: P9
  Note: None
  ```

- **Updated Parameters** Toshiya Nakano

  Date: 2012-03-21
  Data Type: BTL/SUM
  Action: Submitted
  Note:

  ```
  I update sum/bottle data for P9 revisit cruise.

  summary: 20120321_p09su.txt
  ?1st line? 20111209JMAGEMD -> 20120321JMAGEMD

  bottle: 20120321_p09su.csv
  ?parameter name?NITRAT -> NO2+NO3
  ?PH_TS_TMP -> 25.00
  ```

- **Available under 'Files as received'** Carolina Berys

  Date: 2012-03-14
  Data Type: CTD/BTL/SUM
  Action: Website Updated
  Note:

  ```
  Date:  2012-03-14

  Data Type: BTL/SUM/CTD/Documentation

  Action: Website Update

  Summary: Available under 'Files as received'

  Details:

  File 20111209_p09su.txt containing SUM file data, submitted by Toshiya
  Nakano on 2012-02-21, available under 'Files as received', unprocessed
  by CCHDO.

  File 20120118_p09_hy1.csv containing bottle data, submitted by Toshiya
  Nakano on 2012-02-21, available under 'Files as received', unprocessed
  by CCHDO.

  File 20120202_p09_in-vivo.txt containing RAWFLU/FLU/RATIO/CHL data,
  submitted by Toshiya Nakano on 2012-02-21, available under 'Files as
  received', unprocessed by CCHDO.

  File 20120208_p09_ct1.zip containing CTD data, submitted by Toshiya
  Nakano on 2012-02-21, available under 'Files as received', unprocessed
  by CCHDO.

  File P9_revisit_doc_20120222.zip containing Cruise Documentation,
  ```

submitted by Toshiya Nakano on 2012-02-21, available under 'Files as
received', unprocessed by CCHDO.

- **File Merge** Carolina Berys

  P9_revisit_doc_20120222.zip (download) #a62c5
  Date: 2012-03-08
  Current Status: merged
  Notes

  ```
  Documentation
  ```

- **New PDF and Text versions online** Jerry Kappa

  Date: 2012-03-08
  Data Type: CrsRpt
  Action: Website Updated

- **New Text version online** Jerry Kappa

  Date: 2012-03-08
  Data Type: CrsRpt
  Action: Website Updated
  Note:

  ```
  I just added a new text version of the cruise report
  (p09_49UP20100706do.pdf) to the co2clivar/pacific/p09/p09_49UP20100706/
  directory.  This is the final cruise report, although it still lacks
  sections on CO2, pH, CFCs, pCO2 and thermo-salinograph.  Updates will
  be made as they become available.

  This doc is already online because it replaces a doc by the same name
  that was previously online.  The older doc was renamed and moved to the
  "original" dir.
  ```

- **New PDF version online** Jerry Kappa

  Date: 2012-03-01
  Data Type: CrsRpt
  Action: Website Updated
  Note:

  ```
  I just added a new pdf version of the cruise report
  (p09_49UP20100706do.pdf) to the co2clivar/pacific/p09/p09_49UP20100706/
  directory.  This is the final cruise report, although it still lacks
  sections on CO2, pH, CFCs, pCO2 and thermo-salinograph.  Updates will
  be made as they become available.

  This doc is already online because it replaces a doc by the same name
  that was previously online.  The older doc was renamed and moved to the
  "original" dir.
  ```

- **File Submission** Toshiya Nakano

  [20120321_p09su.txt (download)](#) #70a67
  Date: 2012-02-21
  Current Status: merged
  Notes

  ```
  SUM file (update)
  ```

- **File Submission** Toshiya Nakano

  [20120208_p09_ct1.zip (download)](#) #eb915
  Date: 2012-02-21
  Current Status: merged
  Notes

  ```
  CTD
  ```

- **File Submission** Nakano, Toshiya

  [20120208_p09_ct1.zip (download)](#) #eb915
  Date: 2012-02-21
  Current Status: merged
  Notes

  ```
  Expocode: 49RY20100706
  Ship: Ryofu Maru
  Woce Line: P9
  Note: None
  ```

- **File Submission** Toshiya Nakano

  [P9_revisit_doc_20120222.zip (download)](#) #a62c5
  Date: 2012-02-21
  Current Status: merged
  Notes

  ```
  Documentation
  ```

- **File Submission** Nakano, Toshiya

  [P9_revisit_doc_20120222.zip (download)](#) #a62c5
  Date: 2012-02-21
  Current Status: merged
  Notes

  ```
  Expocode: 49RY20100706
  Ship: Ryofu Maru
  Woce Line: P9
  Note: None
  ```

- **File Submission** Toshiya Nakano

  [20120202_p09_in_vivo.txt (download)](#) #4cdee
  Date: 2012-02-21
  Current Status: unprocessed
  Notes

  ```
  RAWFLU, FLU, RATIO, CHL
  ```

- **File Submission** Nakano, Toshiya

  [20120202_p09_in_vivo.txt (download)](download) #4cdee
  Date: 2012-02-21
  Current Status: unprocessed
  Notes

  ```
  Expocode: 49RY20100706
  Ship: Ryofu Maru
  Woce Line: P9
  Note: None
  ```

- **to go online** Toshiya Nakano

  Date: 2012-02-21
  Data Type: CTD/BTL/SUM
  Action: Submitted

- **File Merge** Carolina Berys

  [20101228_WHP-P9_revisit_ct1_doc.zip (download)](download) #8cb8a
  Date: 2011-08-17
  Current Status: merged
  Notes

  ```
  CTDO/Cruise report
  ```

- **Corrected Exchange and new NetCDF files online** Matthew Shen

  Date: 2011-08-17
  Data Type: CTD
  Action: Website Updated
  Note:

  ```
  I made the following updates to the CTD files for
  http://cchdo.ucsd.edu/cruise/49UP20100706:

  Exchange CTD
  * Corrected file format
  _* TIM -> TIME
  ```

```
_* 49UP20100706 -> EXPOCODE = 49UP20100706
_* added END_DATA

NetCDF CTD
* Generated from Exchange CTD
```

- **CTD/Format Steve Diggs**

  Date: 2011-03-14
  Data Type: CTD/CTDO2
  Action: Files need format corrections
  Note:

  ```
  CTD files as received need only a few modifications:
    - TIM -> TIME
    - 49UP20100706 -> EXPOCODE = 49UP20100706
    - END_DATA at the end of each file
  Matt Shen and I will make the corrections and place the data (and
  documentation) online
  ```

- **Available under 'Updates' Carolina Berys**

  Date: 2011-02-02
  Data Type: CTD02/Report
  Action: Website Update
  Note:

  ```
  File 20101228_WHP-P9_revisit_ct1_doc.zip containing CTD data
  and Cruise Report submitted by
  Toshiya Nakano on 2010-12-27, available under 'Files as received',
  unprocessed
  by CCHDO.
  ```

- **File Submission Toshiya Nakano**

  [20101228_WHP-P9_revisit_ct1_doc.zip (download)](download) #8cb8a
  Date: 2010-12-27
  Current Status: merged
  Notes

  ```
  preliminary CTDO2 dataset and document of RF10-05 cruise (WHP-P9
  revisit)
  ```

- **File Submission** Nakano, Toshiya

  [20101228_WHP-P9_revisit_ct1_doc.zip (download)](#) #8cb8a
  Date: 2010-12-27
  Current Status: merged
  Notes

  ```
  Expocode: 49UP20100706 (RF10-05)
  Ship: Ryofu Maru
  Woce Line: P9
  Note: Dear Dr. James H. Swift

  I send the preliminary CTDO2 dataset and document of RF10-05 cruise
  (WHP-P9 revisit).

  Sincerely yours,
  -------------------------------------------
  Dr. Toshiya NAKANO
  Marine Division
  Global Environment and Marine Department
  Japan Meteorological Agency
  1-3-4 Otemachi Chiyoda-ku, Tokyo, 100-8122 Japan
  e-mail: nakano_t@met.kishou.go.jp
  -------------------------------------------
  ```

- **Preliminary** Toshiya Nakano

  Date: 2010-12-27
  Data Type: CTDO2
  Action: Submitted
  Note:

  ```
  I send the preliminary CTDO2 dataset and document of RF10-05 cruise
  (WHP-P9 revisit).
  ```