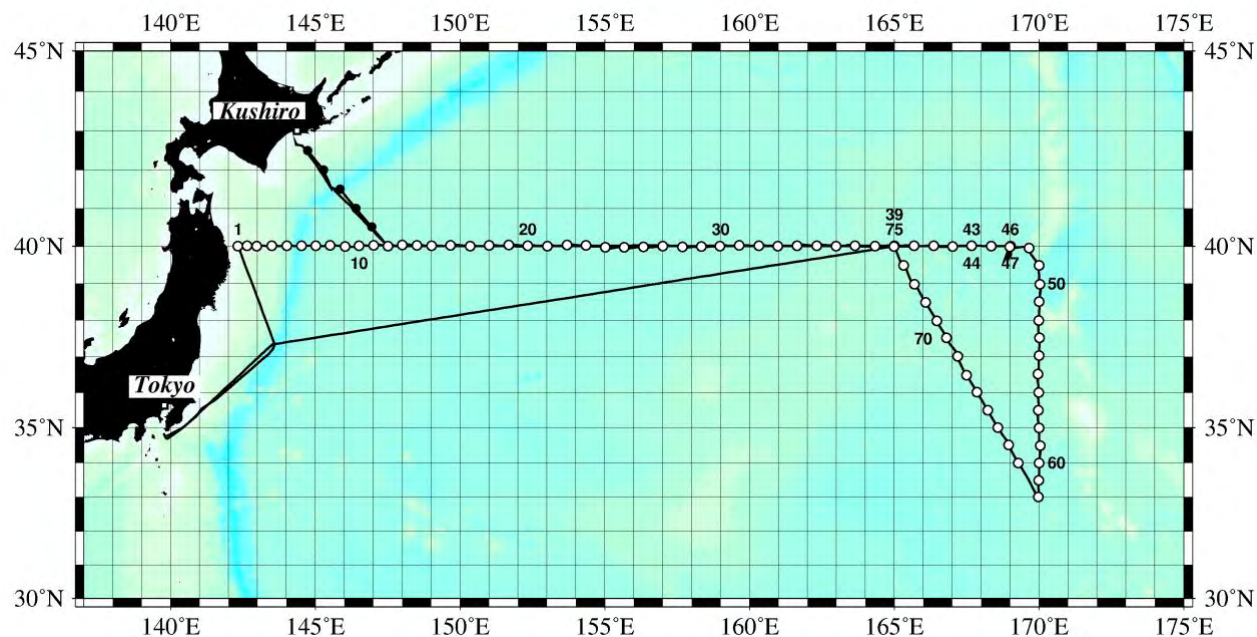


CRUISE REPORT: RF12-06

(Updated JAN 2021)



HIGHLIGHTS

Cruise Summary Information

WOCE Section Designation	RF12-06
Expedition designation (ExpoCodes)	49RY20120726 (aka: 49UP20120726, 40N)
Chief Scientists	Hitomi KAMIYA
Dates	2012 JUL 26 - 2012 AUG 16 Leg 1 2012 AUG 21 - 2012 SEP 13 Leg 2
Ship	<i>R/V Ryofu Maru</i>
Ports of call	Tokyo - Kuroshima - Tokyo
Geographic Boundaries	40° 04.31' N 142° 18.89' E 170° 04.51' E 32° 59.86' N
Stations	75
Floats and drifters deployed	2 profiling floats and 1 drifting ocean data buoy
Moorings deployed or recovered	0

Contact Information:

Hitomi KAMIYA

Marine Environment Monitoring and Analysis Center • Marine Division
Global Environment and Marine Department • Japan Meteorological Agency (JMA)
1-3-4, Otemachi • Chiyoda-ku • Tokyo • 100-8122 • JAPAN

Tel: +81-3-3212-8341 x5131 • Fax: +81-3-3211-6908 • Email: hkamiya@met.kishou.go.jp

Table of Contents

CRUISE REPORT: RF12-06	1
(Updated JAN 2021)	1
Highlights	1
Cruise Summary Information	1
A. Cruise Summary Information	5
C. Hydrographic Measurement Techniques and Calibration	12
1. CTDO₂ Measurements	12
(1) Personnel.....	12
(2) CTDO ₂ measurement system	12
(3) Pre-cruise calibration	13
(3.1) Pressure	13
(3.2) Temperature (ITS-90): SBE 3plus	13
(3.3) Deep Ocean Standards Thermometer Temperature (ITS-90): SBE 35	14
(3.4) Conductivity: SBE 4C	14
(3.5) Oxygen (RINKO III)	15
(4) Data correction and Post-cruise calibration.....	15
(4.1) Temporal change of deck pressure and Post-cruise calibration	15
(4.2) Temperature sensor (SBE 3plus)	15
(4.3) Conductivity sensor (SBE 4C)	18
(4.4) Oxygen sensor (RINKO III).....	22
(4.5) Results of detection of sea floor by the altimeter (PSA-916D)	26
2. Bottle Salinity	27
(1) Personnel.....	27
(2) Salinity measurement.....	27
(3) Sampling and measurement	27
(4) Stations occupied	27
(5) Result.....	29
(5.1) Ambient temperature, bath temperature and SSW measurements	29
(5.2) Replicate and Duplicate Samples.....	29
(5.3) Summary of assigned quality control flags.....	30
3. Bottle Oxygen	31
(1) Personnel.....	31
(2) Stations occupied	31
(3) Instrument.....	32
(4) Sampling and measurement	32
(5) Standardization	33
(6.1) Reagent blank	33
(6.2) Other blanks.....	34
(7) Quality Control	35
(7.1) Replicate and duplicate analyses.....	35
(7.2) Mutual comparison between each standard KIO ₃ solution	36
(7.3) Quality control flag assignment.....	36
(8) Uncertainty.....	37
Appendix.....	38
A1. Methods.....	38
A2. Reagents recipes	38
A3. Other blanks in oxygen measurement.....	39

References.....	39
4. Nutrients	41
(1) Personnel.....	41
(2) Stations occupied	41
(3) Instrument.....	42
(4) Sampling and measurement	42
(5) Nutrients standards.....	42
(5.1) Volumetric laboratory ware of in-house standards	42
(5.2) Reagents of standard	42
(5.3) Low nutrient seawater (LNSW).....	43
(5.4) In-house standard solutions	43
(6) Certified reference material	44
(7) Quality Control	44
(7.1) Replicate and duplicate analyses.....	44
(7.2) Measurement of CRMs	47
(7.3) Precision of analysis in a run.....	48
(7.4) Limit of detection/quantitation of measurement	50
(7.5) Quality control flag assignment.....	50
(8) Uncertainty.....	51
(8.1) Uncertainty associated with concentration level: U_c	51
(8.2) Uncertainty of analysis between runs: U_s	52
(8.3) Uncertainty of analysis in a run: U_a	53
(8.4) Uncertainty of CRM concentration: U_r	53
(8.5) Combined relative standard uncertainty: U	53
Appendix.....	55
A1. Seawater sampling.....	55
A2. Measurement	55
A3. Data processing.....	58
A4. Reagents recipes	59
References	60
5. Phytopigments (chlorophyll-a and phaeopigment).....	61
(1) Personnel.....	61
(2) Stations occupied	61
(3) Reagents.....	62
(4) Instruments	62
(5) Standardization	62
(5.1) Determination of chlorophyll-a concentration of standard solution	62
(5.2) Determination of R and f_{ph}	63
(6) Seawater sampling and measurement	63
(7) Quality control flag assignment	63
References	64
CCHDO Data Processing Notes	65
• File Online Carolina Berys.....	65
• File Online Carolina Berys.....	65
• File Online Carolina Berys.....	65
• File Online Carolina Berys.....	65
• File Submission Toshiya NAKANO	65
• File Submission Toshiya NAKANO	65
• File Submission Toshiya NAKANO	65
• File Submission Toshiya NAKANO	66

• Confirmed as a GO-SHIP Contributor Andrew Barna	66
• File Merge cchdo_admin	66
• Put SUM file online Geetha Ratnam	66
• File Merge cchdo_admin	67
• Exchange and netCDF files online Rox Lee.....	67
• Available under 'Files as received' CCHDO Staff.....	69
• File Submission Robert M. Key.....	69
• File Submission Robert M. Key.....	70
• new PDF version online Jerry Kappa	70
• flags updated Bob Key	70
• change "0" flags to "9999" Bob Key.....	71
• Maps created Rox Lee.....	71
• Available under 'Files as received' CCHDO Staff.....	72
• ExpoCode changed Matt Shen	72
• File Submission Toshiya NAKANO	73
• File Submission Toshiya NAKANO	73
• File Submission Toshiya NAKANO	73
• File Submission Toshiya NAKANO	73
• File Submission Toshiya NAKANO	73
• File Submission Toshiya NAKANO	74
• File Submission Toshiya NAKANO	74
• File Submission Toshiya NAKANO	74
• to go online Toshiya Nakano	74

A. Cruise Summary Information

RF12-06 cruise was carried out during the period from July 26 to September 13, 2012. The cruise started from the east of Honshu, Japan, and sailed towards east along 40°N. This line was not observed in the WOCE (World Ocean Circulation Experiment) Hydrographic Programme.

R/V *Ryofu Maru* departed Tokyo (Japan) on July 26, 2012. Before the observation at the first station, all watch standers were drilled in the method of sample drawing and CTD operations near Izu-Oshima (34°42'N, 139°52'E). The hydrographic cast of CTDO₂ was started at the first station (Stn.1 (40°00'N, 142°19'E; RF4461)) on June 28. Leg 1 consisted of 43 stations from Stn.1 to Stn.43 (40°01'N, 167°40'E; RF4498). She called for Kushiro on August 16, 2012 (Leg 1). She left Kushiro on August 21, 2012 for Tokyo and arrived on September 13, 2012 (Leg 2). Leg 2 consisted of 32 stations from Stn.44 (40°01'N, 167°41'E; RF4504) to Stn.75 (39°59'N, 164°59'E; RF4535). To examine consistency of data, we carried out the observation twice at 40°N, 165°E (Stn.39 and 75), 40°N, 167°40'E (Stn.43 and 44) and 40°N, 169°E (Stn.46 and 47). In order to ensure a controlled spooling of the armored cable, we rewound the cable three times at 37°20'N, 143°35'E (about 7000 m depth), 40°N, 154°20'E (about 5560 m depth) and 41°30'N, 145°35'E (about 6000 m depth). Cruise track and station location are shown in [Figure 1](#).

A total of 75 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).

At each station, full-depth CTDO₂ (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 2](#) (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 phaeopigments). Underway measurements of partial pressure of carbon dioxide ($p\text{CO}_2$), temperature, salinity, chlorophyll-a, subsurface current, bathymetry and meteorological parameters were conducted along the cruise track.

One drifting ocean data buoy (WMO number : 21636) was deployed at 38°45.947'N, 142°50.188'E on June 28, 2012. Two ARGO floats (PROVOR: nke Instrumentation, France) were deployed at the request of JAMSTEC along the cruise track. The information of deployed floats is listed in [Table 1](#).

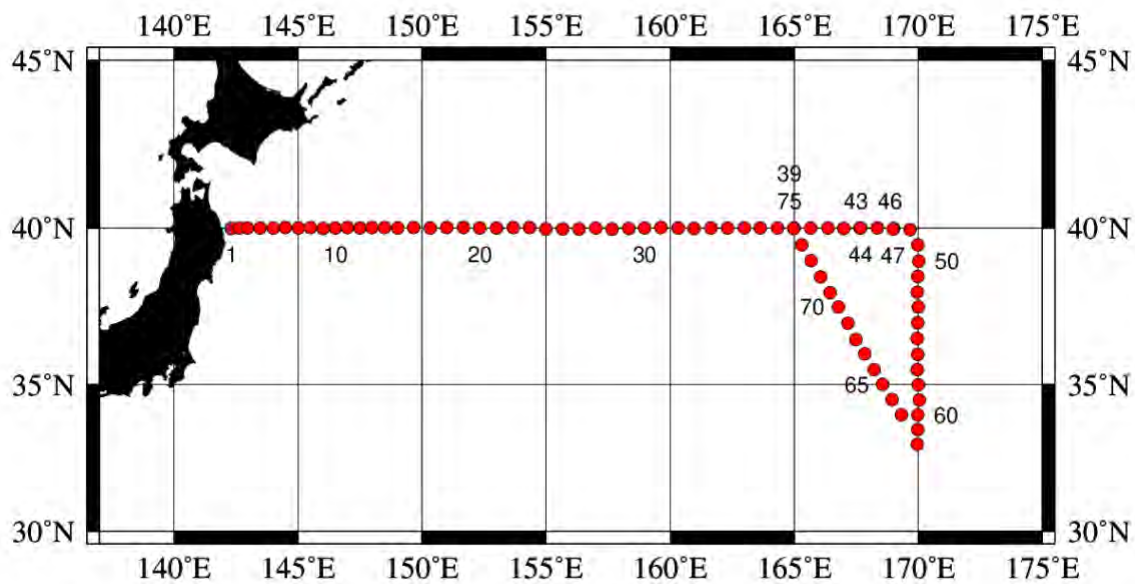


Figure 1: Cruise track of RF13-06 and RF13-07.

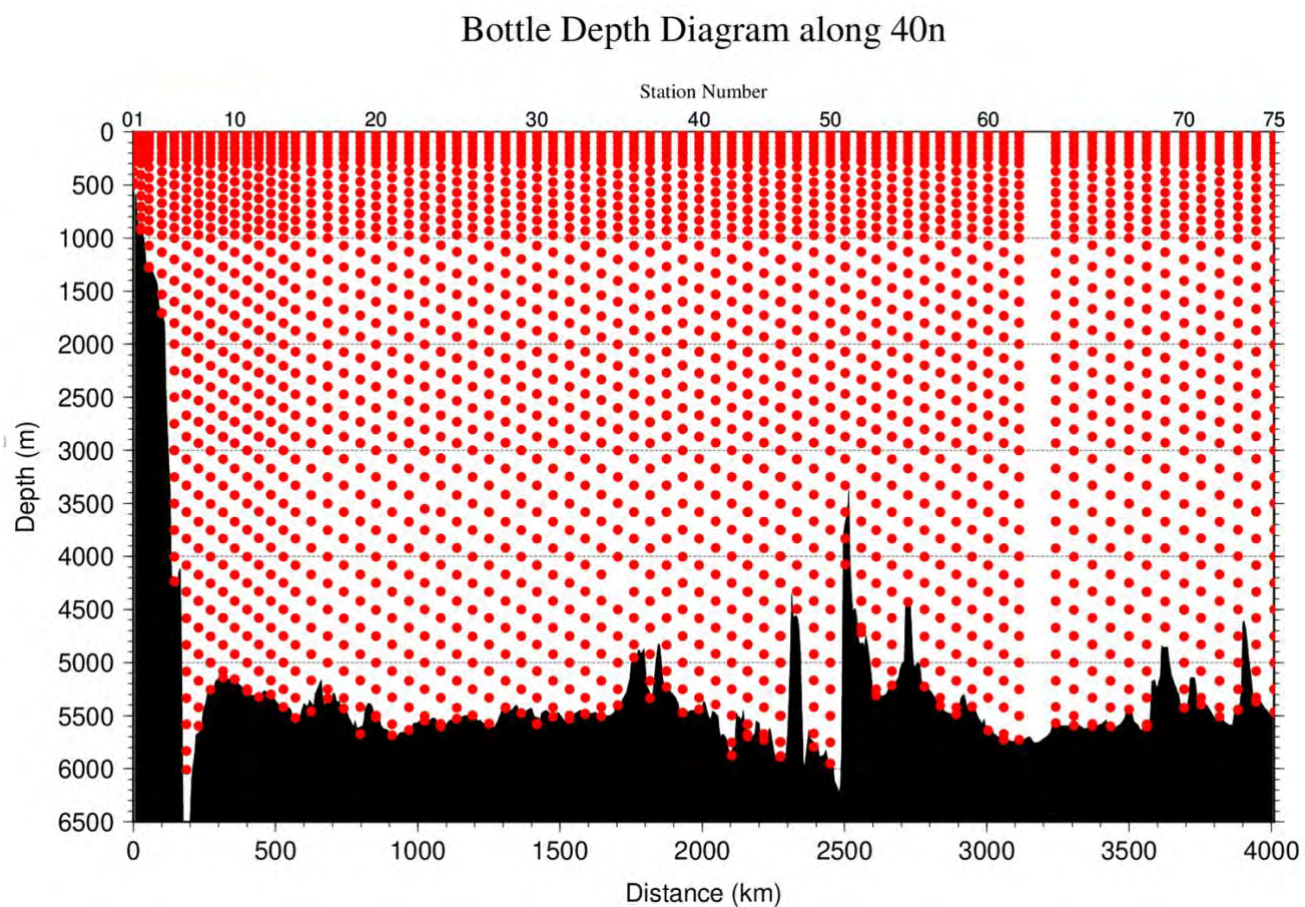


Figure 2: The bottle depth diagram for RF12-06 cruise.

Table 1: Information of deployed floats in RF12-06.

<i>Float</i>	<i>Date and Time of</i>	<i>Position of deployment</i>		<i>PI</i>	
<i>WMO number</i>	<i>Deployment (UTC)</i>	<i>Latitude</i>	<i>Longitude</i>		
2901673	2012 August 9 19:00	39-58.53 N	167-01.77 E	JAMSTEC	PROVOR
2901674	2012 September 3 18:59	37-01.35 N	167-14.03 E	JAMSTEC	PROVOR

PROVOR : nke Instrumentation (France)

Table 2: The scheme of sampling layer in meters.

<i>Bottle count</i>	<i>scheme1</i>	<i>scheme2</i>	<i>scheme3</i>
<i>1</i>	10	10	10
<i>2</i>	50	50	50
<i>3</i>	100	100	100
<i>4</i>	150	150	150
<i>5</i>	200	200	200
<i>6</i>	250	250	250
<i>7</i>	300	330	280
<i>8</i>	400	430	370
<i>9</i>	500	530	470
<i>10</i>	600	630	570
<i>11</i>	700	730	670
<i>12</i>	800	830	770
<i>13</i>	900	930	870
<i>14</i>	1000	1070	970
<i>15</i>	1200	1270	1130
<i>16</i>	1400	1470	1330
<i>17</i>	1600	1670	1530
<i>18</i>	1800	1870	1730
<i>19</i>	2000	2070	1930
<i>20</i>	2200	2270	2130
<i>21</i>	2400	2470	2330
<i>22</i>	2600	2670	2530
<i>23</i>	2800	2870	2730
<i>24</i>	3000	3080	2930
<i>25</i>	3250	3330	3170
<i>26</i>	3500	3580	3420
<i>27</i>	3750	3830	3670
<i>28</i>	4000	4080	3920
<i>29</i>	4250	4330	4170
<i>30</i>	4500	4580	4420
<i>31</i>	4750	4830	4670
<i>32</i>	5000	5080	4920
<i>33</i>	5250	5330	5170
<i>34</i>	5500	5580	5420
<i>35</i>	5750	5830	5670
<i>36</i>	Bottom	Bottom	Bottom

Table 3: Station data of RF12-06 cruise. The ‘RF’ column indicates the JMA station identification number.

<i>Leg</i>	<i>Station</i>		<i>Position</i>	
	<i>Stn.</i>	<i>RF</i>	<i>Latitude</i>	<i>Longitude</i>
1	1	4461	39-59.97 N	142-19.33 E
1	2	4462	40-00.95 N	142-38.12 E
1	3	4463	40-00.23 N	142-58.65 E
1	4	4464	40-00.53 N	143-29.88 E
1	5	4465	40-00.53 N	144-00.60 E
1	6	4466	40-01.02 N	144-30.91 E
1	7	4467	40-00.48 N	145-01.15 E
1	8	4468	40-01.06 N	145-30.62 E
1	9	4469	39-59.20 N	146-01.73 E
1	10	4470	40-00.66 N	146-30.13 E
1	11	4471	40-01.44 N	147-00.81 E
1	12	4472	40-00.10 N	147-30.32 E
1	13	4473	40-01.75 N	147-59.66 E
1	14	4474	40-01.25 N	148-30.73 E
1	15	4475	40-00.88 N	149-01.07 E
1	16	4476	40-01.46 N	149-40.02 E
1	17	4477	40-00.21 N	150-20.61 E
1	18	4478	40-01.08 N	151-00.04 E
1	19	4479	40-01.82 N	151-40.85 E
1	20	4480	40-00.84 N	152-20.37 E
1	21	4481	40-00.28 N	153-00.46 E
1	22	4482	40-01.68 N	153-41.55 E
1	23	4483	40-01.06 N	154-20.87 E
1	24	4484	39-58.09 N	155-00.94 E
1	25	4485	39-58.26 N	155-40.07 E
1	26	4486	39-58.94 N	156-19.75 E
1	27	4487	40-00.36 N	157-00.14 E
1	28	4488	39-58.88 N	157-40.48 E
1	29	4489	39-59.33 N	158-20.16 E
1	30	4490	40-00.41 N	158-58.47 E
1	31	4491	40-01.09 N	159-38.59 E
1	32	4492	40-00.93 N	160-19.04 E
1	33	4493	39-59.98 N	160-58.68 E
1	34	4494	40-00.82 N	161-38.65 E
2	69	4529	37-00.32 N	167-10.85 E
2	70	4530	37-31.04 N	166-47.84 E
2	71	4531	37-58.97 N	166-27.71 E
2	72	4532	38-29.23 N	166-04.53 E

<i>Leg</i>	<i>Station</i>		<i>Position</i>	
	<i>Stn.</i>	<i>RF</i>	<i>Latitude</i>	<i>Longitude</i>
1	35	4495	40-00.62 N	162-19.37 E
1	36	4496	40-00.30 N	162-59.27 E
1	37	4497	40-00.96 N	163-38.49 E
1	38	4503	40-00.29 N	164-20.07 E
1	39	4502	40-00.88 N	164-59.83 E
1	40	4501	40-00.75 N	165-40.62 E
1	41	4500	40-00.77 N	166-21.27 E
1	42	4499	39-59.39 N	167-00.98 E
1	43	4498	40-00.77 N	167-39.80 E
2	44	4504	40-00.58 N	167-40.70 E
2	45	4505	40-00.39 N	168-21.18 E
2	46	4506	39-59.86 N	169-00.81 E
2	47	4507	39-58.64 N	168-59.30 E
2	48	4508	39-57.26 N	169-39.23 E
2	49	4509	39-29.27 N	169-59.80 E
2	50	4510	38-58.61 N	170-01.62 E
2	51	4511	38-30.30 N	169-59.91 E
2	52	4512	37-59.41 N	169-58.98 E
2	53	4513	37-31.18 N	170-00.47 E
2	54	4514	37-01.50 N	169-59.99 E
2	55	4515	36-30.70 N	169-57.52 E
2	56	4516	35-59.50 N	169-59.26 E
2	57	4517	35-29.65 N	169-58.38 E
2	58	4518	34-59.50 N	170-00.06 E
2	59	4519	34-29.33 N	170-02.11 E
2	60	4520	33-59.33 N	169-59.95 E
2	61	4521	33-29.35 N	169-59.09 E
2	62	4522	33-00.03 N	169-58.53 E
2	63	4523	33-59.55 N	169-16.96 E
2	64	4524	34-30.31 N	168-56.76 E
2	65	4525	35-00.12 N	168-34.54 E
2	66	4526	35-29.61 N	168-13.44 E
2	67	4527	36-00.30 N	167-51.49 E
2	68	4528	36-28.99 N	167-29.88 E
2	73	4533	38-59.03 N	165-41.40 E
2	74	4534	39-29.11 N	165-18.94 E
2	75	4535	39-59.48 N	164-59.32 E

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 4.

Table 4: List of principal investigators and the person in charge on the ship for RF12-06.

Item	Principal Investigator (PI)	Person in charge on the ship
<u>Hydrography</u>		
CTDO ₂ / LADCP	Toshiya NAKANO	Keizo SHUTTA
Salinity	Toshiya NAKANO	Keizo SHUTTA
Dissolve oxygen	Toshiya NAKANO	Chihiro KAWAMURA
Nutrients	Toshiya NAKANO	Takashi MIYAO
Phytopigment	Toshiya NAKANO	Takashi MIYAO
DIC	Toshiya NAKANO	Shu SAITO
Total Alkalinity	Toshiya NAKANO	Shu SAITO
pH	Toshiya NAKANO	Shu SAITO
CFCs	Toshiya NAKANO	Etsuro ONO
<u>Underway</u>		
Meteorology	Toshiya NAKANO	Keizo SHUTTA
Thermo-Salinograph	Toshiya NAKANO	Shu SAITO
pCO ₂	Toshiya NAKANO	Shu SAITO
Chlorophyll-a	Toshiya NAKANO	Takashi MIYAO
ADCP	Toshiya NAKANO	Keizo SHUTTA
Bathymetry	Toshiya NAKANO	Keizo SHUTTA
<u>Floats</u>		
Argo float	Toshio SUGA	Hitomi KAMIYA

Toshiya NAKANO (nakano_t@met.kishou.go.jp)
Marine Division, Global Environment and Marine Dept, (JMA)
1-3-4, Otemachi, Chiyoda-ku, Tokyo 100-8122, JAPAN
Phone: +81-3-3212-8341 Ext. 5131

Toshio SUGA (sugat@jamstec.go.jp)
Ocean Climate Change Research Program
Research Institute for Global Change (RIGC)
Japan Agency for Marine-Earth Science and
Technology (JAMSTEC)
2-15 Natsushima, Yokosuka, Kanagawa, Japan 237-0061

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*

C. Hydrographic Measurement Techniques and Calibration

1. CTDO₂ Measurements

Updated 5 March 2020

(1) Personnel

Keizo SHUTTA (GEMD/JMA)
 Nobumi KATO (GEMD/JMA)
 Seiko SHIMOJI (GEMD/JMA)
 Noriyuki OKUNO (GEMD/JMA)
 Koichi WADA (GEMD/JMA)
 Yasunori SASAKI (GEMD/JMA)

(2) CTDO₂ measurement system

(Software: SEASAVEwin32 ver7.18)

<i>Deck unit</i>	<i>Serial Number</i>	<i>Station</i>
SBE 11plus (SBE)	0683	RF4461 – 4535
<i>Under water unit</i>	<i>Serial Number</i>	<i>Station</i>
SBE 9plus (SBE)	35251 (Pressure: 0760)	RF4461 – 4535
<i>Temperature</i>	<i>Serial Number</i>	<i>Station</i>
SBE 3plus (SBE)	4923 (primary)	RF4461 – 4535
	4199 (secondary)	RF4461 – 4535
SBE 35 (SBE)	0069	RF4461 – 4535
<i>Conductivity</i>	<i>Serial Number</i>	<i>Station</i>
SBE 4C (SBE)	3670 (primary)	RF4461 – 4535
	2842 (secondary)	RF4461 – 4535
<i>Pump</i>	<i>Serial Number</i>	<i>Station</i>
SBE 5T (SBE)	5501 (primary)	RF4461 – 4535
	3887 (secondary)	RF4461 – 4535
<i>Oxygen</i>	<i>Serial Number</i>	<i>Station</i>
RINKO III (JFE)	007 (foil number:160002A)	RF4461 – 4535
	008 (foil numner:160003A)	RF4461 – 4535
<i>Water sampler (36 position)</i>	<i>Serial Number</i>	<i>Station</i>
SBE 32 (SBE)	0734	RF4461 – 4535
<i>Altimeter</i>	<i>Serial Number</i>	<i>Station</i>
PSA-916D (TB)	43854	RF4461 – 4535
<i>Water Sampling Bottle</i>		<i>Station</i>
Niskin Bottle (GO)		RF4461 – 4535

SBE: Sea- Bird Electronics, Inc., USA JFE: JFE Advantech Co., Ltd., Japan
 TB: Teledyne Benthos, Inc., USA GO: General Oceanics, Inc., USA

(3) Pre-cruise calibration

(3.1) Pressure

S/N 0760, 25 June 2012

c_1	=	-4.959020e+004	t_1	=	3.006343e+001
c_2	=	5.955454e-001	t_2	=	-1.267270e-004
c_3	=	1.521070e-002	t_3	=	3.974510e-006
d_1	=	3.670600e-002	t_4	=	3.613180e-009
d_2	=	0.000000e+000	t_5	=	0.000000e+000

Formula:

$$c = c_1 + c_2 \times U + c_3 \times U^2$$

$$d = d_1 + d_2 \times U$$

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

$$U (\text{degrees Celsius}) = M \times (12\text{-bit pressure temperature compensation word}) + B$$

U : temperature in degrees Celsius

S/N 0760 coefficients in SEASOFT (configuration sheet dated on 25 June 2012)

$$M = 1.28452e-002, B = -9.05575e+000$$

Finally, pressure is computed as

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

t : pressure period (μsec)

The drift-corrected pressure is computed as

$$\text{Driftcorrected pressure}(\text{dbar}) = \text{slope} \times (\text{computed pressure in dbar}) + \text{offset}$$

$$\text{Slope} = 0.99985, \text{Offset} = -2.1180$$

(3.2) Temperature (ITS-90): SBE 3plus

S/N 4923(primary), 07 June 2012

g	=	4.35306753e-003	j	=	1.77392830e-006
h	=	6.39201272e-004	f_0	=	1000.0
i	=	2.11553579e-005			

S/N 4199(secondary), 07 June 2012

g	=	4.39477018e-003	j	=	2.29541975e-006
h	=	6.50168448e-004	f_0	=	1000.0
i	=	2.42311649e-005			

Formula:

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

f : Instrument freq.[Hz]

(3.3) Deep Ocean Standards Thermometer Temperature (ITS-90): SBE 35

S/N 0069, 23 Oct. 2006

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

Formula:

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

n : instrument output

The slow time drift of the SBE 35

S/N 0069, 11 Sep. 2011 (2nd step: fixed point calibration)

$$Slope = 1.000003, Offset = -0.000378$$

Formula:

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

(3.4) Conductivity: SBE 4C

S/N 3670(primary), 07 June 2012

$$\begin{array}{ll} g = -1.01995535e+001 & j = 2.53978667e-004 \\ h = 1.57607652e+000 & CP_{cor} = -9.5700e-008 \\ i = -2.02177497e-003 & CT_{cor} = 3.2500e-006 \end{array}$$

S/N 2842(secondary), 07 June 2012

$$\begin{array}{ll} g = -1.01277455e+001 & j = 1.95371413e-005 \\ h = 1.38819272e+000 & CP_{cor} = -9.5700e-008 \\ i = 6.13968402e-004 & CT_{cor} = 3.2500e-006 \end{array}$$

Conductivity of a fluid in the cell is expressed as:

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

f : instrument frequency (kHz)

t : water temperature (degrees Celsius)

p : water pressure (dbar).

(3.5) Oxygen (RINKO III)

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.

RINKOIII output is expressed in voltage from 0 to 5 V.

(4) Data correction and Post-cruise calibration

(4.1) Temporal change of deck pressure and Post-cruise calibration

The drift-corrected pressure of post-cruise is computed as

$$\text{Driftcorrected pressure(dbar)} = \text{slope} \times (\text{computed pressure in dbar}) + \text{offset}$$

S/N 0760, 17 Oct. 2012

$$\text{Slope} = 0.99982, \text{ Offset} = -2.1059$$

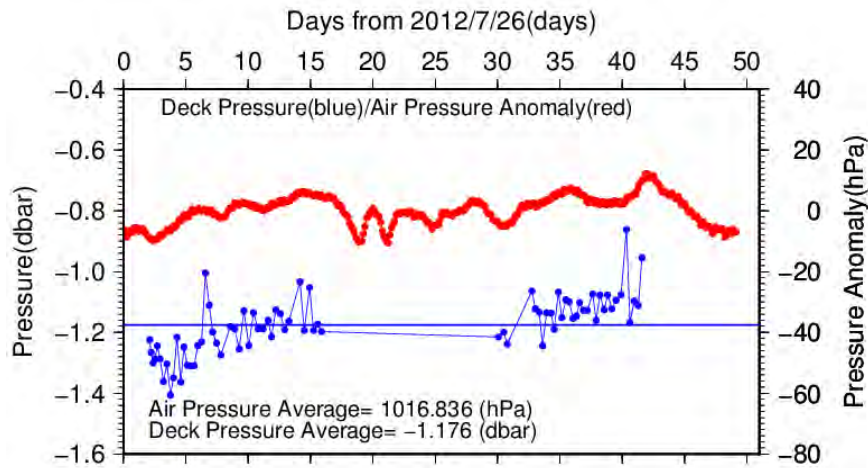


Figure C.1.1: Time series of the CTD deck pressure. Red line indicates atmospheric pressure anomaly. Blue line and dots indicate pre-cast deck pressure and average.

(4.2) Temperature sensor (SBE 3plus)

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 (McTaggart *et al.*, 2010; Uchida *et al.*, 2007).

CTD temperature is corrected as

$$\text{Corrected temperature} = T - (c_0 + c_1 \times P + c_2 \times P^2)$$

T : the CTD temperature (degrees Celsius), P : pressure (dbar) and c_0, c_1, c_2 : coefficients

Table C.1.1: Temperature correction summary (Pressure ≥ 2000 dbar). (Bold : selected sensor)

<i>S/N</i>	<i>Num</i>	$c_0(K)$	$c_1(K/dbar)$	$C_2(K/dbar^2)$	<i>Stations</i>
4923	1116	5.7355493e-4	1.3373866e-7	0.0000000e+0	RF4461 – 4535
4199	1115	1.6317968e-3	-3.2009900e-7	7.1930323e-10	RF4461 – 4535

Table C.1.2: Temperature correction summary for S/N 4923.

Stations	Pressure < 2000dbar			Pressure ≥ 2000 dbar		
	Num	Average (K)	Std (K)	Num	Average (K)	Std (K)
RF4461 – 4503	760	0.0008	0.0315	596	0.0000	0.0001
RF4504 – 4535	576	0.0000	0.0094	520	0.0000	0.0001

Table C.1.3: Temperature correction summary for S/N 4199.

Stations	Pressure < 2000dbar			Pressure ≥ 2000 dbar		
	Num	Average (K)	Std (K)	Num	Average (K)	Std (K)
RF4461 – 4503	760	0.0003	0.0145	597	0.0000	0.0002
RF4504 – 4535	576	0.0001	0.0078	518	0.0000	0.0002

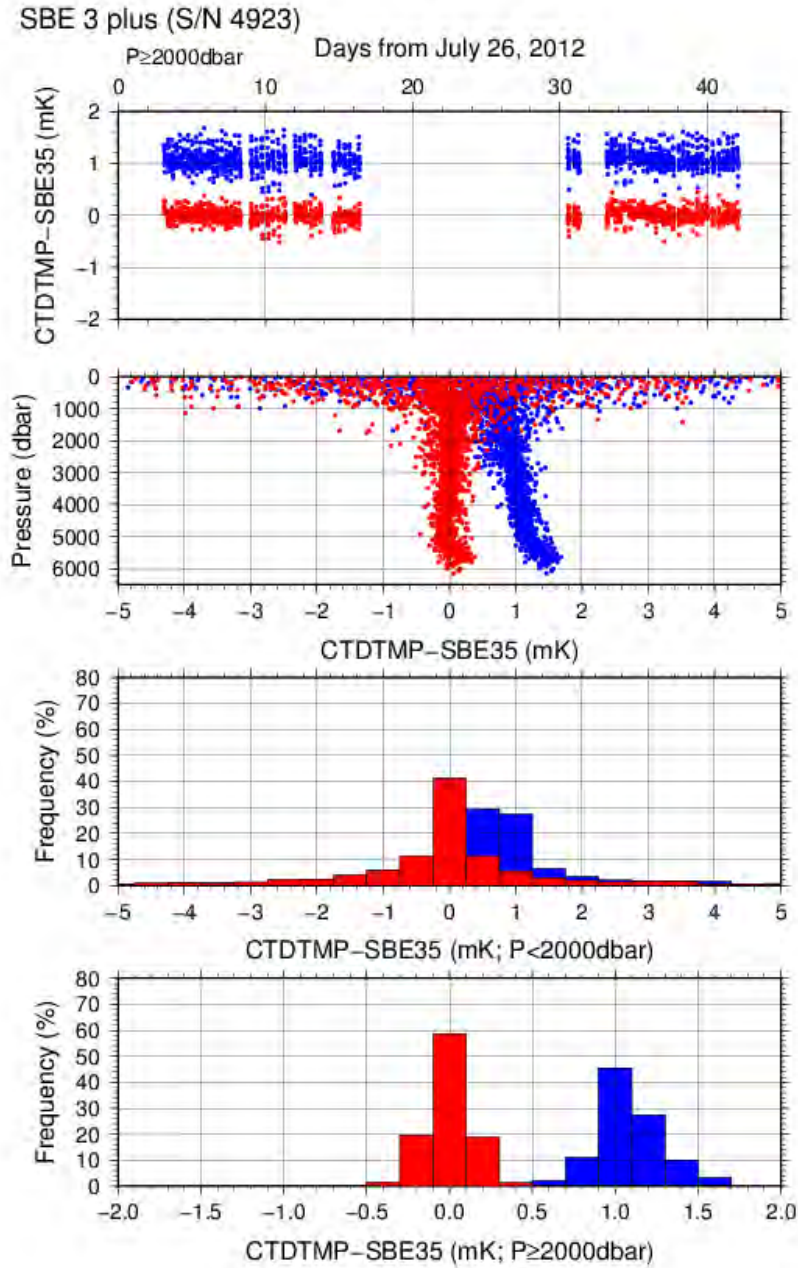


Figure C.1.2: Difference between the CTD temperature (*S/N 4923*) and the Deep Ocean Standards thermometer (SBE 35) at RF12-06. Blue and red dots indicate before and after the correction using SBE 35 data respectively. Lower two panels show histogram of the difference after correction.

Post-cruise sensor calibration for the SBE 3plus

S/N 4923(primary), 04 Oct. 2012

$$\begin{aligned}
 g &= 4.35315593\text{e-}003 & j &= 1.80068115\text{e-}006 \\
 h &= 6.39388379\text{e-}004 & f_0 &= 1000.0 \\
 i &= 2.12796459\text{e-}005
 \end{aligned}$$

S/N 4199(secondary), 05 Oct. 2012

$$\begin{aligned} g &= 4.39449032\text{e-}003 & j &= 2.19010408\text{e-}006 \\ h &= 6.49542198\text{e-}004 & f_0 &= 1000.0 \\ i &= 2.37799205\text{e-}005 \end{aligned}$$

Formula:

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

f : Instrument freq.[Hz]

Post-cruise sensor calibration for the SBE 35

S/N 0069, 12 Oct. 2012 (2nd step: fixed point calibration)

$$\text{Slope} = 1.000002, \text{Offset} = 0.000498$$

Formula:

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

(4.3) Conductivity sensor (SBE 4C)

The practical corrections for CTD conductivity data can be made by using a bottle salinity data, correcting the SBE 4C to agree with measured conductivity (McTaggart *et al.*, 2010).

CTD conductivity is corrected

$$\text{Corrected Conductivity} = C - \left(\sum_{i=0}^I c_i \times C^i + \sum_{j=1}^J p_j \times P^j \right)$$

C : CTD conductivity, c_i and p_j : calibration coefficients

i, j : determined by referring to AIC (Akaike, 1974). According to McTaggart *et al.* (2010), maximum of I and J are 2.

Table C.1.4: Conductivity correction coefficient summary. (Bold : selected sensor)

S/N	Num	$c_0(S/m)$	c_1	$c_2(m/S)$	Stations
			$p_1(S/m/dbar)$	$p_2(S/m/dbar^2)$	
3670	810	1.5903e-4	0.0000e+0	0.0000e+0	RF4461 – 4503
			8.4024e-8	-1.2424e-11	
3670	616	2.2746e-4	0.0000e+0	0.0000e+0	RF4504 – 4535
			4.2797e-8	-4.8510e-12	
2842	814	1.5063e-4	0.0000e+0	0.0000e+0	RF4461 – 4503
			9.4583e-8	-1.2004e-11	
2842	615	2.5754e-4	0.0000e+0	0.0000e+0	RF4504 – 4535
			2.9613e-8	0.0000e+0	

Table C.1.5: Conductivity correction and salinity summary for S/N 3670.

Stations	Pressure < 1900dbar					
	Conductivity			Salinity		
	Num	Average (S/m)	Std (S/m)	Num	Average	Std
RF4461 – 4503	446	0.0000	0.0004	446	0.0002	0.0041
RF4504 – 4535	304	0.0000	0.0001	304	0.0000	0.0013
Stations	Pressure \geq 1900 dbar					
	Conductivity			Salinity		
	Num	Average (S/m)	Std (S/m)	Num	Average	Std
RF4461 – 4503	364	0.0000	0.0001	364	–0.0001	0.0007
RF4504 – 4535	312	0.0000	0.0000	312	0.0000	0.0006

Table C.1.6. Conductivity correction and salinity summary for S/N 2842.

Stations	Pressure < 1900dbar					
	Conductivity			Salinity		
	Num	Average (S/m)	Std (S/m)	Num	Average	Std
RF4461 – 4503	446	0.0000	0.0004	446	0.0002	0.0046
RF4504 – 4535	303	0.0000	0.0001	303	0.0000	0.0013
Stations	Pressure \geq 1900 dbar					
	Conductivity			Salinity		
	Num	Average (S/m)	Std (S/m)	Num	Average	Std
RF4461 – 4503	365	0.0000	0.0001	365	–0.0001	0.0007
RF4504 – 4535	312	0.0000	0.0000	312	0.0000	0.0006

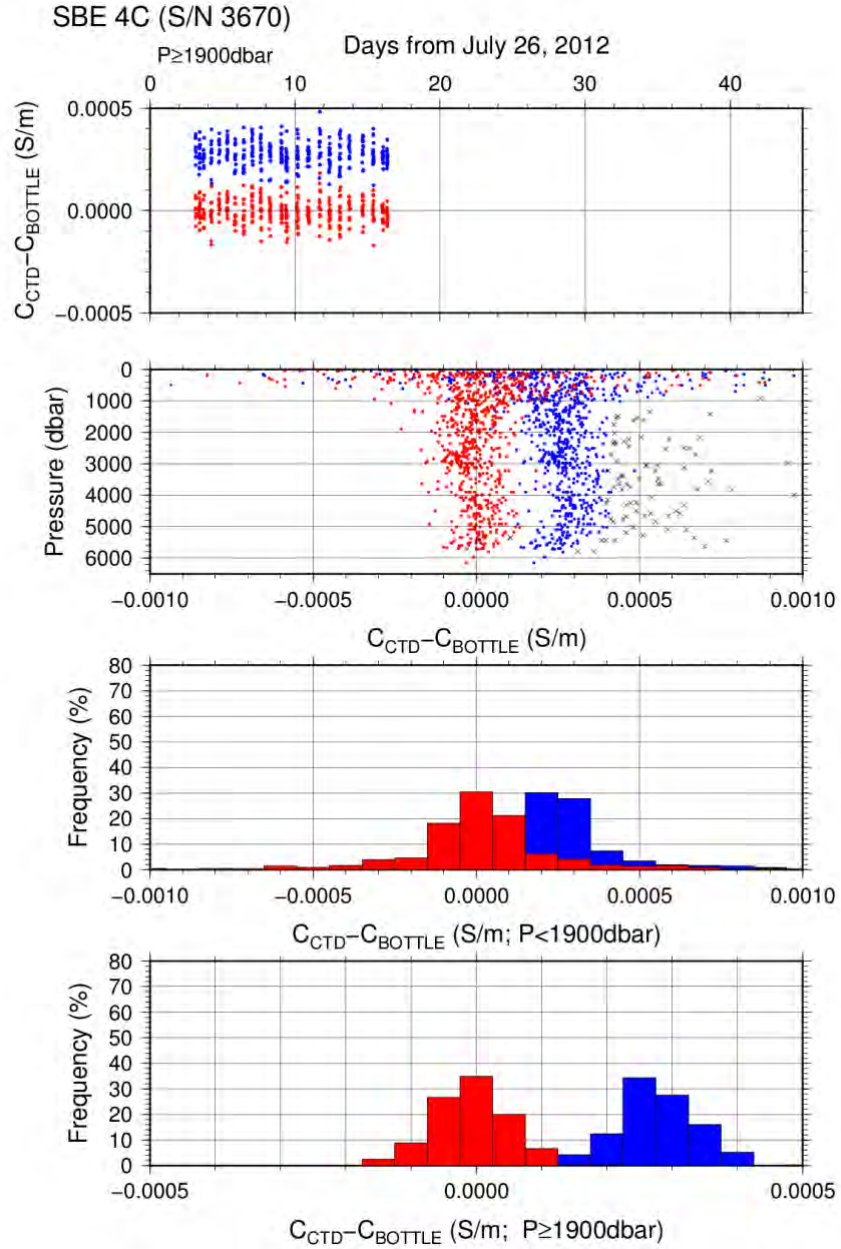


Figure C.1.3: Difference between the CTD conductivity (*S/N 3670*) and the bottle conductivity at Leg 1. Blue and red dots indicate before and after the calibration using bottle data respectively. Lower two panels show histogram of the difference before and after calibration.

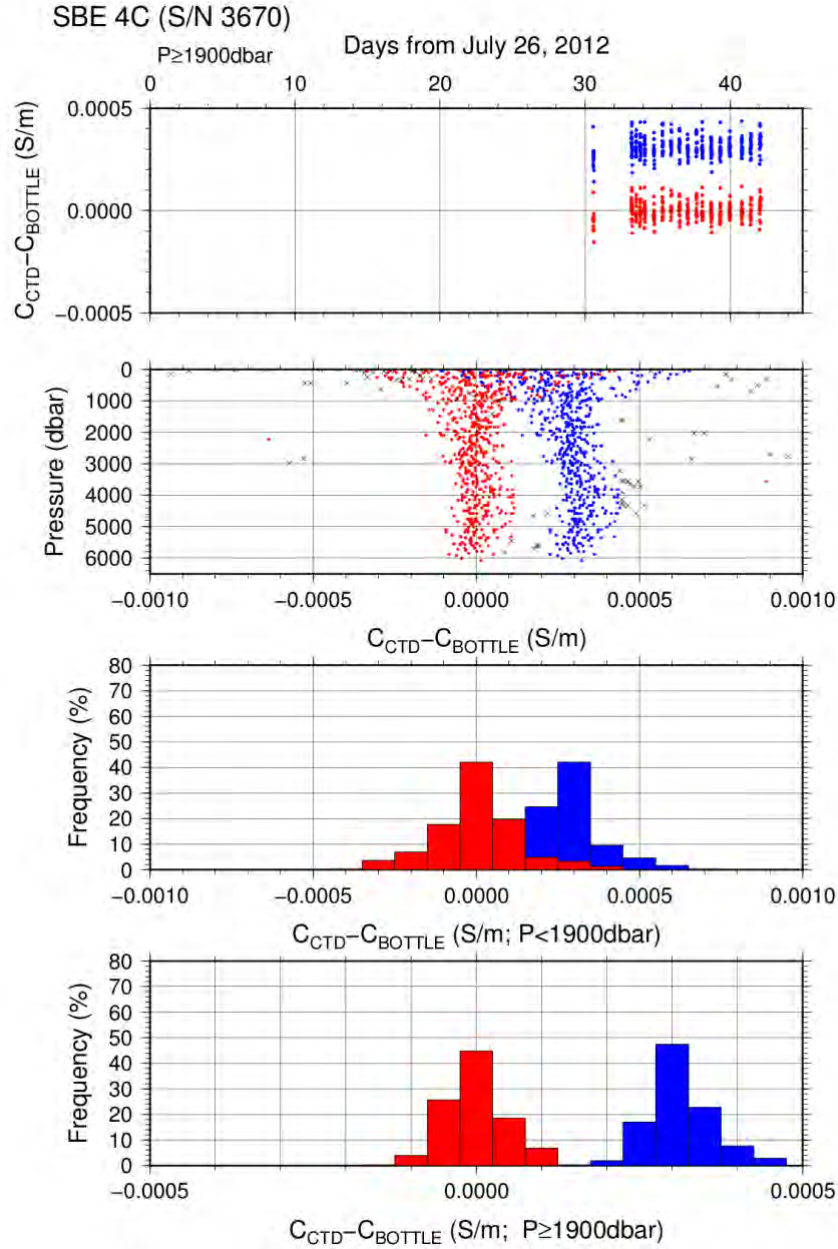


Figure C.1.4: Difference between the CTD conductivity (S/N 3670) and the bottle conductivity at Leg 2. Blue and red dots indicate before and after the calibration using bottle data respectively. Lower two panels show histogram of the difference before and after calibration.

Post-cruise sensor calibration for the SBE 4C

S/N 3670(primary), 04 Oct. 2012

g	$= -1.02008629\text{e}+001$	j	$= 2.65177344\text{e}-004$
h	$= 1.57654876\text{e}+000$	CP_{cor}	$= -9.5700\text{e}-008$
i	$= -2.16327892\text{e}-003$	CT_{cor}	$= 3.2500\text{e}-006$

S/N 2842(secondary), 04 Oct. 2012

$$\begin{aligned} g &= -1.01282248\text{e}+001 & j &= 2.44828241\text{e}-005 \\ h &= 1.38836986\text{e}+000 & CP_{cor} &= -9.5700\text{e}-008 \\ i &= 5.53283965\text{e}-004 & CT_{cor} &= 3.2500\text{e}-006 \end{aligned}$$

Conductivity of a fluid in the cell is expressed as:

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

f : instrument frequency (kHz)

t : water temperature (degrees Celsius)

p : water pressure (dbar).

(4.4) Oxygen sensor (RINKO III)

The CTD oxygen is calculated using RINKO III output (voltage) by the Stern-Volmer equation, according to a method by *Uchida et al. (2008)* and *Uchida et al. (2010)*. The pressure hysteresis for the RINKO III output (voltage) is corrected according to a method by *Sea-bird Electronics (2009)* and *Uchida et al. (2010)*. The formulas are as follows:

$$P_0 = 1.0 + c_4 \times t$$

$$P_c = c_5 + c_6 \times v + c_7 \times T + c_8 \times T \times v$$

$$K_{sv} = c_1 + c_2 \times t + c_3 \times t^2$$

$$coef = (1.0 + c_9 \times P/1000)^{1/3}$$

$$[O_2] = O_2^{\text{sat}} \times \{(P_0/P_c - 1.0)/K_{sv} \times coef\}$$

P : pressure (dbar), t : potential temperature, v : RINKO output voltage (volt)

T : elapsed time of the sensor from the beginning of first station in calculation group in day

O_2^{sat} : dissolved oxygen saturation by *Garcia and Gordon (1992)* ($\mu\text{mol/kg}$)

$[O_2]$: dissolved oxygen concentration ($\mu\text{mol/kg}$)

c_1 – c_9 : determined by minimizing difference between CTD oxygen and bottle dissolved oxygen by quasi-newton method (*Shanno, 1970*).

Table C.1.7: Dissolved oxygen correction coefficient summary. (Bold: selected sensor)

S/N	Stations	c_1	c_2	c_3	c_4	c_5
		c_6	c_7	c_8	c_9	
007	RF4461 – 4503	1.52760e+0	2.91968e–2	2.86993e–4	1.73464e–3	–2.00194e–1
		3.24160e–1	–4.34986e–4	7.17883e–4	9.34545e–2	
007	RF4504 – 4535	1.51865e+0	1.78606e–2	2.93187e–4	–6.67446e–4	–1.77500e–1
		3.16880e–1	–6.38358e–4	7.30758e–4	1.02766e–1	
008	RF4461 – 4503	1.65967e+0	3.24203e–2	1.32570e–4	1.41117e–3	–1.08751e–1
		3.02507e–1	–3.75917e–4	5.65218e–4	8.32538e–2	
008	RF4504 – 4535	1.65702e+0	2.31065e–2	1.89197e–4	–6.51385e–4	–1.00474e–1
		2.99167e–1	–2.94419e–4	5.13555e–4	8.74394e–2	

Table C.1.8: Dissolved oxygen correction summary for S/N 007.

Stations	Pressure < 950dbar			Pressure \geq 950dbar		
	Num	Average ($\mu\text{mol/kg}$)	Std ($\mu\text{mol/kg}$)	Num	Average ($\mu\text{mol/kg}$)	Std ($\mu\text{mol/kg}$)
RF4461 – 4503	303	–0.38	1.39	436	0.02	0.40
RF4504 – 4535	387	–0.26	1.56	590	0.02	0.40

Table C.1.9: Dissolved oxygen correction summary for S/N 008.

Stations	Pressure < 950dbar			Pressure \geq 950dbar		
	Num	Average ($\mu\text{mol/kg}$)	Std ($\mu\text{mol/kg}$)	Num	Average ($\mu\text{mol/kg}$)	Std ($\mu\text{mol/kg}$)
RF4461 – 4503	303	–0.16	1.08	436	0.01	0.35
RF4504 – 4535	387	–0.06	1.35	590	0.01	0.35

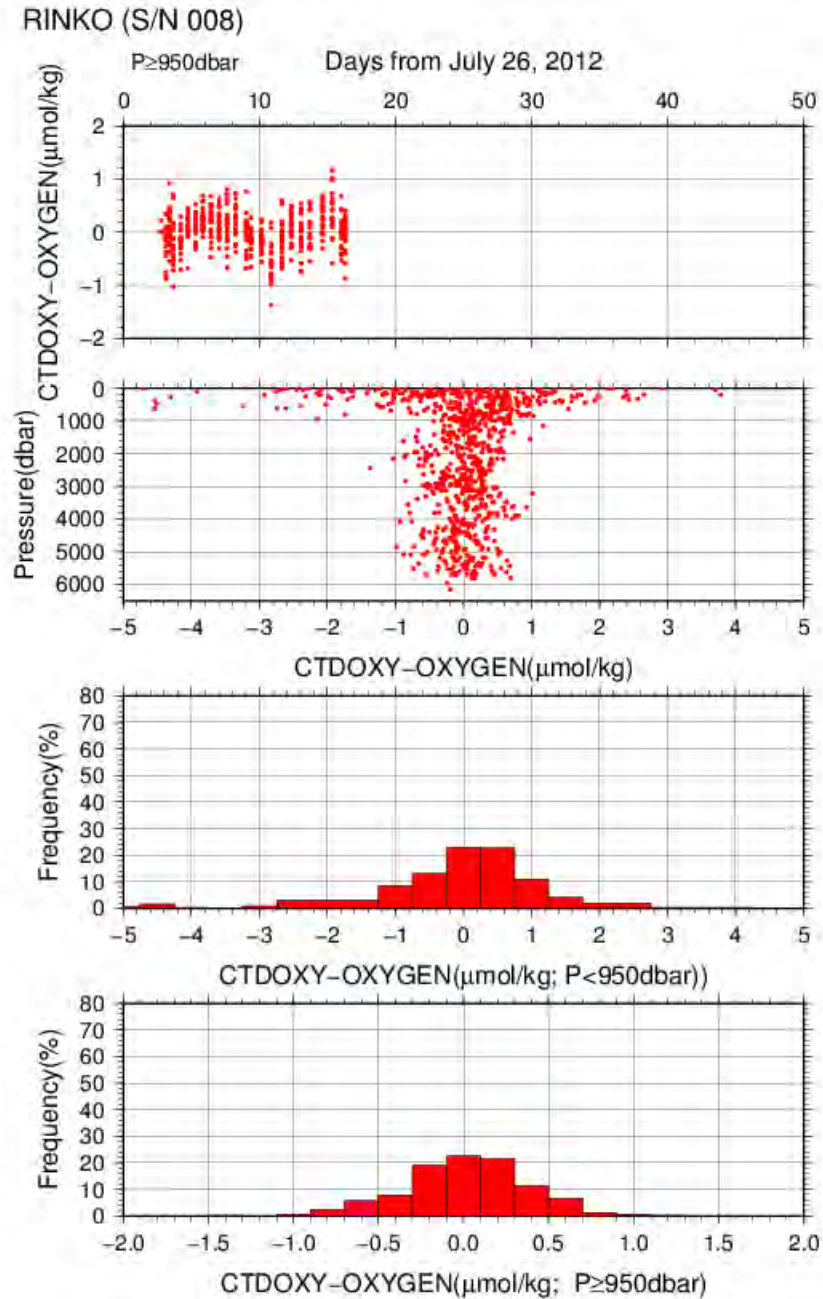


Figure C.1.5: Difference between the CTD oxygen (*S/N 008*) and bottle dissolved oxygen at Leg 1. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.

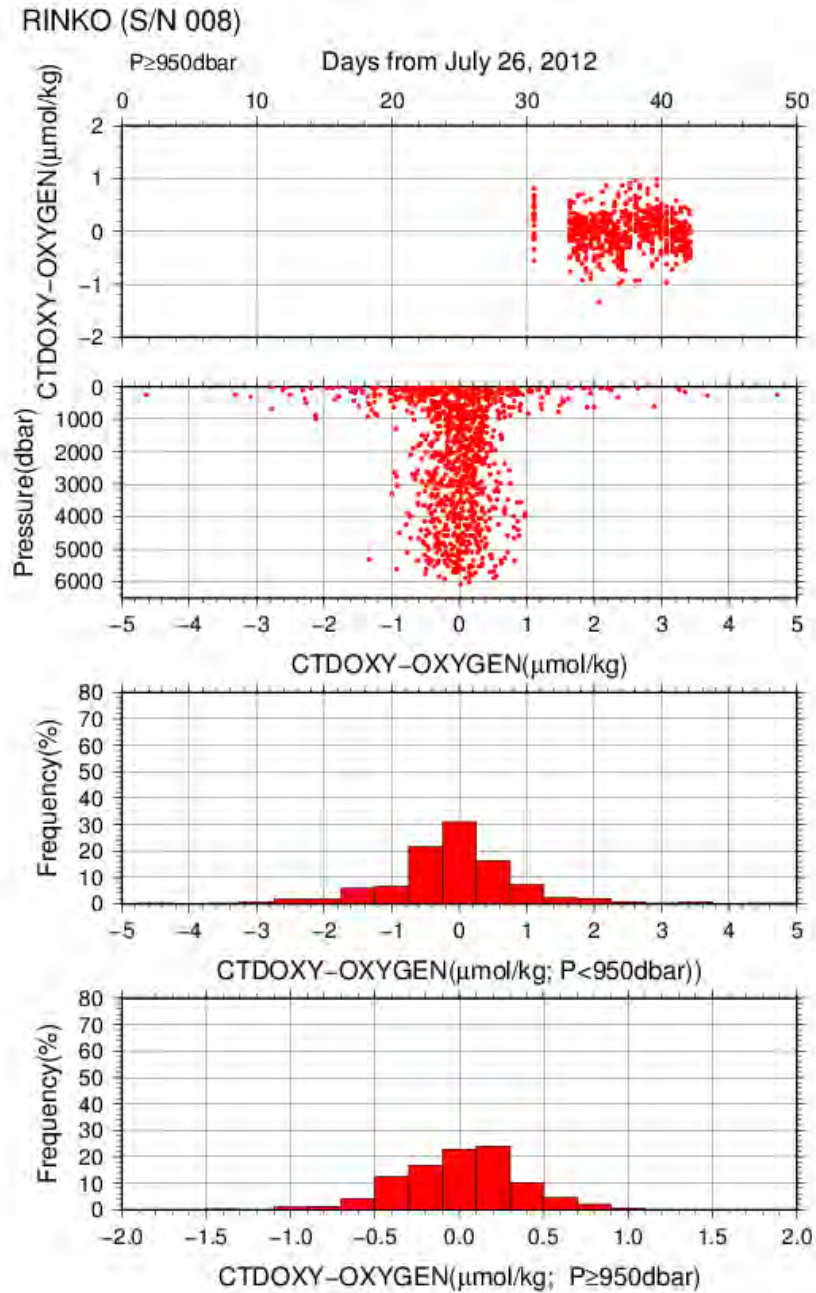


Figure C.1.6: Difference between the CTD oxygen (*S/N 008*) and bottle dissolved oxygen at Leg 2. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.

(4.5) Results of detection of sea floor by the altimeter (PSA-916D)

The altimeter detected the sea floor at 72 of 75 stations, the average distance of beginning detecting the sea floor was 34.1m, and that of final detection of sea floor was 6.0m. The summary of detection of PSA-916D was shown in Figure C.1.7.

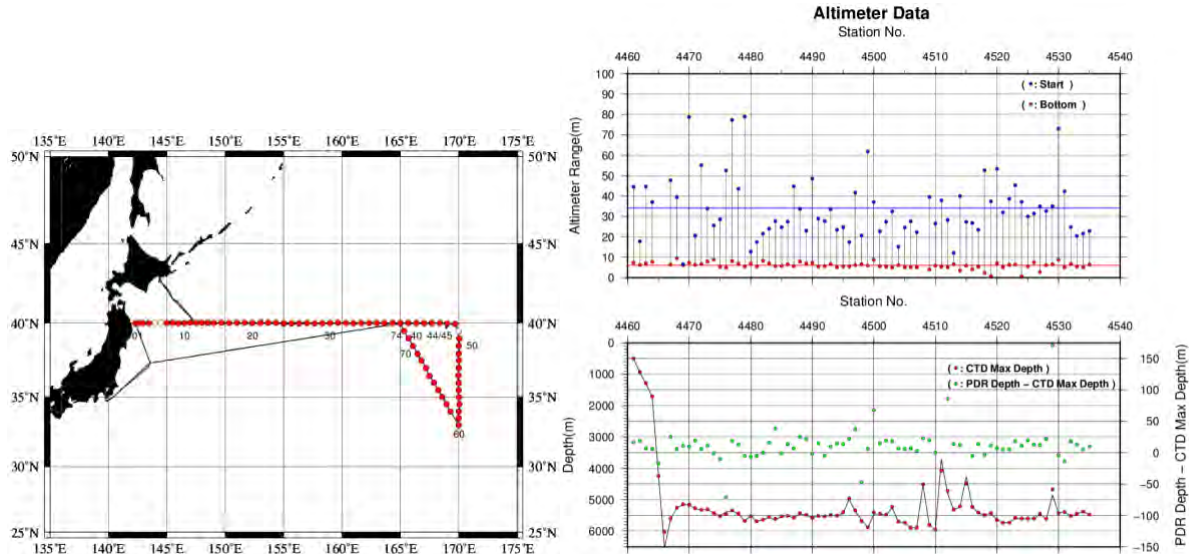


Figure C.1.7: The summary of detection of PSA-916D. The left panel shows the stations of detection, the right panel shows the relationship among PSA-916D, bathymetry and CTD depth. In the left panel, closed and open circles indicate react and no-react stations, respectively.

References

- Akaike, H. (1974): A new look at the statistical model identification. *IEEE Transactions on Automatic Control*, **19**:716–722.
- García, H. E., and L. I. Gordon (1992): Oxygen solubility in seawater: Better fitting equations. *Limnol. Oceanogr.*, **37**, 1307–1312.
- 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.
- 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.
- Uchida, H., G. C. Johnson, McTaggart, K. E. (2010): CTD oxygen sensor calibration procedures. In: 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.
- 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-

2. Bottle Salinity

1 November 2019

(1) Personnel

Keizo SHUTTA (GEMD/JMA)
Nobumi KATO (GEMD/JMA)
Seiko SHIMOJI (GEMD/JMA)
Noriyuki OKUNO (GEMD/JMA)
Koichi WADA (GEMD/JMA)
Yasunori SASAKI (GEMD/JMA)

(2) Salinity measurement

Salinometer: AUTOSAL 8400B (S/N66286 (Leg 1), S/N67642 (Leg 2); Guildline Instruments Ltd., Canada)

Thermometer: Guildline platinum thermometers model 9450 (to monitor an ambient temperature and bath temperature)

IAPSO Standard Sea Water: P154 ($K_{15}=0.99990$)

(3) Sampling and measurement

The measurement system was almost same as *Kawano* (2010).

Algorithm for practical salinity scale, 1978 (PSS-78, UNESCO, 1981) was employed to convert the conductivity ratios to salinities.

(4) Stations occupied

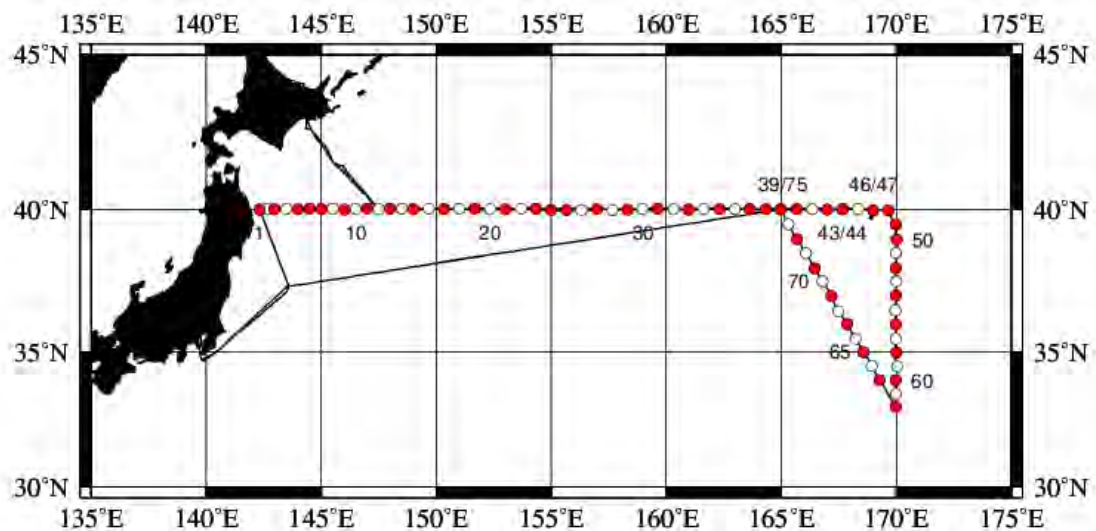


Figure C.2.1: Location of observation stations of bottle salinity. Closed and open circles indicate sampling and no-sampling station, respectively.

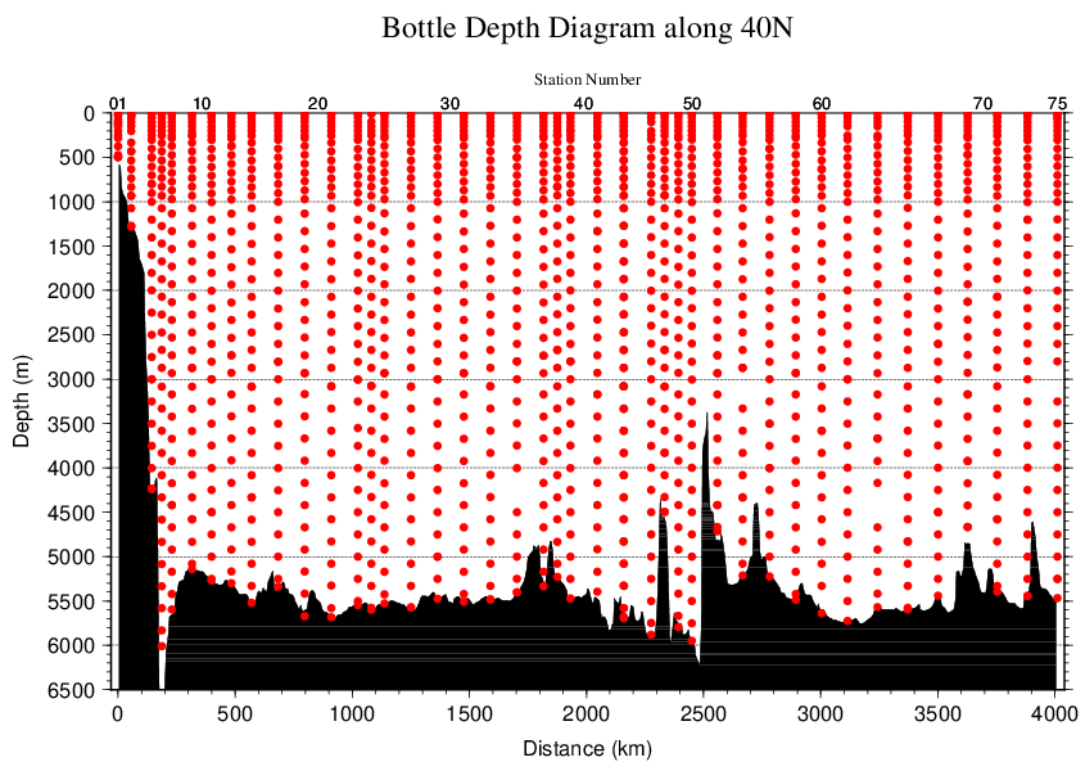


Figure C.2.2: Distance-depth distribution of sampling layers of bottle salinity.

(5) Result

(5.1) Ambient temperature, bath temperature and SSW measurements

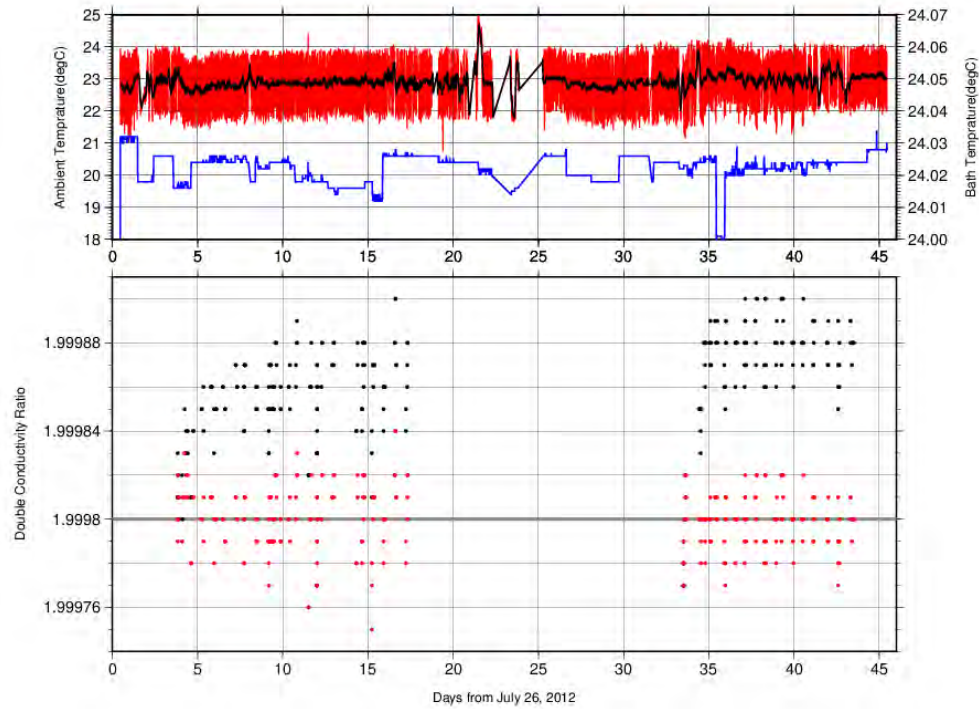


Figure C.2.3: The upper panel, red line, black line and blue line indicate time-series of ambient temperature, ambient temperature average and bath temperature during cruise. The lower panel, black dots and red dots indicate raw and corrected time-series of the double conductivity ratio of the standard sea water (P154).

(5.2) Replicate and Duplicate Samples

We took replicate (pair of water samples taken from a single Niskin bottle) and duplicate (pair of water samples taken from different Niskin bottles closed at the same depth) samples of bottle salinity through the cruise. Results of the analyses are summarized in Table C.2.1. Detailed results of them are shown in [Figure C.2.4](#). The calculation of the standard deviation from the difference of sets was based on a procedure (SOP 23) in *DOE* (1994).

Table C.2.1: Summary of replicate and duplicate analyses.

Measurement	Ave. \pm S.D.
Replicate	0.0005 \pm 0.0005 (N=100)
Duplicate	0.0007 \pm 0.0007 (N=67)

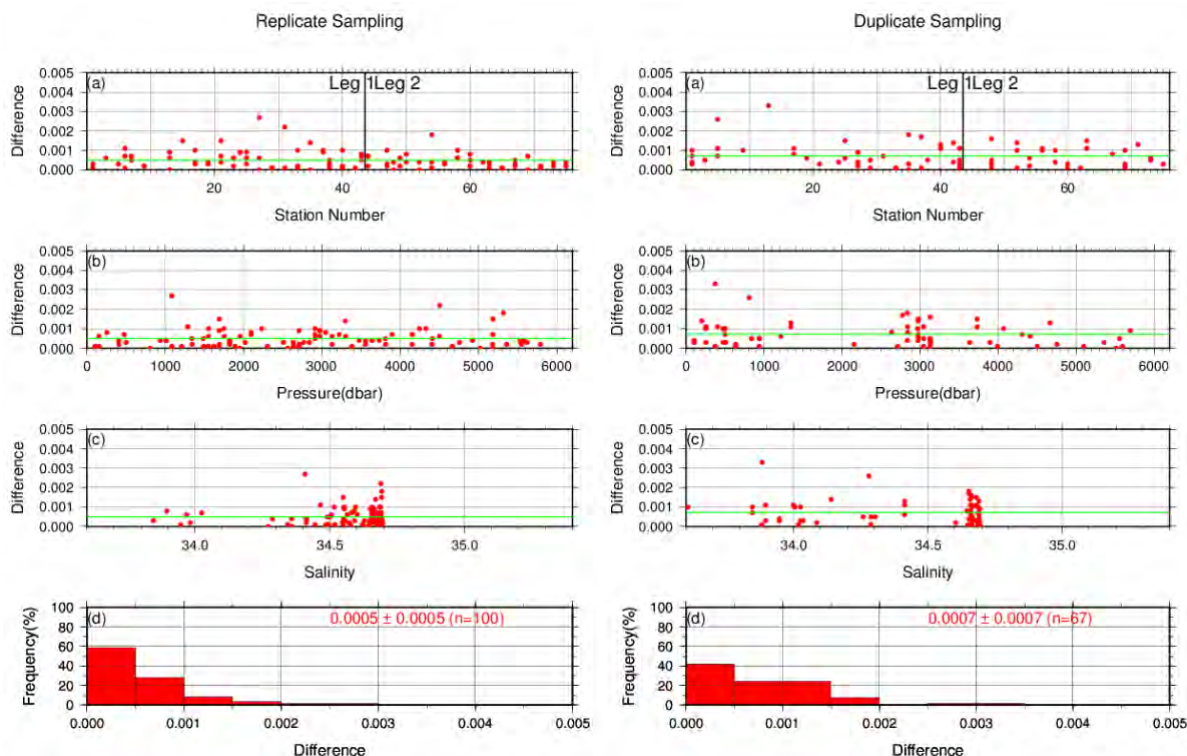


Figure C.2.4: Result of (left) replicate and (right) duplicate analyses during the cruise against (a) station number, (b) pressure and (c) salinity, and (d) histogram of the measurements. Green line indicates the mean of the differences of salinity of replicate/duplicate.

(5.3) Summary of assigned quality control flags

Table C.2.2. Summary of assigned quality control flags

Flag	Definition	Salinity
2	Good	1260
3	Questionable	0
4	Bad (Faulty)	175
6	Replicate measurements	105
Total number of samples		1540

References

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

3. Bottle Oxygen

1 November 2019

(1) Personnel

Chihiro KAWAMURA (GEMD/JMA)

Sho HIBINO (GEMD/JMA)

Hiroki SHIOZURU (GEMD/JMA)

(2) Stations occupied

A total of 55 stations (Leg 1: 25, Leg 2: 30) were occupied for dissolved oxygen measurements. Station location and sampling layers of bottle oxygen are shown in Figures C.3.1 and C.3.2, respectively.

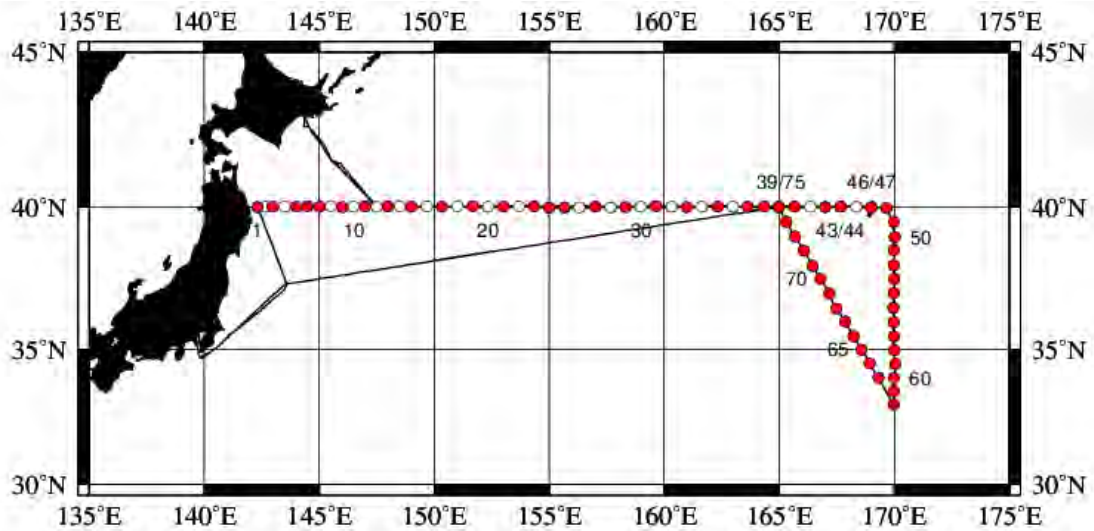


Figure C.3.1: Location of observation stations of bottle oxygen. Closed and open circles indicate sampling and no-sampling stations, respectively.

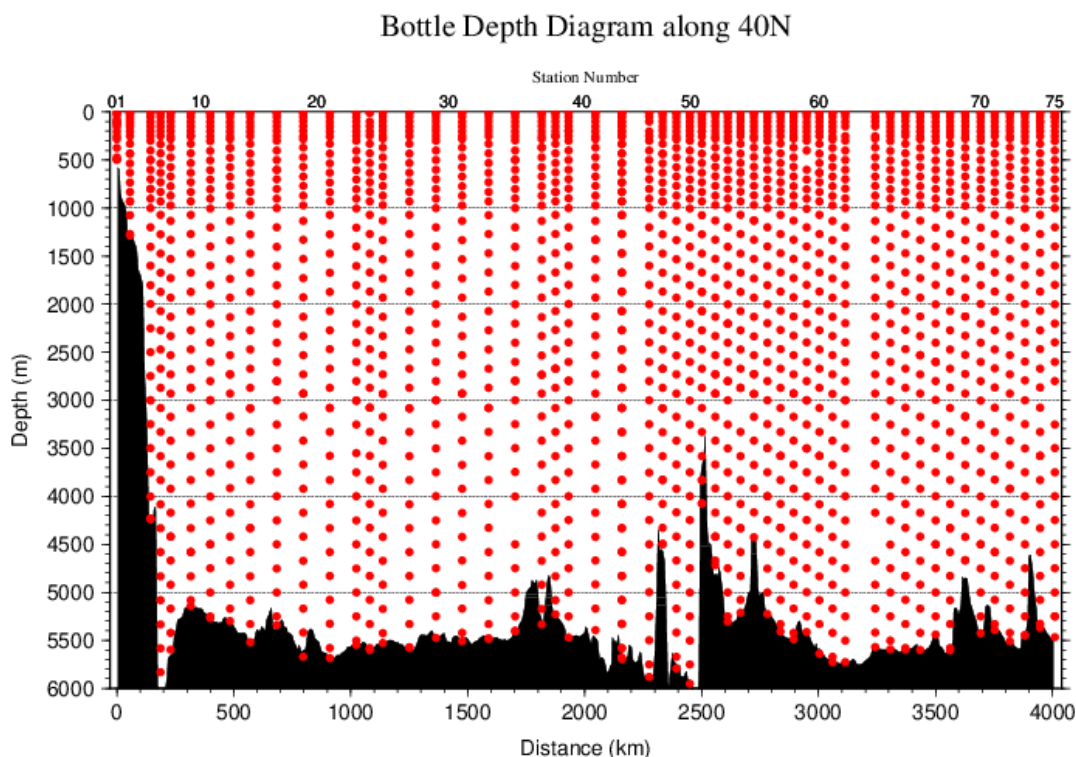


Figure C.3.2: Distance-depth distribution of sampling layers of bottle oxygen.

(3) Instrument

Detector: DOT-01X (Kimoto Electronic, Japan)

Burette: APB-510 (Kyoto Electronic, Japan)

(4) Sampling and measurement

Methods of seawater sampling, measurement, and calculation of dissolved oxygen concentration were based on IOCCP Report (Langdon, 2010). Details of the methods are shown in Appendix A1.

The reagents for the measurement were prepared according to recipes described in Appendix A2. It is noted that standard KIO_3 solutions were prepared gravimetrically using the highest purity standard substance KIO_3 (Lot. No. 92404G, Merck KGaA, Germany). Batch list of prepared standard KIO_3 solutions is shown in Table C.3.1. The normality of the standard potassium iodate solution made by Merck reagent was corrected by the factor as 1.0026 from the result of the inter-laboratory comparison with the standard potassium iodate solution made by National Metrology Institute of Japan reagent (JMA, 2010).

Table C.3.1: Batch list of the standard KIO_3 solutions.

KIO_3 batch	Concentration and uncertainty (k=2) at 20 °C. Unit is normality (N).	Purpose of use
20120222	0.010120±0.000005	Standardization (main use)
20120404-2	0.010189±0.000005	Mutual comparison

(5) Standardization

Concentration of $\text{Na}_2\text{S}_2\text{O}_3$ titrant was determined with the standard KIO_3 solution “20120222”, based on the methods of IOCCP Report (Langdon, 2010). The results of standardization during the cruise are shown in Figure C.3.3. Standard deviation of its concentration at 20 °C determined through standardization was used in calculation of an uncertainty.

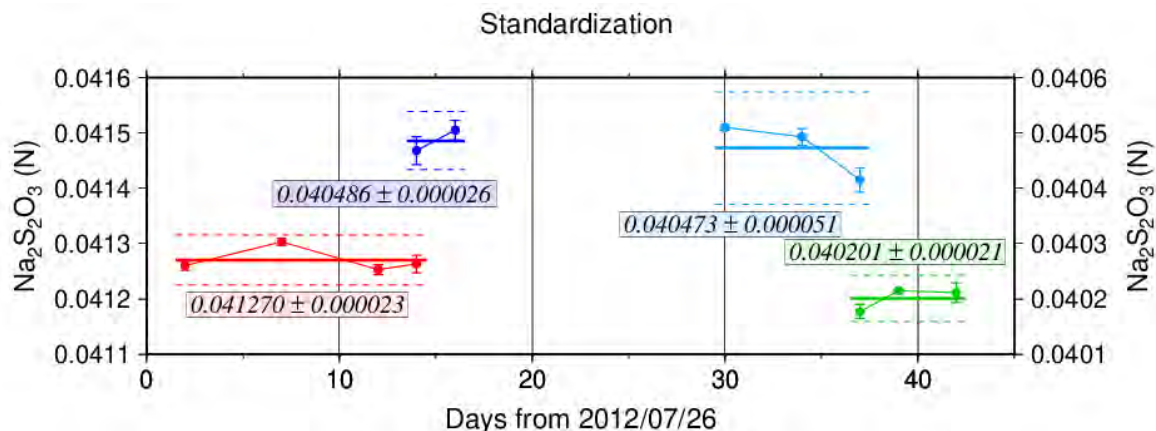


Figure C.3.3: Calculated concentration of $\text{Na}_2\text{S}_2\text{O}_3$ solution at 20 °C in standardization during the cruise. Different colors of plots indicate different batches of $\text{Na}_2\text{S}_2\text{O}_3$ solution; red (blue, light blue, and green) plots correspond to the left (right) y-axis. Error bars of plots show standard deviation of concentration of $\text{Na}_2\text{S}_2\text{O}_3$ in the measurement. Thick and dashed lines denote the mean and 2 times of standard deviations for the batch measurements, respectively.

(6) Blank

(6.1) Reagent blank

Blank in oxygen measurement (reagent blank; $V_{\text{blk}, \text{dw}}$) can be represented as follows:

$$V_{\text{blk}, \text{dw}} = V_{\text{blk}, \text{ep}} + V_{\text{blk}, \text{reg}} \quad (\text{C3.1})$$

where $V_{\text{blk}, \text{ep}}$ represents a blank due to differences between the measured endpoint and the equivalence point, and $V_{\text{blk}, \text{reg}}$ a blank associated with oxidants or reductants in the reagent. The reagent blank $V_{\text{blk}, \text{dw}}$ was determined by the methods described in IOCCP Report (Langdon, 2010). Because we used two sets (set A and B) of pickling reagent-I and -II, the blanks in each set were determined (Figure C.3.4).

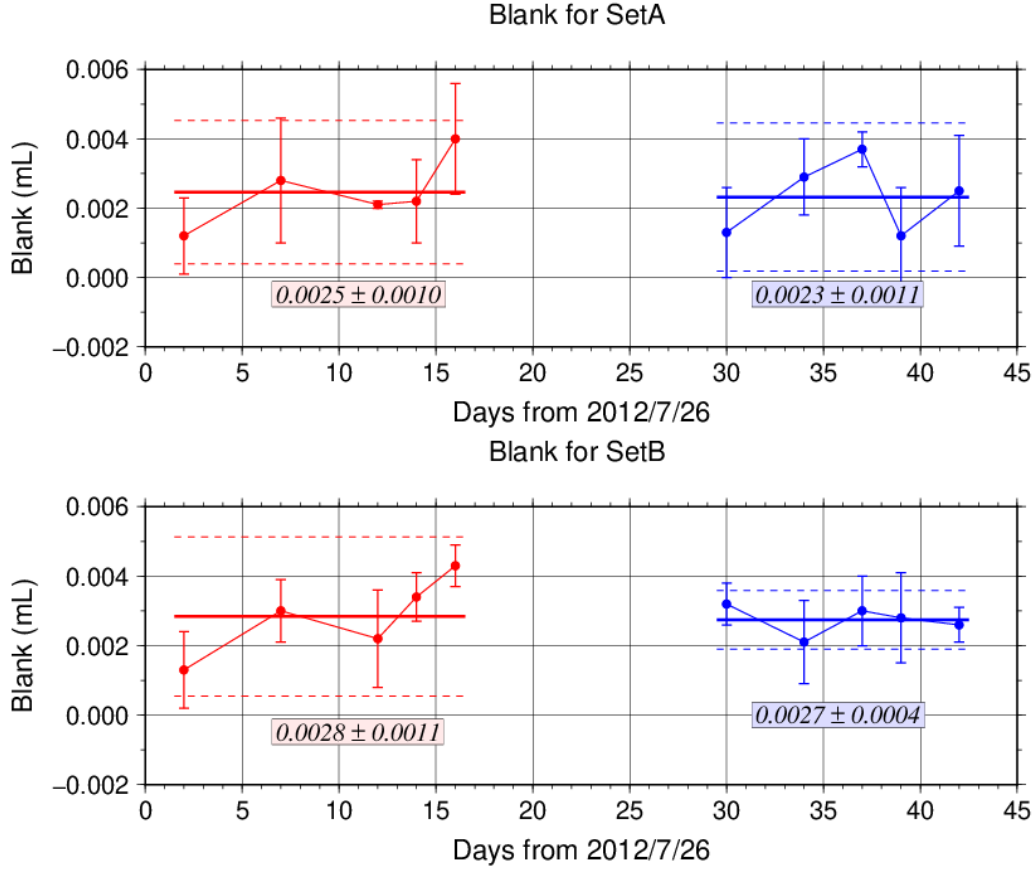


Figure C.3.4: Reagent blank ($V_{\text{blk, dw}}$) determination for set A (top) and set B (bottom). Error bars of plots show standard deviation of the measurement. Thick and dashed lines denote the mean and 2 times of standard deviations for the batch measurement, respectively.

(6.2) Other blanks

We also determined other blanks related to oxygen measurement; the blank $V_{\text{blk, reg}}$. Details are described in Appendix A3.

(7) Quality Control

(7.1) Replicate and duplicate analyses

We took replicate (pair of water samples taken from a single Niskin bottle) and duplicate (pair of water samples taken from different Niskin bottles closed at the same depth) samples of dissolved oxygen through the cruise. Results of the analyses are summarized in Table C.3.2. Detailed results of them are shown in Figure C.3.5. The calculation of the standard deviation from the difference of sets was based on a procedure (SOP 23) in DOE (1994).

Table C.3.2: Summary of replicate and duplicate analyses.

Measurement	Ave. \pm S.D. ($\mu\text{mol kg}^{-1}$)
Replicate	0.22 ± 0.21 (N=213)
Duplicate	0.35 ± 0.33 (N=87)

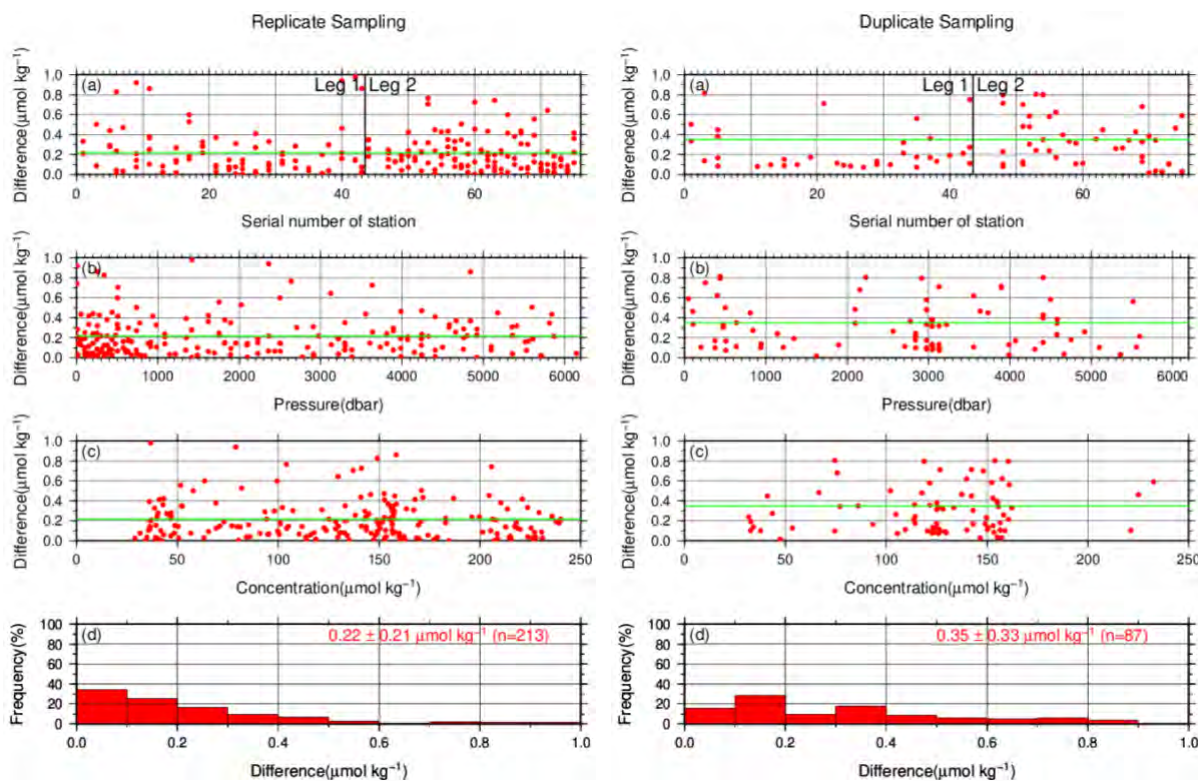


Figure C.3.5: Results of (left) replicate and (right) duplicate analyses during the cruise against (a) station number, (b) pressure and (c) concentration of dissolved oxygen. Green line denotes the average of the measurements. Bottom panels (d) show histogram of the measurements.

(7.2) Mutual comparison between each standard KIO_3 solution

During the cruise, mutual comparison between different lots of standard KIO_3 solution was performed to confirm the accuracy of our oxygen measurement and the bias of a standard KIO_3 solution. A concentration of the standard KIO_3 solution “20120404-2” was determined using $\text{Na}_2\text{S}_2\text{O}_3$ solution standardized with the KIO_3 solution “20120222”, and the difference between measurement value and theoretical one. A good agreement among two standards confirmed that there was no systematic shift in our oxygen measurements during the cruise (Figure C.3.6).

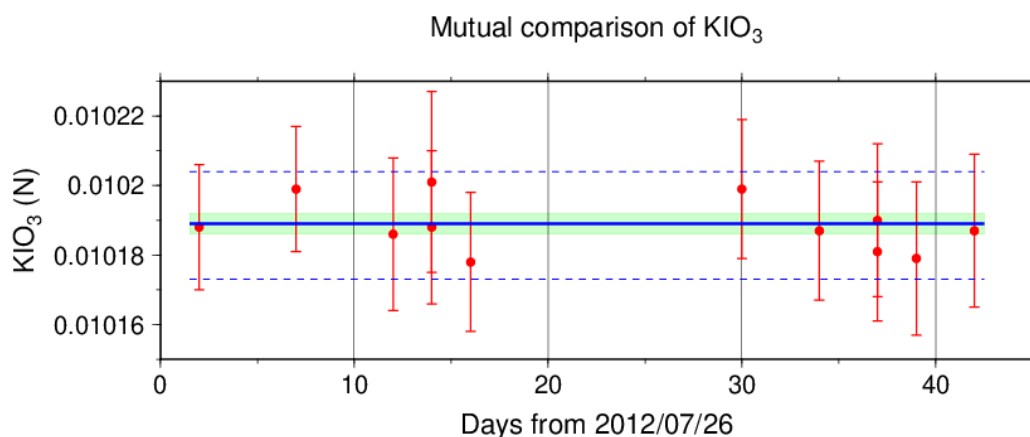


Figure C.3.6: Result of mutual comparison of standard KIO_3 solutions during the cruise. Circles and error bars show mean of the measurement value and its uncertainty ($k=2$), respectively. Thick and dashed lines in blue denote the mean and 2 times of standard deviations, respectively, for the measurement. Green thin line and light green thick line denote nominal concentration and its uncertainty ($k=2$) of standard KIO_3 solution “20120404-2”.

(7.3) Quality control flag assignment

Quality flag value was assigned to oxygen measurements as shown in Table C.3.3, using the code defined in IOCCP Report No.14 (Swift, 2010).

Table C.3.3: Summary of assigned quality control flags.

Flag	Definition	Number of samples
2	Good	1699
3	Questionable	26
4	Bad (Faulty)	52
5	Not reported	0
6	Replicate measurements	204
Total number of samples		1981

(8) Uncertainty

Oxygen measurement involves various uncertainties; determination of glass bottles volume, repeatability and systematic error of burette discharge, repeatability of pickling reagents discharge, determination of reagent blank, standardization of $\text{Na}_2\text{S}_2\text{O}_3$ solution, and uncertainty of KIO_3 concentration. Considering evaluable uncertainties as above, expanded uncertainty of bottle oxygen concentration ($T=20$, $S=34.5$) was estimated as shown in Table C.3.4. However, it is difficult to determine a strict uncertainty for oxygen concentration because there is no reference material for oxygen measurement.

Table C.3.4: Expanded uncertainty ($k=2$) of bottle oxygen in the cruise.

O ₂ conc. ($\mu\text{mol kg}^{-1}$)	Uncertainty ($\mu\text{mol kg}^{-1}$)
20	0.35
30	0.36
50	0.39
70	0.42
100	0.49
150	0.62
200	0.76
250	0.92
300	1.07
400	1.40

Appendix

A1. Methods

(A1.1) Seawater sampling

Following procedure is based on a determination method in IOCCP Report (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 bottle and a stainless steel bucket to a volumetrically calibrated dry glass bottles. At least three times the glass volume water was overflowed. Then, pickling reagent-I 1 mL and reagent-II 1mL were added immediately, and sample temperature was measured using a thermometer. After a stopper was inserted carefully into the glass, it was shaken vigorously to mix the content and to disperse the precipitate finely. After the precipitate has settled at least halfway down the glass, the glass was shaken again. The sample glasses containing pickled samples were stored in a laboratory until they were titrated. To prevent air from entering the glass, deionized water (DW) was added to its neck after sampling.

(A1.2) Sample measurement

At least 15 minutes after the re-shaking, the samples were measured on board. Added 1 mL H_2SO_4 solution and a magnetic stirrer bar into the sample glass, samples were titrated with $\text{Na}_2\text{S}_2\text{O}_3$ solution whose molarity was determined with KIO_3 solution. During the titration, the absorbance of iodine in the solution was monitored using a detector. Also, temperature of $\text{Na}_2\text{S}_2\text{O}_3$ solution during the titration was recorded using a thermometer. Dissolved oxygen concentration ($\mu\text{mol kg}^{-1}$) was calculated from sample temperature at the fixation, CTD salinity, glass volume, and titrated volume of the $\text{Na}_2\text{S}_2\text{O}_3$ solution, and oxygen in the pickling reagents-I (1 mL) and II (1 mL) (7.6×10^{-8} mol; Murray *et al.*, 1968).

A2. Reagents recipes

Pickling reagent-I; Manganous chloride solution (3 mol L^{-1})

Dissolve 600 g of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in DW, then dilute the solution with DW to a final volume of 1 L.

Pickling reagent-II; Sodium hydroxide (8 mol L^{-1}) / sodium iodide solution (4 mol L^{-1})

Dissolve 320 g of NaOH in about 500 mL of DW, allow to cool, then add 600 g NaI and dilute with DW to a final volume of 1 L.

H_2SO_4 solution; Sulfuric acid solution (5 mol L^{-1})

Slowly add 280 mL concentrated H_2SO_4 to roughly 500 mL of DW. After cooling the final volume should be 1 L.

$\text{Na}_2\text{S}_2\text{O}_3$ solution; Sodium thiosulfate solution (0.04 mol L^{-1})

Dissolve 50 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ and 0.4 g of Na_2CO_3 in DW, then dilute the solution with DW to a final volume of 5 L.

KIO_3 solution; Potassium iodate solution ($0.001667 \text{ mol L}^{-1}$)

Dry high purity KIO_3 for two hours in an oven at 130°C . After weight out accurately KIO_3 , dissolve it in DW in a 5 L flask. Concentration of potassium iodate is determined by a gravimetric method.

A3. Other blanks in oxygen measurement

(A3.1) Blank associated with oxidants or reductants in the reagents

The blank $V_{\text{blk, reg}}$, associated with oxidants or reductants in the reagent, was determined as follows. Using a calibrated pipette, 1 mL of the standard KIO_3 solution and 100 mL of DW were added to two glasses each. Then, 1 mL H_2SO_4 solution, 1 mL of pickling reagent-II and 1 mL reagent-I were added in sequence into the first glass. Next, added two times volume of the reagents (2 mL of H_2SO_4 solution, pickling reagent-II and I each) into the second one. After that, the sample was titrated to the end-point with $\text{Na}_2\text{S}_2\text{O}_3$ solution. $V_{\text{blk, reg}}$ was determined with difference of titrated volume of $\text{Na}_2\text{S}_2\text{O}_3$ between the first (total reagents volume is 3 mL) and the second (total reagents volume is 6 mL) one, also, experiments for three times and four times volume of them were carried out. The results are shown in Figure C.3.A1.

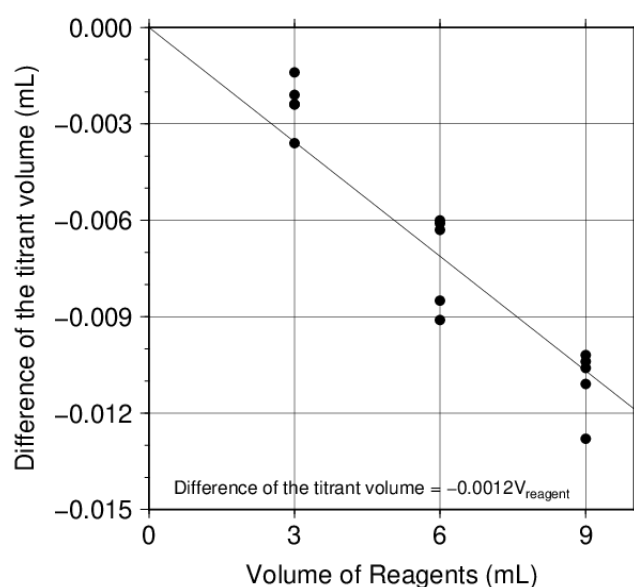


Figure C.3.A1: Blank (mL) due to redox species other than oxygen in the reagents.

The relation between difference of the titrant volume and the reagents of the volume (V_{reg}) is expressed as follows:

$$\text{Difference of the titrant volume} = -0.0012 V_{\text{reg}}. \quad (\text{C3.A1})$$

Therefore, $V_{\text{blk, reg}}$ was estimated to be +0.004 mL.

References

- Culberson, A.H. (1994) Dissolved oxygen, in WHPO Pub. 91-1 Rev. 1, November 1994, Woods Hole, Mass., USA.
- Culberson, 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.*
- Japan Meteorological Agency (2010), WHP P09 REVISIT CRUISE REPORT.
- 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.*
- 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.
- 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)

(Leg 1) Minoru HAMANA (GEMD/JMA)

(Leg 2) Takashi MIYAO (GEMD/JMA)

(2) Stations occupied

A total of 74 stations (Leg 1: 43, Leg 2: 31) were occupied for nutrients measurements. Station location and sampling layers of nutrients are shown in Figures C.4.1 and C.4.2.

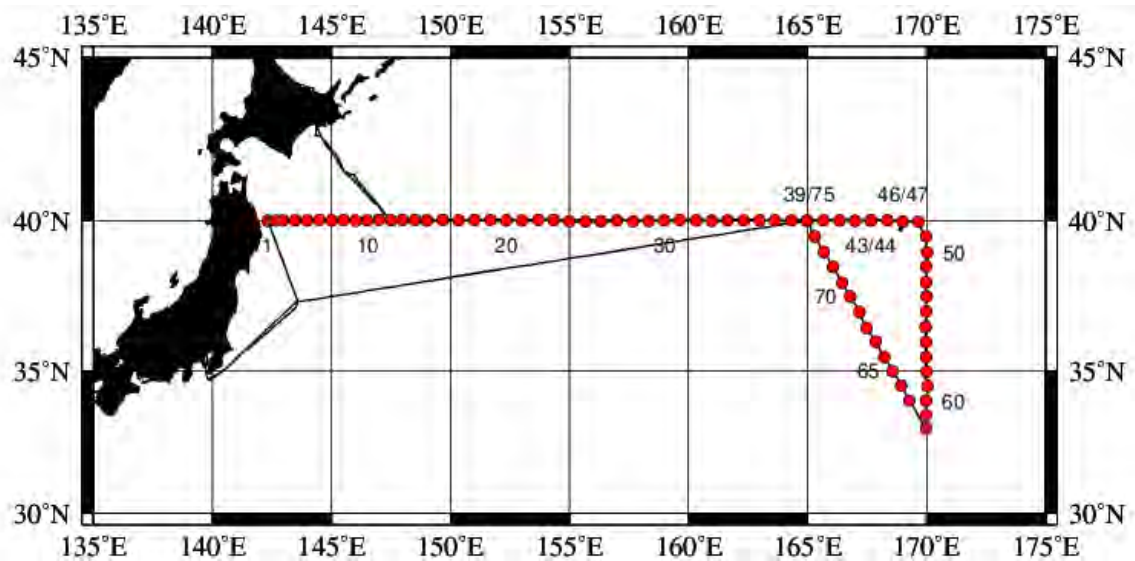


Figure C.4.1: Location of observation stations of nutrients. Closed and open circles indicate sampling and no-sampling stations, respectively.

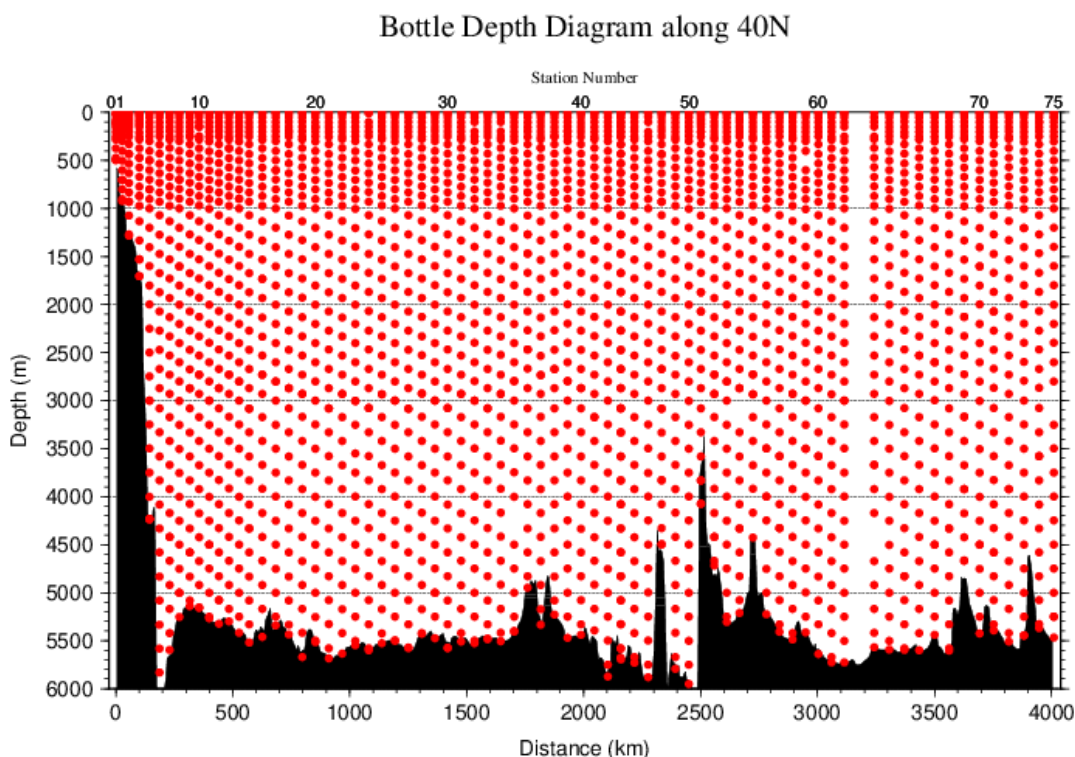


Figure C.4.2: Distance-depth distributions of sampling layers of nutrients.

(3) Instrument

The nutrients analysis was carried out on 4-channel Auto Analyzer III (BL TEC K.K., Japan) for 4 parameters; nitrate+nitrite, nitrite, phosphate, and silicate.

(4) Sampling and measurement

Methods of seawater sampling, measurement, and data processing of nutrient concentration were described in Appendixes A1, A2, and A3, respectively. The reagents for the measurement were prepared according to recipes shown in Appendix A4.

(5) Nutrients standards

(5.1) Volumetric laboratory ware of in-house standards

All volumetric wares were gravimetrically calibrated. The weights obtained in the calibration weighing were corrected for the density of water and for air buoyancy. Polymethylpenten volumetric flasks were gravimetrically calibrated at the temperature of use within 4–6 °C. 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.

(5.2) Reagents of standard

The batches of the reagents used for standard are listed in [Table C.4.1](#).

Table C.4.1: List of reagents of standard used in the cruise.

	Name	CAS No	Lot. No	Industries
Nitrate	potassium nitrate 99.995 suprapur®	7757-79-1	B0158765	Merck KGaA
Nitrite	sodium nitrite GR for analysis ACS, Reag. Ph Eur	7632-00-0	A0113649	Merck KGaA
Phosphate	potassium dihydrogen phosphate anhydrous 99.995 suprapur®	7778-77-0	B0442908	Merck KGaA
Silicate	Silicon standard solution 1000 mg/l Si*	-	HC122701** HC247279***	Merck KGaA

* Traceable to NIST-SRM3150
 ** Used before Station RF4519
 *** Used after Station RF4520

(5.3) Low nutrient seawater (LNSW)

Surface water with sufficiently low nutrient concentration was taken and filtered using 10 µm pore size membrane filter in our previous cruise. This water was stored in 20-liter flexible container with paper box.

(5.4) In-house standard solutions

Nutrient concentrations for A, B and C standards were set as shown in Table C.4.2. A and B standards were prepared with deionized water (DW). C standard (full scale of working standard) was mixture of B-1 and B-2 standards and was prepared with LNSW. C-1 standard, whose concentrations of nutrient were nearly zero, was prepared as LNSW slightly added with DW to be equal with mixing ratio of LNSW and DW in C standard. The C-2 to -5 standards were prepared with mixture of C-1 and C standards in stages as 1/4, 2/4, 3/4, and 4/4 (i.e., pure “C standard”) concentration for full scale, respectively. The actual concentration of nutrients in each standard was calculated based on the solution temperature and factors of volumetric laboratory wares calibrated prior to use. Nominal zero concentration of nutrient was determined in measurement of DW after refraction error correction. The calibration curves for each run were obtained using 5 levels of C-1 to -5 standards. These standard solutions were periodically renewed as shown in Table C.4.3.

Table C.4.2: Nominal concentrations of nutrients for A, B, and C standards at 20 °C. Unit is µmol L⁻¹.

	A	B	C
Nitrate	27480	550	43.6
Nitrite	12480	250	2.0
Phosphate	2120	42.3	3.38
Silicate	35600	2300	183.9
	35680	2310	184.2

Table C.4.3: Schedule of renewal of in-house standards.

Standard	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-1 std. (mixture of A-1, A-3, and A-4 stds.)	Maximum 8 days
B-2 std. (diluted A-2 std.)	Maximum 15 days
C-std. (mixture of B-1 and B-2 stds.)	Every measurement
C-1 to -5 stds.	Every measurement

(6) Certified reference material

Certified reference material (CRM) and reference material (RM) for nutrients in seawater, which were prepared by the General Environmental Technos (KANISO Technos, Japan), was used every analysis at each hydrographic station. Using CRM and RMs for the analysis of seawater, stable comparability and uncertainty of our data are secured.

CRM and RMs used in the cruise are shown in Table C.4.4.

Table C.4.4: Certified concentration and uncertainty (k=2) of RMs. Unit is $\mu\text{mol kg}^{-1}$.

	Nitrate	Phosphate	Silicate
RM-BS	0.058±0.028*	0.054±0.010	2.411±0.236
RM-BT	18.15±0.24	1.296±0.027	42.02±0.64
CRM-BV	35.36±0.35	2.498±0.023	102.2±1.1
RM-BF**	41.39±0.05	2.809±0.06	150.61±0.14

* Reference value because concentration is under limit of quantitation

** Assigned by Aoyama et al. (2010)

It is noted that nutrient data in our report are calibrated not on CRM and RM but on in-house standard solutions. Therefore, to calculate data based on CRM and RM, it is necessary that values of nutrient concentration in our report are correlated with CRM and RM values measured in the same analysis run. The result of CRM and RM measurements is attached as 49UP20120726_40N_nut_RM_measurement.csv.

(7) Quality Control

(7.1) Replicate and duplicate analyses

We took replicate (pair of water samples taken from a single Niskin bottle) and duplicate (pair of water samples taken from different Niskin bottles closed at the same depth) samples of nutrient through the

cruise. Results of the analyses are summarized in Table C.4.5. Detailed results of them are shown in Figures C.4.3–C.4.5. The calculation of the standard deviation from the difference of sets was based on a procedure (SOP 23) in *DOE* (1994).

Table C.4.5: Average and standard deviation of difference of replicate and duplicate analyses through the cruise. Unit is $\mu\text{mol kg}^{-1}$.

Measurement	Nitrate+nitrite	Phosphate	Silicate
Replicate	0.063 ± 0.064 (N=275)	0.003 ± 0.003 (N=282)	0.104 ± 0.098 (N=287)
Duplicate	0.092 ± 0.086 (N=130)	0.004 ± 0.005 (N=130)	0.178 ± 0.193 (N=129)

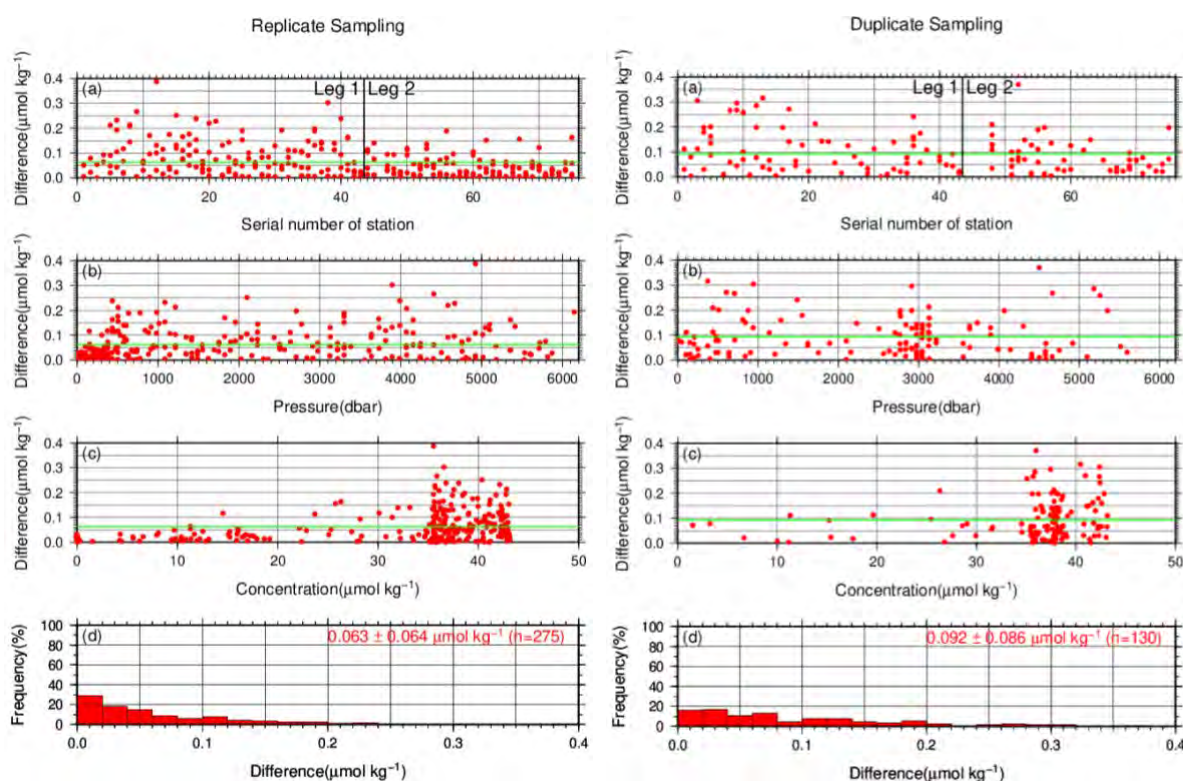


Figure C.4.3. Result of (left) replicate and (right) duplicate analyses of nitrate+nitrite through the cruise versus (a) station number, (b) sampling pressure, (c) concentration, and (d) histogram of the measurements. Green line indicates the mean of the differences of concentration of replicate/duplicate analyses.

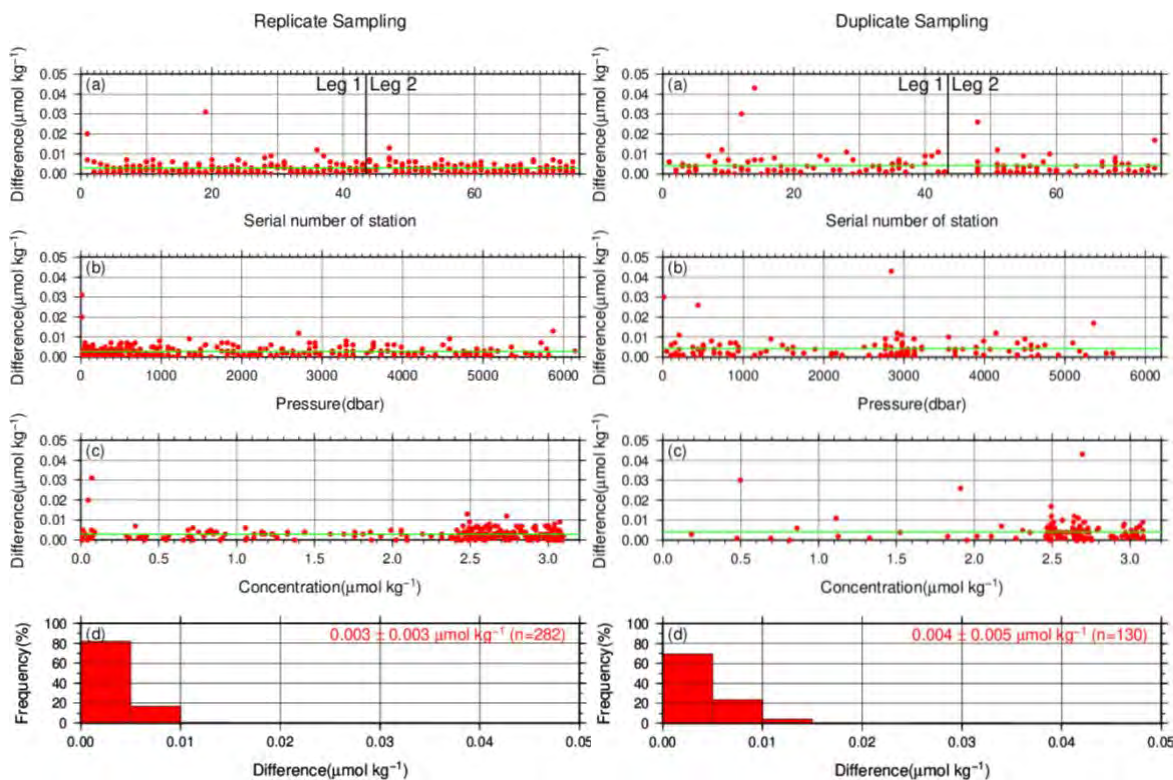


Figure C.4.4: Same as Figure C.4.3 but for phosphate.

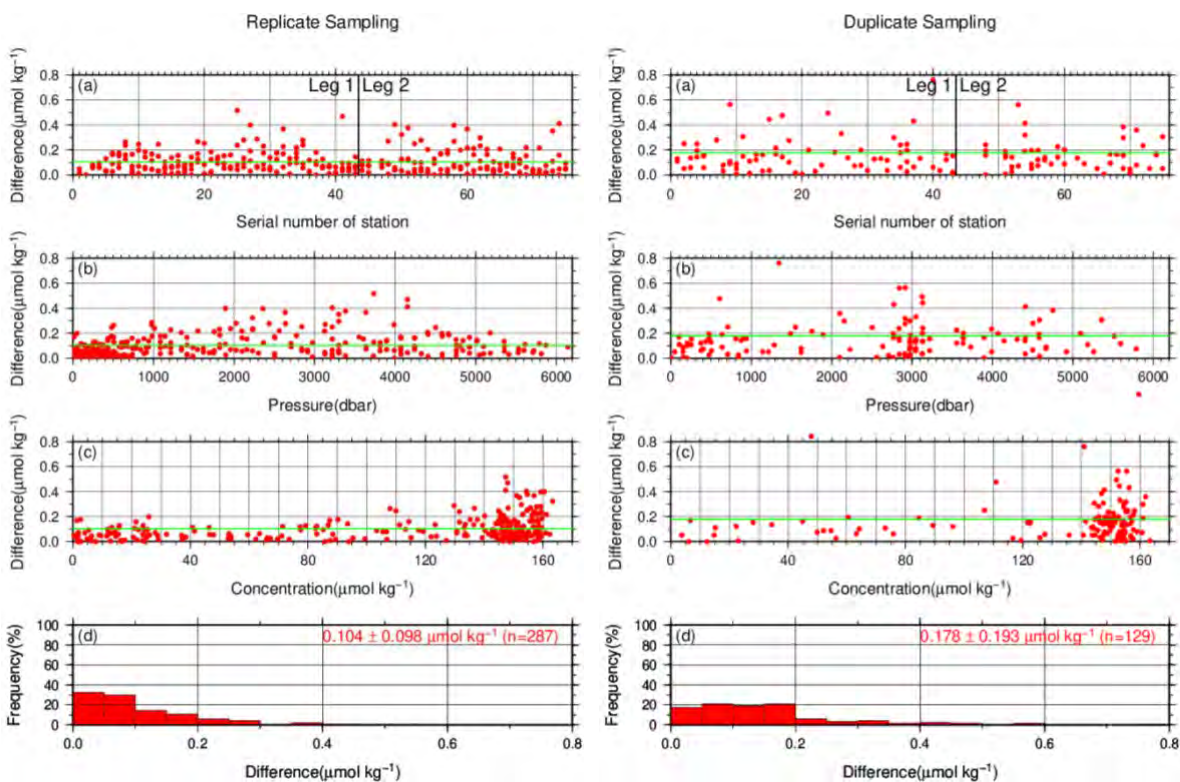


Figure C.4.5: Same as Figure C.4.3 but for silicate.

(7.2) Measurement of CRMs

CRM and RM measurements during the cruise are summarized in Table C.4.6, whose concentrations were assigned with in-house standard solutions. The measured concentrations of CRM-BV through the cruise are shown in Figures C.4.6–C.4.9.

Table C.4.6: Summary of (upper) mean concentration and its standard deviation (unit: $\mu\text{mol kg}^{-1}$), (middle) coefficient of variation (%), and (lower) total number of CRM and RMs measurements through the cruise.

	Nitrate+nitrite	Nitrite	Phosphate	Silicate
RM-BS	0.073 \pm 0.037 50.86% (N=147)	0.013 \pm 0.003 22.42% (N=144)	0.029 \pm 0.006 19.18% (N=147)	1.78 \pm 0.10 5.86% (N=147)
RM-BT	18.63 \pm 0.07 0.39% (N=112)	0.046 \pm 0.028 6.04% (N=112)	1.29 \pm 0.01 0.76% (N=112)	42.00 \pm 0.14 0.34% (N=112)
CRM-BV	35.39 \pm 0.10 0.28% (N=147)	0.040 \pm 0.003 6.65% (N=145)	2.50 \pm 0.01 0.45% (N=147)	102.26 \pm 0.27 0.26% (N=147)
RM-BF	41.38 \pm 0.11 0.26% (N=112)	0.017 \pm 0.003 16.02% (N=112)	2.79 \pm 0.01 0.37% (N=112)	153.73 \pm 0.37 0.24% (N=112)

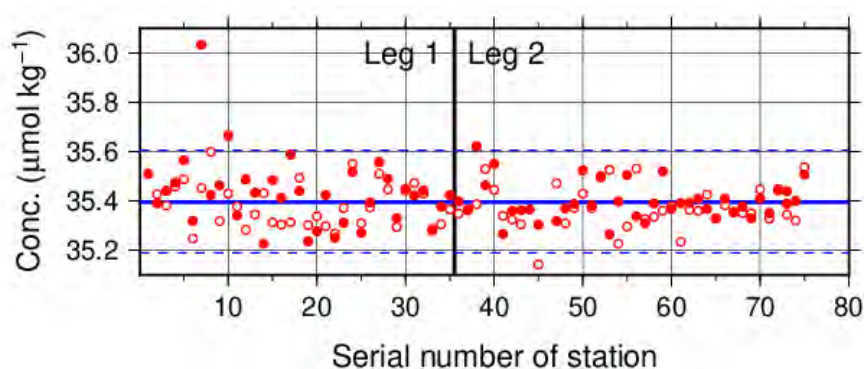


Figure C.4.6: Time-series of measured concentration of nitrate+nitrite of CRM-BV through the cruise. Closed and open circles indicate the newly and previously opened bottle, respectively. Thick and dashed lines denote the mean and 2 times of standard deviations of the measurements through the cruise, respectively.

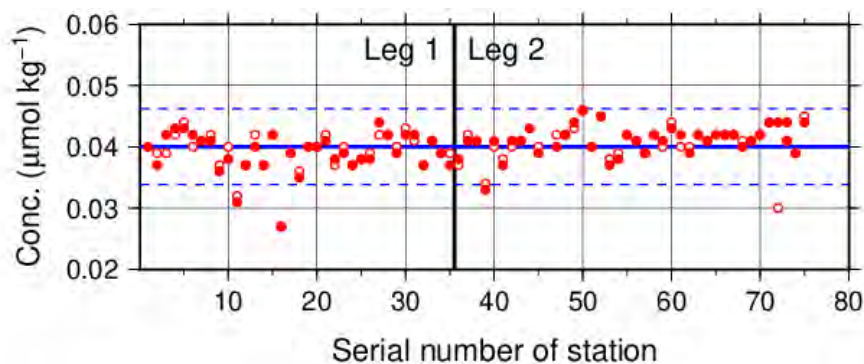


Figure C.4.7: Same as [Figure C.4.6](#) but for nitrite.

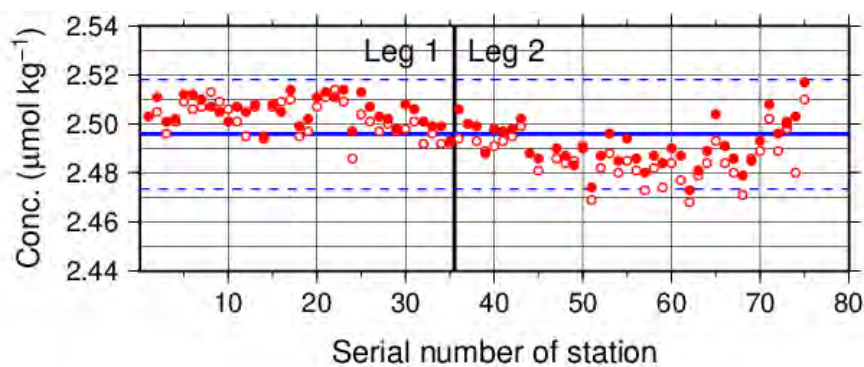


Figure C.4.8: Same as [Figure C.4.6](#) but for phosphate.

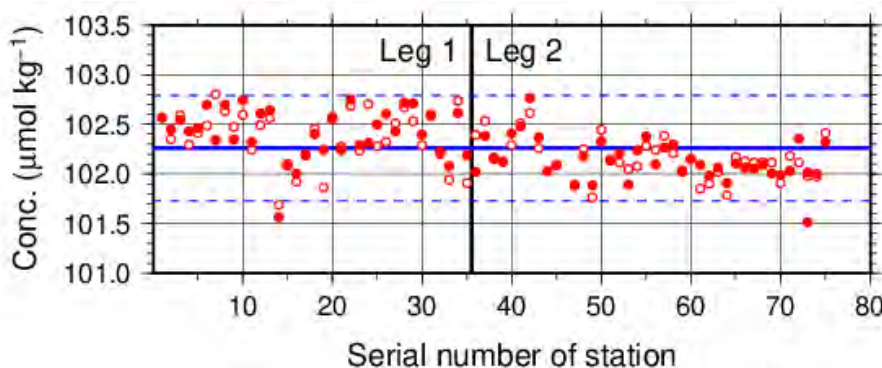


Figure C.4.9: Same as [Figure C.4.6](#) but for silicate.

(7.3) Precision of analysis in a run

To monitor precision of analysis, the same samples were repeatedly measured in a sample array in a run. For this, C-5 standard solutions were randomly arrayed in every 2–10 samples as “check standard” (the number of the standard is about 8–9) in the run. The precision was estimated as coefficient of variation

of the measurements. The results are summarized in [Table C.4.7](#). The time series are shown in [Figures C.4.10–C.4.13](#).

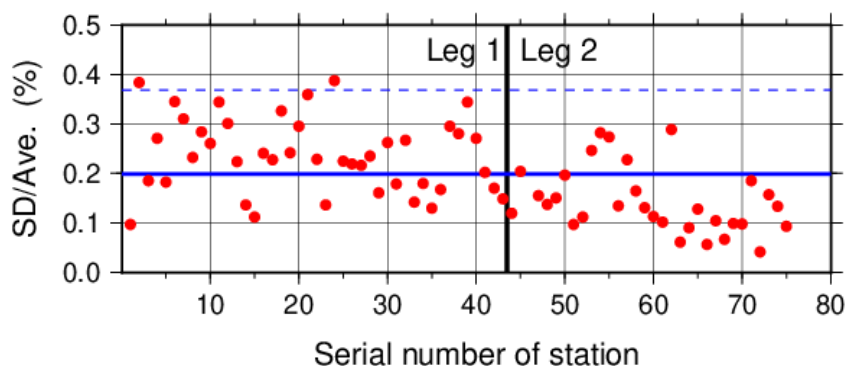


Figure C.4.10: Time-series of coefficient of variation of “check standard” measurement of nitrate+nitrite through the cruise. Thick and dashed lines denote the mean and 2 times of standard deviations of the measurements through the cruise, respectively.

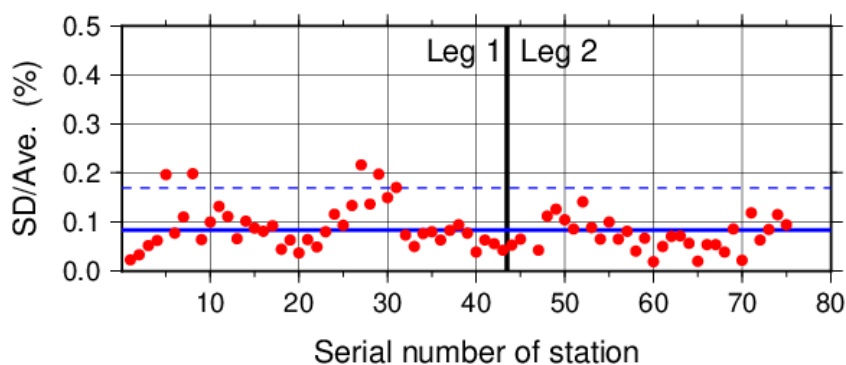


Figure C.4.11: Same as Figure C.4.10 but for nitrite.

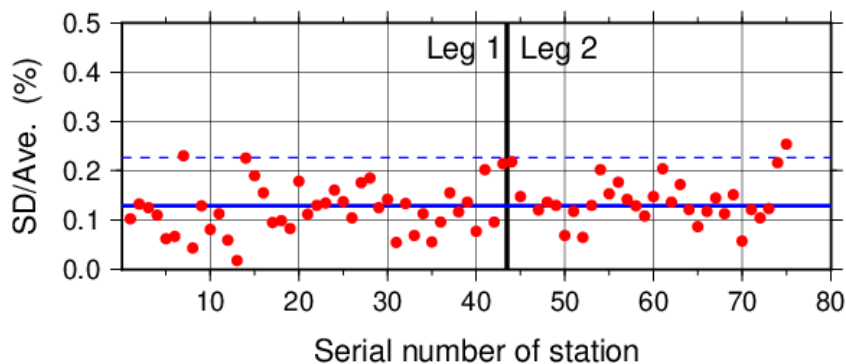


Figure C.4.12: Same as Figure C.4.10 but for phosphate.

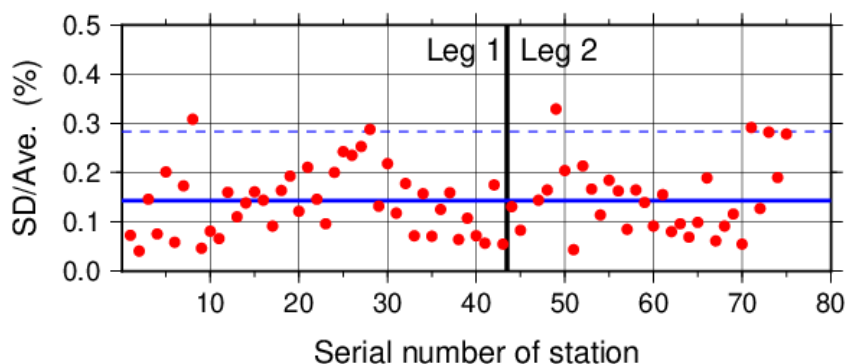


Figure C.4.13: Same as [Figure C.4.10](#) but for silicate.

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

	Nitrate+nitrite	Nitrite	Phosphate	Silicate
Median	0.19%	0.08%	0.13%	0.14%
Mean	0.20%	0.08%	0.13%	0.14%
Minimum	0.04%	0.02%	0.02%	0.04%
Maximum	0.39%	0.22%	0.25%	0.33%
Number	74	74	74	74

(7.4) Limit of detection/quantitation of measurement

Limit of detection (LOD) and quantitation (LOQ) of nutrient measurement were estimated from standard deviation (σ) of repeated measurements of nutrients concentration in C-1 standard as 3σ and 10σ , respectively. Summary of LOD and LOQ are shown in Table C.4.8.

Table C.4.8: Limit of detection (LOD) and quantitation (LOQ) of nutrient measurement in the cruise. Unit is $\mu\text{mol kg}^{-1}$.

	LOD	LOQ
Nitrate+nitrite	0.045	0.150
Nitrite	0.002	0.005
Phosphate	0.012	0.041
Silicate	0.130	0.435

(7.5) Quality control flag assignment

Quality flag value was assigned to nutriment measurements as shown in [Table C.4.9](#), using the code defined in IOCCP Report No.14 (Swift, 2010).

Table C.4.9: Summary of assigned quality control flags.

Flag	Definition	Nitrate+nitrite	Nitrite	Phosphate	Silicate
2	Good	2310	2331	2315	2325
3	Questionable	31	0	19	2
4	Bad (Faulty)	32	30	32	34
5	Not reported	4	6	4	4
6	Replicate measurements	275	285	282	287
Total number of samples		2652	2652	2652	2652

(8) Uncertainty

(8.1) Uncertainty associated with concentration level: U_c

Generally, an uncertainty of nutrient measurement is expressed as a function of its concentration level which reflects that some components of uncertainty are relatively large in low concentration. Empirically, the uncertainty associated with concentrations level (U_c) can be expressed as follows:

$$U_c (\%) = a + b \cdot (1/C_x) + c \cdot (1/C_x)^2, \quad (C4.1)$$

where C_x is the concentration of sample for parameter X.

Using the coefficients of variation of the CRM measurements throughout the cruise, uncertainty associated with concentrations of nitrate+nitrite, phosphate, and silicate were determined as follows:

$$U_{c-no3} (\%) = 0.158 + 4.299 \times (1/C_n) - 0.043 \times (1/C_n)^2 \quad (C4.2)$$

$$U_{c-po4} (\%) = 0.080 + 0.886 \times (1/C_p) - 0.0097 \times (1/C_p)^2 \quad (C4.3)$$

$$U_{c-sil} (\%) = 0.203 + 5.573 \times (1/C_s) + 8.073 \times (1/C_s)^2, \quad (C4.4)$$

where C_n , C_p , and C_s represent concentrations of nitrate+nitrite, phosphate, and silicate, respectively, in $\mu\text{mol kg}^{-1}$. Figures C.4.14–C.4.16 show the calculated uncertainty graphically.

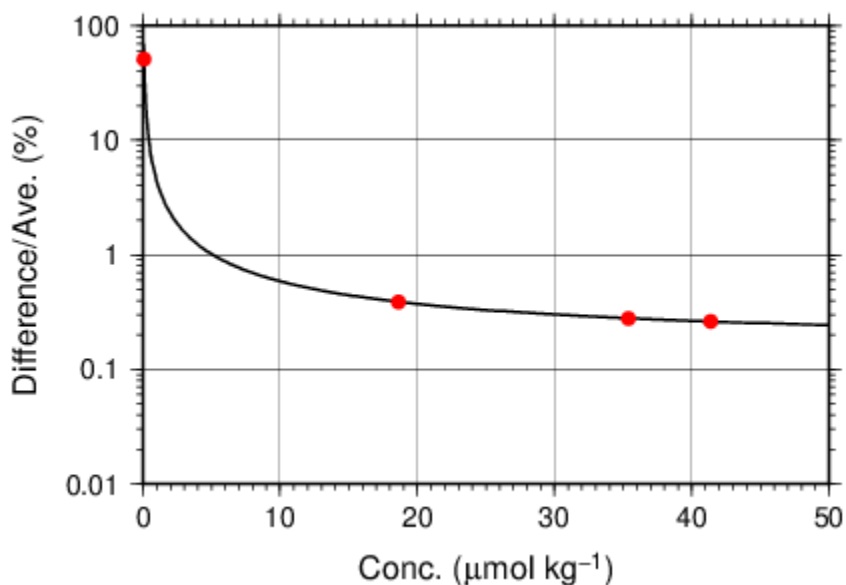


Figure C.4.14: Uncertainty of nitrate+nitrite associated with concentration level.

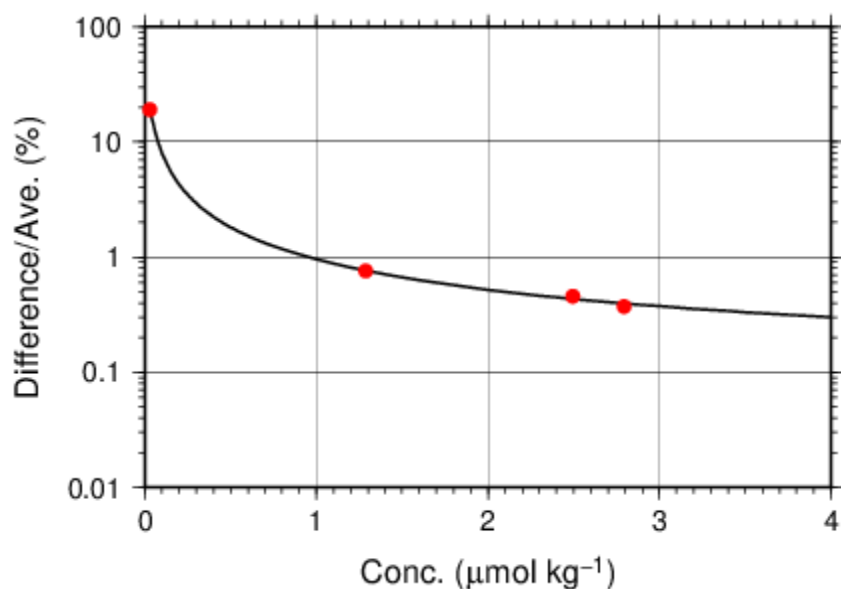


Figure C.4.15: Same as Figure C.4.14 but for phosphate.

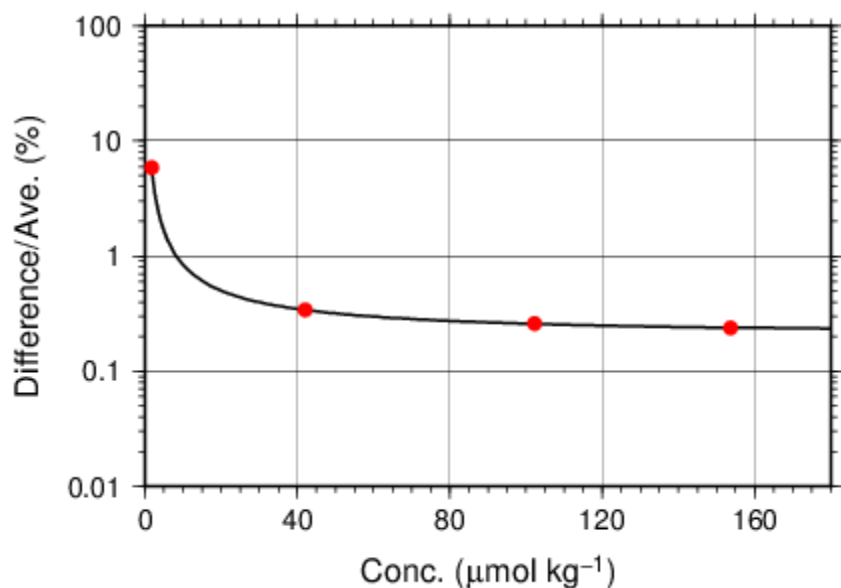


Figure C.4.16: Same as Figure C.4.14 but for silicate.

(8.2) Uncertainty of analysis between runs: U_s

Uncertainty of analysis among runs (U_s) was evaluated based on the coefficient of variation of measured concentrations of CRM-BV with high concentration among the CRM lots throughout the cruise, as shown in subsection (7.2). The reason for using the CRM lot BV to state $\underline{U_s}$ is to exclude the effect of uncertainty associated with lower concentration described previously. As is clear from the definition of U_c , U_s is equal to U_c at nutrients concentrations of lot BV. It is important to note that U_s includes all of uncertainties during the measurements throughout stations, namely uncertainties of concentrations of in-

house standard solutions prepared for each run, uncertainties of slopes and intercepts of the calibration curve in each run if first order calibration curve applied, precision of measurement in a run (U_a), and between-bottle homogeneity of the CRM.

(8.3) *Uncertainty of analysis in a run: U_a*

Uncertainty of analysis in a run (U_a) was evaluated based on the coefficient of variation of repeated measurements of the “check standard” solution, as shown in subsection (7.3). The U_a reflects the conditions associated with chemistry of colorimetric measurement of nutrients, and stability of electronic and optical parts of the instrument throughout a run. Under a well-controlled condition of the measurements, U_a might show Poisson distribution with a mean as shown in [Figures C.4.10–C.4.13](#) and [Table C.4.7](#) and treated as a precision of measurement. U_a is a part of U_c at the concentration as stated in a previous section for U_c .

However, U_a may show larger value which was not expected from Poisson distribution of U_a due to the malfunction of the instruments, larger ambient temperature change, human errors in handling samples and chemistries and contaminations of samples in a run. In the cruise, we observed that U_a of our measurement was usually small and well-controlled in most runs as shown in [Figures C.4.10–C.4.13](#) and [Table C.4.7](#). However, in a few runs, U_a showed high values which were over the mean \pm twice the standard deviations of U_a , suggesting that the measurement system might have some problems.

(8.4) *Uncertainty of CRM concentration: U_r*

In the certification of CRM, the uncertainty of CRM concentrations (U_r) was stated by the manufacturer ([Table C.4.4](#)) as expanded uncertainty at $k=2$. This expanded uncertainty reflects the uncertainty of the Japan Calibration Service System (JCSS) solutions, characterization in assignment, between-bottle homogeneity, and long-term stability. We have ensured comparability between cruises by ensuring that at least two lots of CRMs overlap between cruises. In comparison of nutrient concentrations between cruises using KANSO CRMs in an organization, it was not necessary to include U_r in the conclusive uncertainty of concentration of measured samples because comparability of measurements was ensured in an organization as stated previously.

(8.5) *Combined relative standard uncertainty: U*

To determine the conclusive uncertainty of nutrient measurements of samples (U), 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:

$$U = U_c. \quad (C4.5)$$

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:

$$U = \sqrt{U_c^2 + U_a^2}. \quad (C4.6)$$

When U_a was relatively large and the measurement might have some problems, the equation of U is defined as to include U_a to evaluate U , although U_a partly overlaps with U_c . It means that the equation overestimates the conclusive uncertainty of samples. On the other hand, for low concentration there is a possibility that the equation not only overestimates but also underestimates the conclusive uncertainty because the functional shape of U_c in lower concentration might not be the same and cannot be verified.

However, we believe that the applying the above function might be better way to evaluate the conclusive uncertainty of nutrient measurements of samples because we can do realistic evaluation of uncertainties of nutrient concentrations of samples which were obtained under relatively unstable conditions, larger U_a as well as the evaluation of them under normal and good conditions of measurements of nutrients.

Appendix

A1. Seawater sampling

Seawater samples were collected from 10-liters Niskin bottle attached CTD-system and a stainless steel bucket for the surface. Samples were drawn into 10 mL polymethylpenten vials using sample drawing tubes. The vials were rinsed three times before water filling and were capped immediately after the drawing.

No transfer was made and the vials were set on an auto sampler tray directly. Samples were analyzed immediately after collection.

A2. Measurement

(A2.1) General

Auto Analyzer III is based on Continuous Flow Analysis method and consists of sampler, pump, manifolds, and colorimeters. As a baseline, we used artificial seawater (ASW).

(A2.2) Nitrate+nitrite and nitrite

Nitrate+nitrite and nitrite were analyzed according to the modification method of Armstrong (1967). The sample nitrate was reduced to nitrite in a glass tube which was filled with granular cadmium coated with copper. The sample stream with its equivalent nitrite was 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 was added to the sample stream then coupled with the diazonium ion to produce a red, azo dye. With reduction of the nitrate to nitrite, sum of nitrate and nitrite were measured; without reduction, only nitrite was measured. Thus, for the nitrite analysis, no reduction was performed and the alkaline buffer was not necessary. The flow diagrams for each parameter are shown in [Figures C.4.A1 and C.4.A2](#). If the reduction efficiency of the cadmium column became lower than 95 %, the column was replaced.

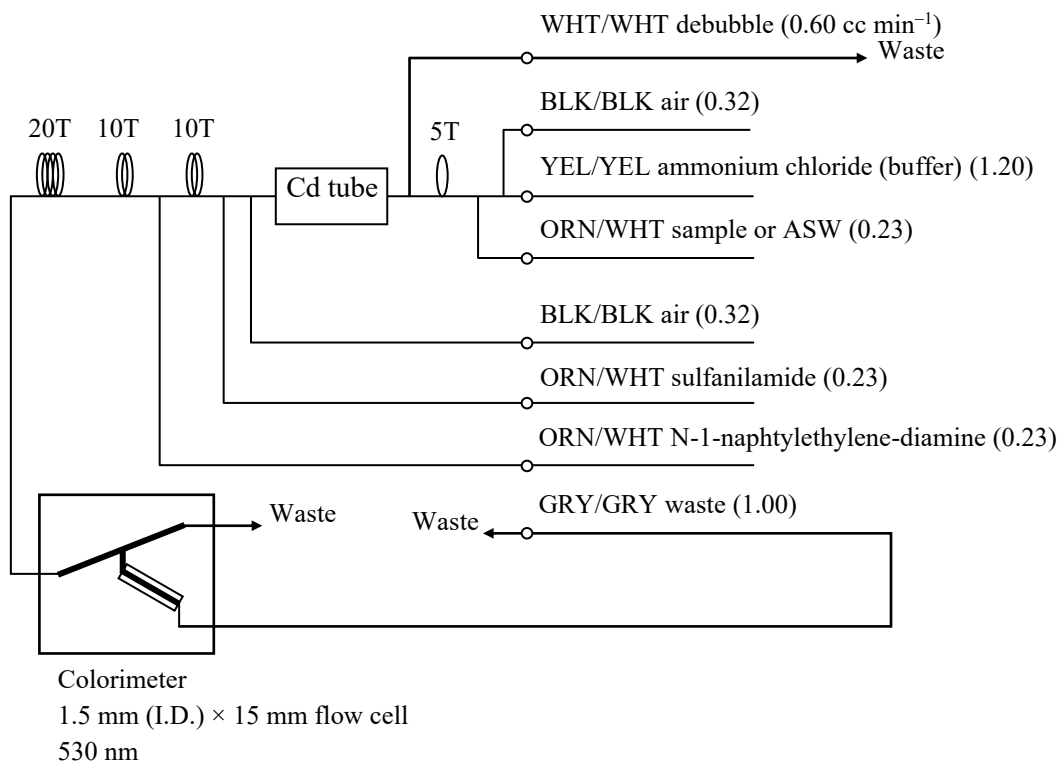


Figure C.4.A1: Nitrate+nitrite (1ch.) flow diagram.

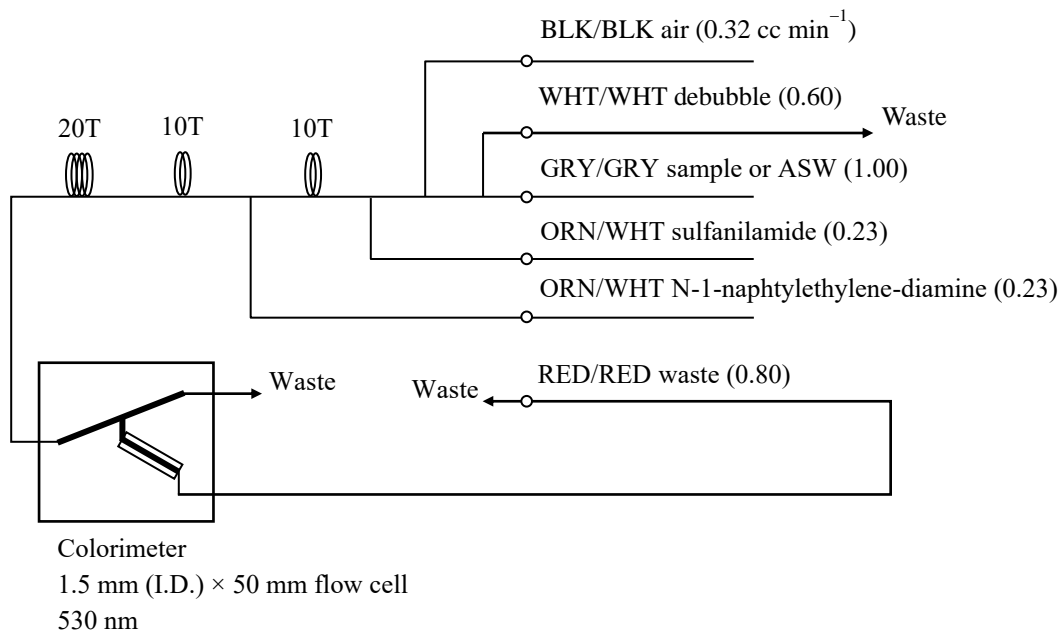


Figure C.4.A2: Nitrite (2ch.) flow diagram.

(A2.3) Phosphate

The phosphate analysis was a modification of the procedure of Murphy and Riley (1962). Molybdic acid was added to the seawater sample to form phosphomolybdic acid which was in turn reduced to phosphomolybdous acid using L-ascorbic acid as the reductant. The flow diagram for phosphate is shown in Figure C.4.A3.

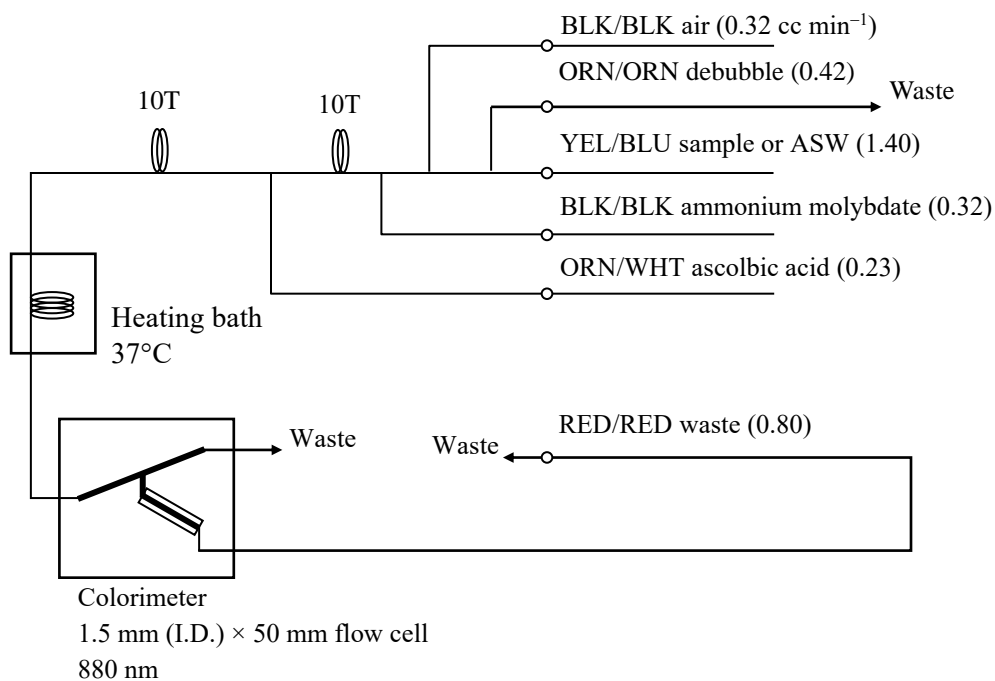


Figure C.4.A3. Phosphate (3ch.) flow diagram.

(A2.4) Silicate

The silicate was analyzed according to the modification method of Grasshoff *et al.* (1983), wherein silicomolybdic acid was first formed from the silicate in the sample and added molybdic acid, then the silicomolybdic acid was reduced to silicomolybdous acid, or "molybdenum blue," using L-ascorbic acid as the reductant. The flow diagram for silicate is shown in Figure C.4.A4.

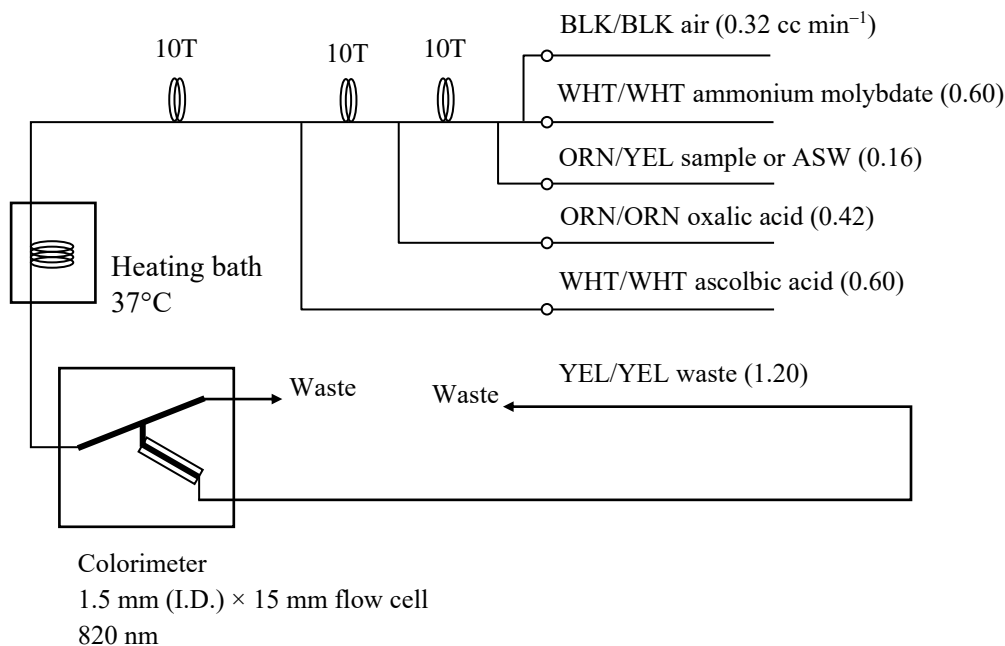


Figure C.4.A4. Silicate (4ch.) flow diagram.

A3. Data processing

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

- 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.
- Carryover 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.
- Concentrations were converted from $\mu\text{mol L}^{-1}$ to $\mu\text{mol kg}^{-1}$ using seawater density.

A4. Reagents recipes

(A4.1) Nitrate+nitrite

Ammonium chloride (buffer), $0.7 \mu\text{mol L}^{-1}$ (0.04 % w/v);

Dissolve 190 g ammonium chloride, NH_4Cl , in ca. 5 L of DW, add about 5 mL ammonia(aq) to adjust pH of 8.2–8.5.

Sulfanilamide, $0.06 \mu\text{mol L}^{-1}$ (1 % w/v);

Dissolve 5 g sulfanilamide, $4\text{-NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$, in 430 mL DW, add 70 mL concentrated HCl. After mixing, add 1 mL Brij-35 (22 % w/w).

N-1-naphtylethylene-diamine dihydrochloride (NEDA), $0.004 \mu\text{mol L}^{-1}$ (0.1 % w/v);

Dissolve 0.5 g NEDA, $\text{C}_{10}\text{H}_7\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \cdot 2\text{HCl}$, in 500 mL DW.

(A4.2) Nitrite

Sulfanilamide, $0.06 \mu\text{mol L}^{-1}$ (1 % w/v); Shared from nitrate reagent.

N-1-naphtylethylene-diamine dihydrochloride (NEDA), $0.004 \mu\text{mol L}^{-1}$ (0.1 % w/v); Shared from nitrate reagent.

(A4.3) Phosphate

Ammonium molybdate, $0.005 \mu\text{mol L}^{-1}$ (0.6 % w/v);

Dissolve 3 g ammonium molybdate(VI) tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and 0.05 g potassium antimonyl tartrate, $\text{C}_8\text{H}_4\text{K}_2\text{O}_{12}\text{Sb}_2 \cdot 3\text{H}_2\text{O}$, in 400 mL DW and add 40 mL concentrated H_2SO_4 . After mixing, dilute the solution with DW to final volume of 500 mL and add 2 mL sodium dodecyl sulfate (15 % solution in water).

L(+)-ascorbic acid, $0.08 \mu\text{mol L}^{-1}$ (1.5 % w/v);

Dissolve 4.5 g L(+)-ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$, in 300 mL DW. After mixing, add 10 mL acetone. This reagent was freshly prepared before every measurement.

(A4.4) Silicate

Ammonium molybdate, $0.005 \mu\text{mol L}^{-1}$ (0.6 % w/v);

Dissolve 3 g ammonium molybdate(VI) tetrahydrate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in 500 mL DW and added concentrated 2 mL H_2SO_4 . After mixing, add 2 mL sodium dodecyl sulfate (15 % solution in water).

Oxalic acid, $0.4 \mu\text{mol L}^{-1}$ (5 % w/v);

Dissolve 25 g oxalic acid dihydrate, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, in 500 mL DW.

L(+)-ascorbic acid, $0.08 \mu\text{mol L}^{-1}$ (1.5 % w/v); Shared from phosphate reagent.

(A4.5) Baseline

Artificial seawater (salinity is ~34.7);

Dissolve 160.6 g sodium chloride, NaCl , 35.6 g magnesium sulfate heptahydrate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.84 g sodium hydrogen carbonate, NaHCO_3 , in 5 L DW.

References

- 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.
- 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.*
- Grasshoff, K., Ehrhardt, M., Kremling K. et al. (1983), Methods of seawater analysis. 2nd rev, *Weinheim: Verlag Chemie, Germany, West.*
- Murphy, J. and Riley, J.P. (1962), *Analytica chimica Acta*, 27, 31-36.
- 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.*

5. Phytopigments (chlorophyll-a and phaeopigment)

1 November 2019

(1) Personnel

Chihiro KAWAMURA (GEMD/JMA)

Takashi MIYAO (GEMD/JMA)

(2) Stations occupied

A total of 41 stations (Leg 1: 24, Leg 2: 17) were occupied for phytopigment measurements. Station location and sampling layers of phytopigment are shown in Figures C.5.1 and C.5.2.

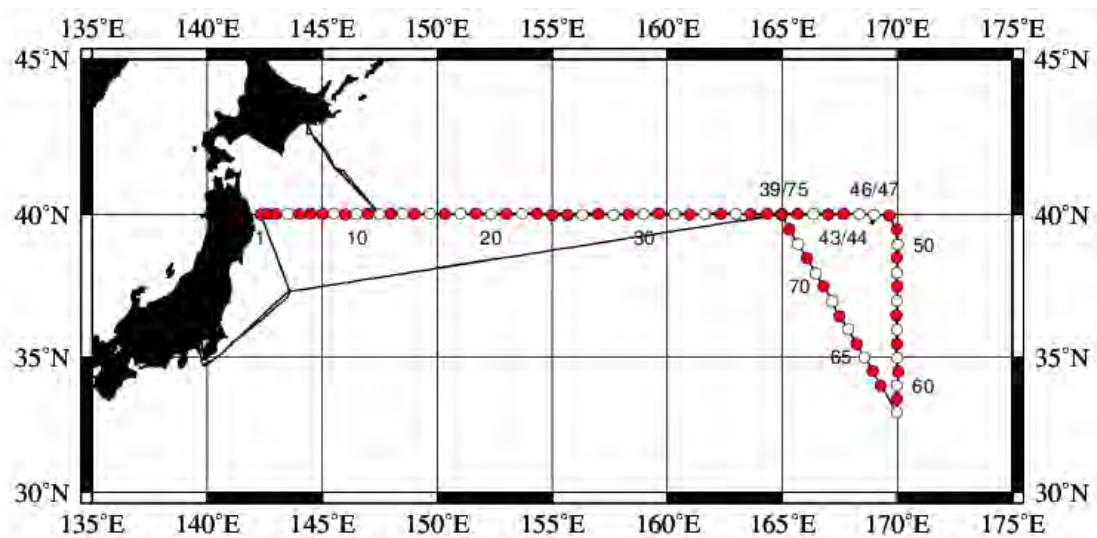


Figure C.5.1: Location of observation stations of chlorophyll-a. Closed and open circles indicate sampling and no-sampling stations, respectively.

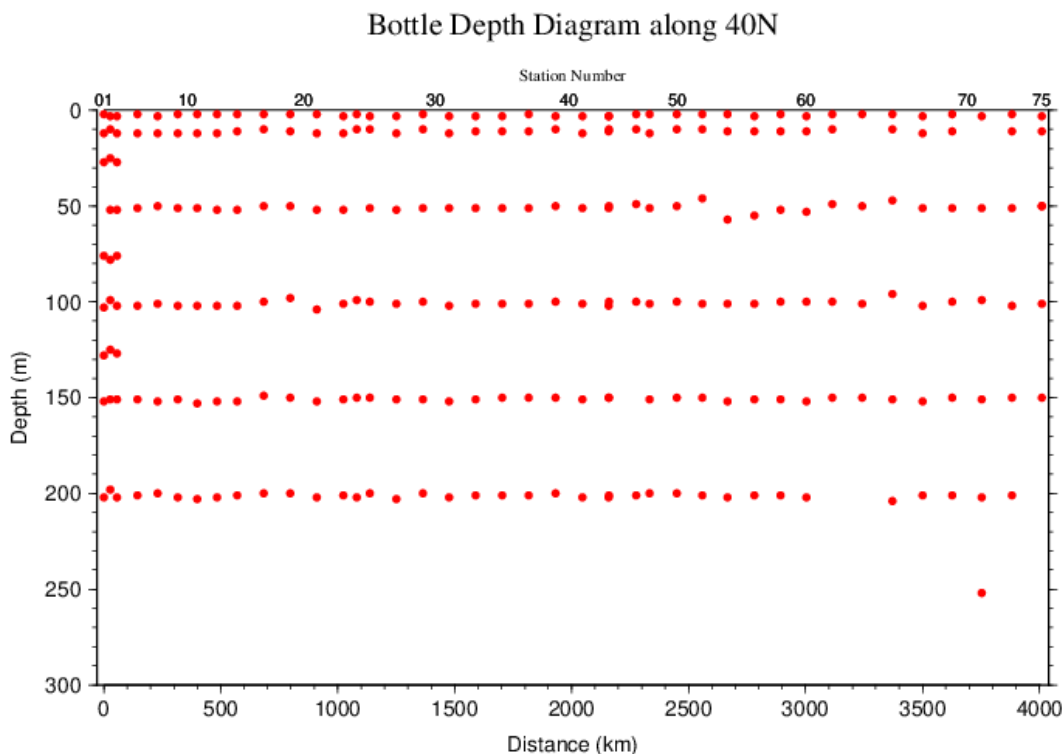


Figure C.5.2. Distance-depth distribution of sampling layers of chlorophyll-*a*.

(3) Reagents

N,N-dimethylformamide (DMF)

Hydrochloric acid (HCl), 0.5 mol L⁻¹

Chlorophyll-*a* standard from *Anacystis nidulans* algae (Sigma-Aldrich, United States)

Rhodamine WT (Turner Designs, United States)

(4) Instruments

Fluorometer: 10-AU (Turner Designs, United States)

Spectrophotometer: UV-1800 (Shimadzu, Japan)

(5) Standardization

(5.1) Determination of chlorophyll-*a* concentration of standard solution

To prepare the pure chlorophyll-*a* standard solution, reagent powder of chlorophyll-*a* standard was dissolved in DMF. A concentration of the chlorophyll-*a* solution was determined with the spectrophotometer as follows:

$$\text{chl } a \text{ concentration } (\mu\text{g mL}^{-1}) = A_{\text{chl}} / a_{\text{phy}}^* \quad (\text{C5.1})$$

where A_{chl} is the difference between absorbance at 663.8 nm and 750 nm, and a_{phy}^* is specific absorption coefficient (UNESCO, 1994). The specific absorption coefficient is 88.74 L g⁻¹ cm⁻¹ (Porra *et al.*, 1989).

(5.2) Determination of R and f_{ph}

Before measurements, sensitivity of the fluorometer was calibrated with pure DMF and a rhodamine 1 ppm solution (diluted with deionized water).

The chlorophyll- a standard solution, whose concentration was precisely determined in subsection (5.1), was measured with the fluorometer, and after acidified with 1–2 drops $0.5 \text{ mol L}^{-1} \text{ HCl}$ the solution was also measured. The acidification coefficient (R) of the fluorometer was also calculated as the ratio of the unacidified and acidified readings of chlorophyll- a standard solution. The linear calibration factor (f_{ph}) of the fluorometer was calculated as the slope of the acidified reading against chlorophyll- a concentration. The R and f_{ph} in the cruise are shown in Table C.5.1.

Table C.5.1. R and f_{ph} in the cruise.

Acidification coefficient (R)	1.764
Linear calibration factor (f_{ph})	7.8333

(6) Seawater sampling and measurement

Water samples were collected from 10-liters Niskin bottle attached the CTD-system and a stainless steel bucket for the surface. A 200 mL seawater sample was immediately filtered through 25 mm GF/F filters by low vacuum pressure below 15 cmHg, the particulate matter collected on the filter. Phytopigments were extracted in vial with 9 mL of DMF. The extracts were stored for 24 hours in the refrigerator at -30°C until analysis.

After the extracts were put on the room temperature for at least one hour in the dark, the extracts were decanted from the vial to the cuvette. Fluorometer readings for each cuvette were taken before and after acidification with 1–2 drops $0.5 \text{ mol L}^{-1} \text{ HCl}$. Chlorophyll- a and phaeopigment concentrations ($\mu\text{g mL}^{-1}$) in the sample are calculated as follows:

$$\text{chl } a \text{ conc.} = \frac{F_0 - F_a}{f_{ph} \cdot (R - 1)} \cdot \frac{v}{V} \quad (\text{C5.2})$$

$$\text{phaeo. conc.} = \frac{R \cdot F_0 - F_a}{f_{ph} \cdot (R - 1)} \cdot \frac{v}{V} \quad (\text{C5.3})$$

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 value was assigned to oxygen measurements as shown in [Table C.5.2](#), using the code defined in IOCCP Report No.14 (Swift, 2010).

Table C.5.2: Summary of assigned quality control flags.

Flag	Definition	Chl <i>a</i>	Phaeo.
2	Good	247	247
3	Questionable	0	0
4	Bad (Faulty)	0	0
5	Not reported	2	2
Total number		249	249

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 absorption spectroscopy. *Biochem. Biophys. 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*.

CCHDO Data Processing Notes

- **File Online Carolina Berys**

[40nsu.txt \(download\)](#) #8cb36

Date: 2018-06-08

Current Status: unprocessed

- **File Online Carolina Berys**

[ct1.zip \(download\)](#) #5b415

Date: 2018-06-08

Current Status: unprocessed

- **File Online Carolina Berys**

[40n_hyl.csv \(download\)](#) #9551a

Date: 2018-06-08

Current Status: unprocessed

- **File Online Carolina Berys**

[A_cruise_narrative_2012_40N_20180502.doc \(download\)](#) #656a8

Date: 2018-06-08

Current Status: unprocessed

- **File Submission Toshiya NAKANO**

[ct1.zip \(download\)](#) #5b415

Date: 2018-05-12

Current Status: unprocessed

Notes

Cruise Narrative and Bottle data were updated.

- **File Submission Toshiya NAKANO**

[40nsu.txt \(download\)](#) #8cb36

Date: 2018-05-12

Current Status: unprocessed

Notes

Cruise Narrative and Bottle data were updated.

- **File Submission Toshiya NAKANO**

[40n_hyl.csv \(download\)](#) #9551a

Date: 2018-05-12

Current Status: unprocessed

Notes

Cruise Narrative and Bottle data were updated.

- **File Submission Toshiya NAKANO**

[A_cruise_narrative_2012_40N_20180502.doc \(download\)](#) #656a8

Date: 2018-05-12

Current Status: unprocessed

Notes

Cruise Narrative and Bottle data were updated.

- **Confirmed as a GO-SHIP Contributor Andrew Barna**

Date: 2017-05-12

Data Type:

Action: Metadata Confirmation

Note:

I have confirmed this cruise is a contributor to the GO-SHIP colaboration via the cruise overview.

http://www.data.jma.go.jp/gmd/kaiyou/data/db/vessel_obs/data-report/data/2012/ship/RF1206/RF1206.SUM

- **File Merge cchdo_admin**

[20131206_40nsu.txt \(download\)](#) #c5e35

Date: 2014-09-08

Current Status: merged

Notes

SUM

- **Put SUM file online Geetha Ratnam**

Date: 2014-09-08

Data Type: SUM

Action: Website Update

Note:

```
=====
RF12-06 2012 49RY20120726 processing - SUM
=====
```

2014-09-08

G Ratnam

.. contents:: :depth: 2

Submission

=====

filename	submitted by	date	data type	id
20131206_40nsu.txt	Toshiya NAKANO	2013-12-05	SUM	1114

Process

=====

Changes

-Put SUM file online.

20131206_40nsu.txt

~~~~~

.. \_merge:

Merge

-----

20131206\_40nsu.txt

~~~~~

Directories

=====

:working directory:

/data/co2clivar/pacific/49RY20120726_RF1206/original/2014.09.08_SUM_GR

:cruise directory:

/data/co2clivar/pacific/49RY20120726_RF1206

Updated Files Manifest

=====

=====

file stamp

=====

49RY20120726su.txt

=====

- **File Merge cchdo_admin**

[49RY20120726.exc.csv \(download\)](#) #04c28

Date: 2014-03-03

Current Status: merged

Notes

BTL

- **Exchange and netCDF files online Rox Lee**

Date: 2014-03-03

Data Type: BTL

Action: Website Update

Note:

=====

49RY20120726 processing - BTL

=====

2014-03-03

R Lee

.. contents:: :depth: 2

Submission

=====

filename	submitted by	date	data type	id
49RY20120726.exc.csv	Robert M. Key	2014-02-06	BTL	1140

Parameters

49RY20120726.exc.csv

~~~~~

CTDPRS

CTDTMP

CTDSAL [1]\_

SALNTY [1]\_

CTDOXY [1]\_

OXYGEN [1]\_

SILCAT [1]\_

NITRAT [1]\_

NITRIT [1]\_

PHSPHT [1]\_

TCARBON [1]\_

ALKALI [1]\_

PH\_TOT [1]\_

PH\_TMP

CHLORA [1]\_

PPHYTN [1]\_

BTL\_TIME [3]\_

SBE35 [1]\_ [3]\_

.. [1] parameter has quality flag column

.. [2] parameter only has fill values/no reported measured data

.. [3] not in WOCE bottle file

## Process

=====

## Changes

-----

- NITRAT empty data value flag 2 changed to flag 9

- PHAEO changed to PPHYTN



49RY20120726.exc.csv  
~~~~~

Conversion

file	converted from	software
49RY20120726_nc_hyd.zip	49RY20120726_hy1.csv	hydro 0.8.0-100-g92744bf

All converted files opened in JOA with no apparent problems.

Directories
=====

:working directory:
 /data/co2clivar/pacific/49RY20120726_RF1206/original/2014.03.03_BTL_RJL
:cruise directory:
 /data/co2clivar/pacific/49RY20120726_RF1206

Updated Files Manifest
=====

file	stamp
49RY20120726_hy1.csv	20140303SIOCCHRJL
49RY20120726_nc_hyd.zip	20140303SIOCCHRJL

• Available under 'Files as received' CCHDO Staff

Date: 2014-02-13

Data Type: BTL

Action: Website Update

Note:

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

49RY20120726.exc.csv

• File Submission Robert M. Key

[49RY20120726.exc.csv \(download\)](#) #04c28

Date: 2014-02-06

Current Status: merged

Notes

Bottle data file, updates by Bob Key:

1. Assigned bottle # 9999 to bucket samples
2. Set bottle flag for bucket samples to 2
3. Calculated nitrate via NO3+NO2 - nitrate
4. PHTS and flag value of 1 for good samples, changed to 2
5. Reset 1 ph flag to 4 (bad borttle)
6. Deleted non standard columns (flags fo theta, sigma)
7. added header

• **File Submission Robert M. Key**

[49RY20120726.exc.csv \(download\)](#) #04c28

Date: 2014-02-06

Current Status: merged

Notes

Expocode: 49RY20120726

Ship: Ryofu Maru

Woce Line: 40N

Note: Started with the file you posted earlier today:

1. Assigned bottle # 9999 to bucket samples
2. Set bottle flag for bucket samples to 2
3. Calculated nitrate via NO3+NO2 - nitrate
4. PHTS and flag value of 1 for good samples, changed to 2
5. Reset 1 ph flag to 4 (bad borttle)
6. Deleted non standard columns (flags fo theta, sigma)
7. added header

This is a really nice data set!

• **new PDF version online Jerry Kappa**

Date: 2014-02-06

Data Type: CrsRpt

Action: Website Update

Note:

I've placed a new PDF version of the cruise report: 49RY20120726do.pdf

into the directory:
http://cchdo.ucsd.edu/data/co2clivar/pacific/49RY20120726_RF1206 .

It includes all the reports provided by the cruise PIs, summary pages and CCHDO data processing notes, as well as a linked Table of Contents and links to figures and tables.

• **flags updated Bob Key**

Date: 2014-02-06

Data Type: BTL

Action: Submitted

Note:

Started with the file you posted earlier today:

1. Assigned bottle # 9999 to bucket samples
2. Set bottle flag for bucket samples to 2
3. Calculated nitrate via $\text{NO}_3 + \text{NO}_2$ - nitrate
4. PHTS and flag value of 1 for good samples, changed to 2
5. Reset 1 ph flag to 4 (bad borttle)
6. Deleted non standard columns (flags fo theta, sigma)
7. added header

• **change "0" flags to "9999" Bob Key**

Date: 2014-02-06

Data Type: BTL

Action: update needed

Note:

When you import this one you will find some bottle flags set to 0. For these the bottle number is set to "missing". These are bucket samples. Historically, we always set the bottle number for these (and surface soaks and similar) to 99, however this file already has bottle numbers of 99 and 999.

I recommend that the bucket samples be reset to have a bottle number of 9999 and a bottle flag of 2. This way they are still identified and existing software will function normally. Recall that a zero flag (0) is generally used to mean "a value that could have been measured but was somehow approximated". Zero flag also implies "good".

Regardless of procedure, a header note of some sort will be needed.

• **Maps created Rox Lee**

Date: 2014-02-05

Data Type: maps

Action: Website Update

Note:

```
=====
49RY20120726 processing - Maps
=====
```

2014-02-05

R Lee

.. contents:: :depth: 2

Process
=====

Changes

- Maps created from 20131206_40n_hy1.csv

Directories

=====

:working directory:

/data/co2clivar/pacific/49RY20120726_RF1206/original/2014.02.05_maps_RJL

:cruise directory:

/data/co2clivar/pacific/49RY20120726_RF1206

Updated Files Manifest

=====

===== =====

file	stamp
------	-------

===== =====

49RY20120726_trk.jpg

49RY20120726_trk.gif

===== =====

• Available under 'Files as received' CCHDO Staff

Date: 2014-02-05

Data Type: BTL

Action: Website Update

Note:

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

20131206_40n_ct1.zip

20131206_40nsu.txt

A_cruise_narrative_20131206.doc

epcRF1206_in-vivo.txt

20131206_40n_hy1.csv

• ExpoCode changed Matt Shen

Date: 2013-12-10

Data Type: ExpoCode

Action: Website Update

Note:

=====
49RY20120726 processing
=====

2013-12-10

M Shen

.. contents:: :depth: 2

Process

=====

ExpoCode changed from 49UP20120726 to 49RY20120726. 49UP20120726 added as an alias for the cruise.

- **File Submission Toshiya NAKANO**

[epcRF1206_in-vivo.txt \(download\)](#) #fbc5c

Date: 2013-12-05

Current Status: unprocessed

Notes

FLU and CHL data file

- **File Submission Toshiya NAKANO**

[epcRF1206_in-vivo.txt \(download\)](#) #fbc5c

Date: 2013-12-05

Current Status: unprocessed

Notes

Expocode: 49UP20120726

Ship: Ryofu Maru

Woce Line: None

Note: None

- **File Submission Toshiya NAKANO**

[20131206_40nsu.txt \(download\)](#) #c5e35

Date: 2013-12-05

Current Status: merged

Notes

SUM file

- **File Submission Toshiya NAKANO**

[20131206_40nsu.txt \(download\)](#) #c5e35

Date: 2013-12-05

Current Status: merged

Notes

Expocode: 49UP20120726

Ship: Ryofu Maru

Woce Line: None

Note: None

- **File Submission Toshiya NAKANO**

[20131206_40n_ct1.zip \(download\)](#) #463dd

Date: 2013-12-05

Current Status: unprocessed

Notes

CTD files

- **File Submission Toshiya NAKANO**

[20131206_40n_ct1.zip \(download\)](#) #463dd

Date: 2013-12-05

Current Status: unprocessed

Notes

Expocode: 49UP20120726

Ship: Ryofu Maru

Woce Line: None

Note: None

- **File Submission Toshiya NAKANO**

[A_cruise_narrative_20131206.doc \(download\)](#) #9b142

Date: 2013-12-05

Current Status: unprocessed

Notes

Cruise documentation

- **File Submission Toshiya NAKANO**

[A_cruise_narrative_20131206.doc \(download\)](#) #9b142

Date: 2013-12-05

Current Status: unprocessed

Notes

Expocode: 49UP20120726

Ship: Ryofu Maru

Woce Line: None

Note: None

- **to go online Toshiya Nakano**

Date: 2013-12-05

Data Type: CTD/BTL/SUM/CrsRpt

Action: Submitted