# C. Hydrographic Measurement Techniques and Calibration

## CTDO2 Measurements

### Personnel

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### CTDO2 measurement system

(*Software* : SEASAVEwin32 ver7.18)

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

### Pre-cruise calibration

#### (3.1) Pressure

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 0760, 25 June 2012* | | | | | | |
| *c1* | = | –4.959020e+004 |  | *t1* | = | 3.006343e+001 |
| *c2* | = | 5.955454e–001 |  | *t2* | = | –1.267270e–004 |
| *c3* | = | 1.521070e–002 |  | *t3* | = | 3.974510e–006 |
| *d1* | = | 3.670600e–002 |  | *t4* | = | 3.613180e–009 |
| *d2* | = | 0.000000e+000 |  | *t5* | = | 0.000000e+000 |

Formula:



*U* (*degrees Celsius*) *=* *M* × (*12-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



*t*: pressure period (μsec)

The drift–corrected pressure is computed as



*Slope = 0.99985****,*** *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 |  | *f0* | = | 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 |  | *f0* | = | 1000.0 |
| *i* | = | 2.42311649e–005 |  |  |  |  |

Formula:



*f* : Instrument freq.[Hz]

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 0069, 23 Oct. 2006* | | | | | | |
| *a0* | = | 4.96812728e–003 |  | *a3* | = | –1.14827915e–005 |
| *a1* | = | –1.39341438e–003 |  | *a4* | = | 2.44200422e–007 |
| *a2* | = | 2.06596098e–004 |  |  |  |  |

Formula:



*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:



#### (3.4) Conductivity: SBE 4C

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 3670(primary), 07 June 2012* | | | | | | |
| *g* | = | –1.01995535e+001 |  | *j* | = | 2.53978667e–004 |
| *h* | = | 1.57607652e+000 |  | *CPcor* | = | –9.5700e–008 |
| *i* | = | –2.02177497e–003 |  | *CTcor* | = | 3.2500e–006 |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 2842(secondary), 07 June 2012* | | | | | | |
| *g* | = | –1.01277455e+001 |  | *j* | = | 1.95371413e–005 |
| *h* | = | 1.38819272e+000 |  | *CPcor* | = | –9.5700e–008 |
| *i* | = | 6.13968402e–004 |  | *CTcor* | = | 3.2500e–006 |

Conductivity of a fluid in the cell is expressed as:



*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.

### 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



*S/N 0760, 17 Oct. 2012*

*Slope = 0.99982，Offset =* –*2.1059*

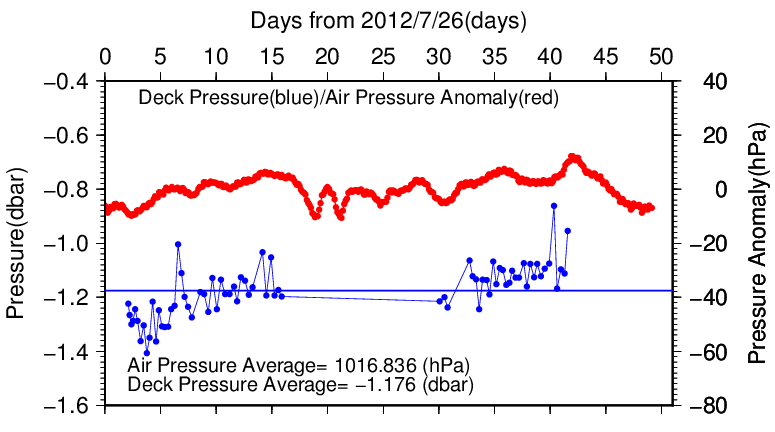


Figure C.1.1. Time series of the CTD deck pressure. Red line indicates atmospheric pressure anomaly. Blue line and dots indicate pre-cast deck pressure and average.

#### (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



*T* : the CTD temperature (degrees Celsius), *P:* pressure (dbar) and *c0*, *c1*, *c2* : coefficients

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

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| *S/N* | *Num* | *c0(K)* | *c1(K/dbar)* | *C2(K/dbar2)* | *Stations* |
| **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 ≥ 2000dbar | | |
| 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 ≥ 2000dbar | | |
| 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 |

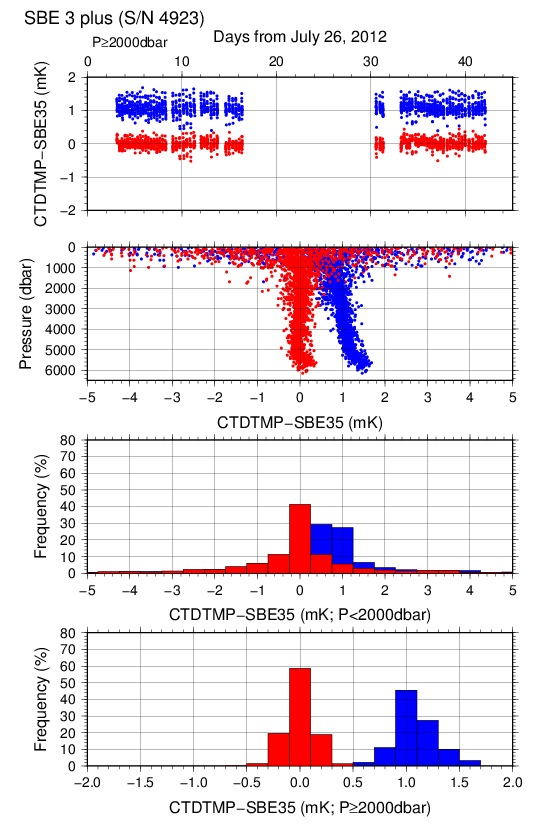


Figure C.1.2. Difference between the CTD temperature (*S/N 4923*) and the Deep Ocean Standards thermometer (SBE 35) at RF12-06. Blue and red dots indicate before and after the correction using SBE 35 data respectively. Lower two panels show histogram of the difference after correction.

Post-cruise sensor calibration for the SBE 3plus

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 4923(primary), 04 Oct. 2012* | | | | | | |
| *g* | = | 4.35315593e–003 |  | *j* | = | 1.80068115e–006 |
| *h* | = | 6.39388379e–004 |  | *f0* | = | 1000.0 |
| *i* | = | 2.12796459e–005 |  |  |  |  |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 4199(secondary), 05 Oct. 2012* | | | | | | |
| *g* | = | 4.39449032e–003 |  | *j* | = | 2.19010408e–006 |
| *h* | = | 6.49542198e–004 |  | *f0* | = | 1000.0 |
| *i* | = | 2.37799205e–005 |  |  |  |  |

Formula:



*f* : Instrument freq.[Hz]

Post-cruise sensor calibration for the SBE 35

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

*Slope = 1.000002, Offset = 0.000498*

Formula:



#### (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



*C*: CTD conductivity, *ci* and *pj* : 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* | *c0(S/m)* | *c1* | *c2(m/S)* | *Stations* |
|  | *p1(S/m/dbar)* | *p2(S/m/dbar2)* |
| **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 ≥ 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 ≥ 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 |

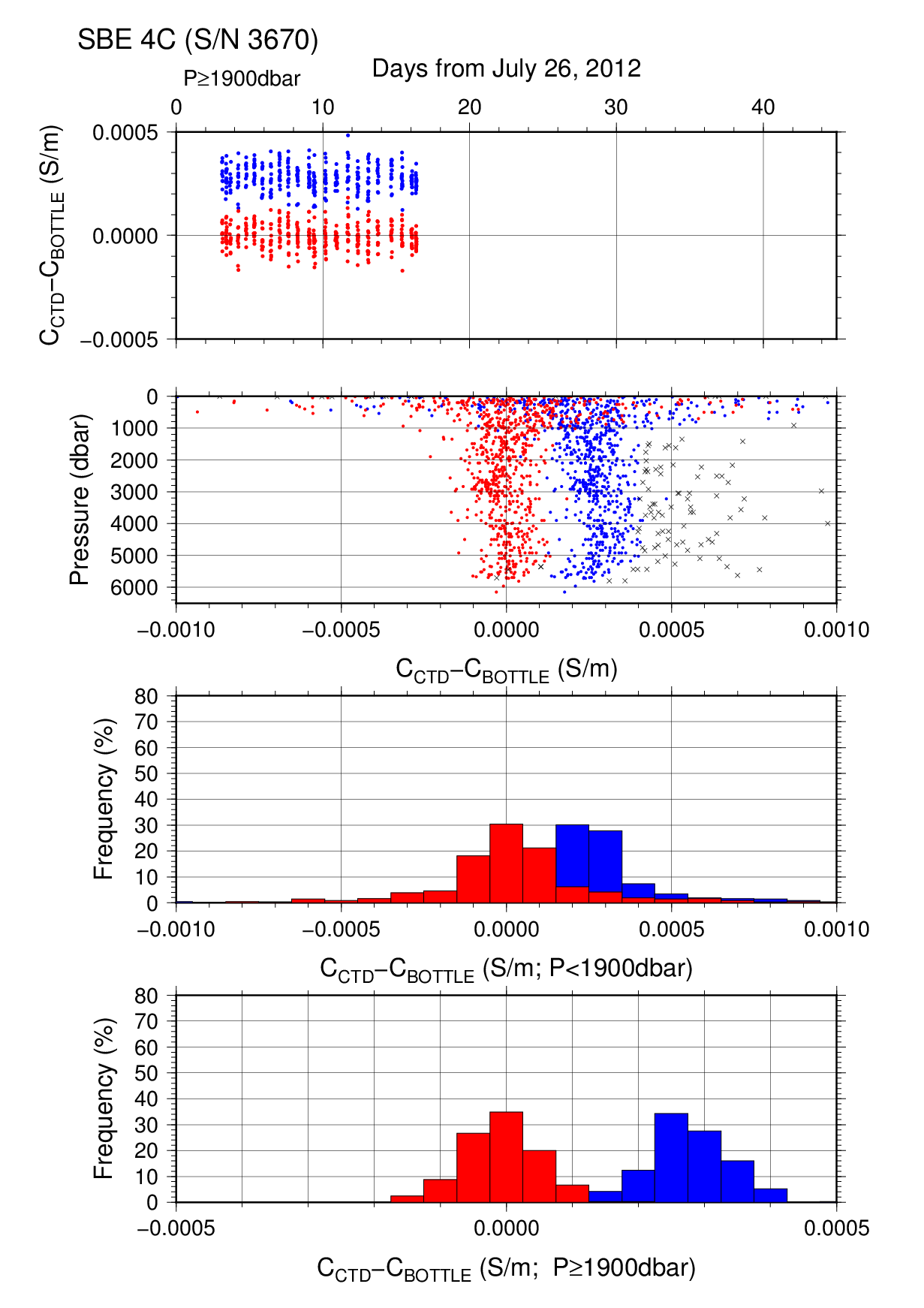


Figure C.1.3. Difference between the CTD conductivity (*S/N 3670*) and the bottle conductivity at Leg 1. Blue and red dots indicate before and after the calibration using bottle data respectively. Lower two panels show histogram of the difference before and after calibration.

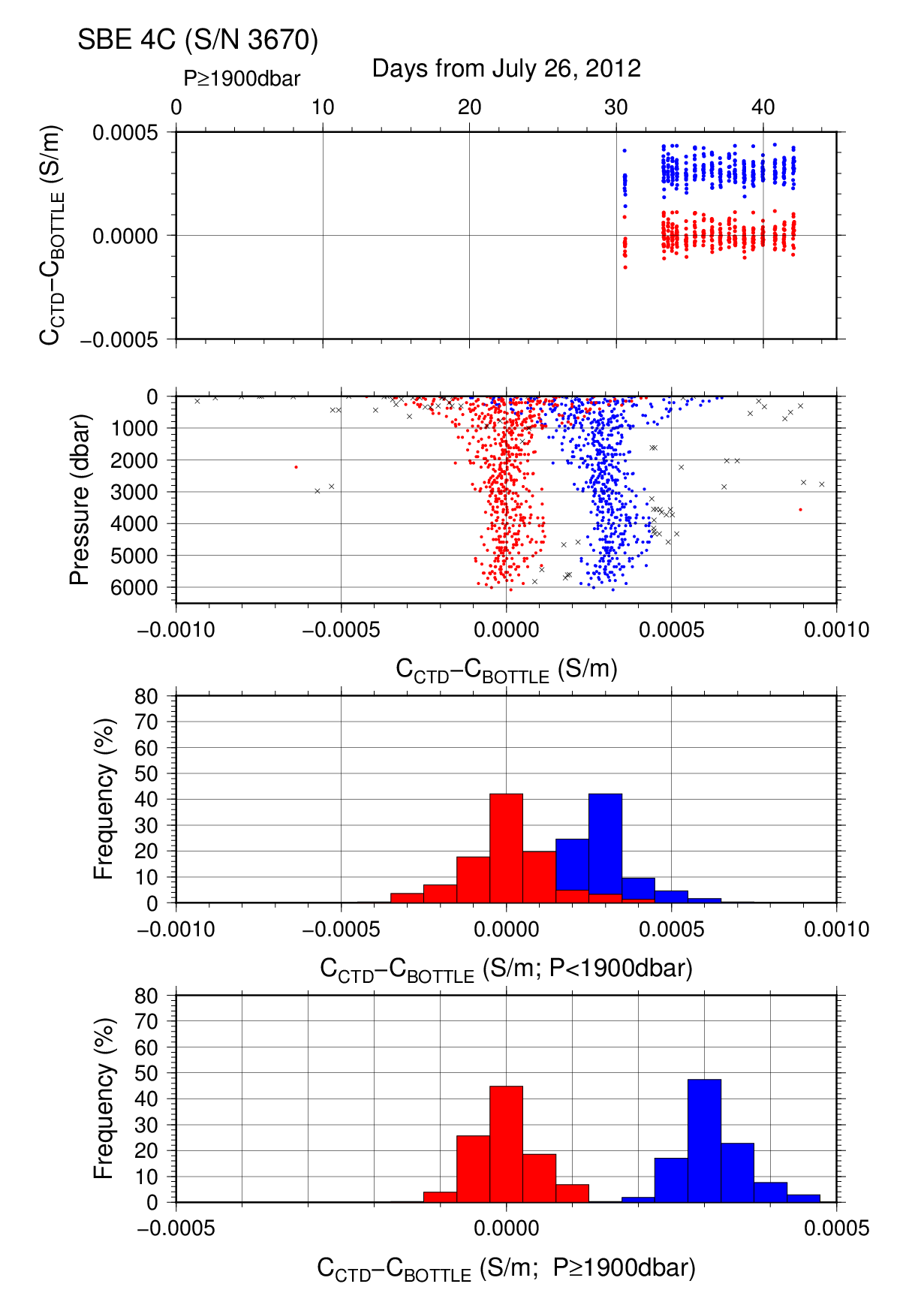


Figure C.1.4. Difference between the CTD conductivity (*S/N 3670*) and the bottle conductivity at Leg 2. Blue and red dots indicate before and after the calibration using bottle data respectively. Lower two panels show histogram of the difference before and after calibration.

Post-cruise sensor calibration for the SBE 4C

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| *S/N 3670(primary), 04 Oct. 2012* | | | | | | | |
| *g* | = | –1.02008629e+001 | |  | *j* | = | 2.65177344e–004 |
| *h* | = | | 1.57654876e+000 |  | *CPcor* | = | –9.5700e–008 |
| *i* | = | | –2.16327892e–003 |  | *CTcor* | = | 3.2500e–006 |

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| *S/N 2842(secondary), 04 Oct. 2012* | | | | | | |
| *g* | = | –1.01282248e+001 |  | *j* | = | 2.44828241e–005 |
| *h* | = | 1.38836986e+000 |  | *CPcor* | = | –9.5700e–008 |
| *i* | = | 5.53283965e–004 |  | *CTcor* | = | 3.2500e–006 |

Conductivity of a fluid in the cell is expressed as:



*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 Electornics (2009)* and *Uchida et al. (2010).* The formulas are as follows:

*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

O2sat: dissolved oxygen saturation by *Garcìa and Gordon* (1992) (μmol/kg)

[O2]: dissolved oxygen concentration (μmol/kg)

*c1*–*c9*: 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* | *c1* | *c2* | *c3* | *c4* | *c5* |
| *c6* | *c7* | *c8* | *c9* |  |
| 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 ≥ 950dbar | | |
| Num | Average  (μmol/kg) | Std  (μmol/kg) | Num | Average  (μmol/kg) | Std  (μmol/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 ≥ 950dbar | | |
| Num | Average  (μmol/kg) | Std  (μmol/kg) | Num | Average  (μmol/kg) | Std  (μmol/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 |

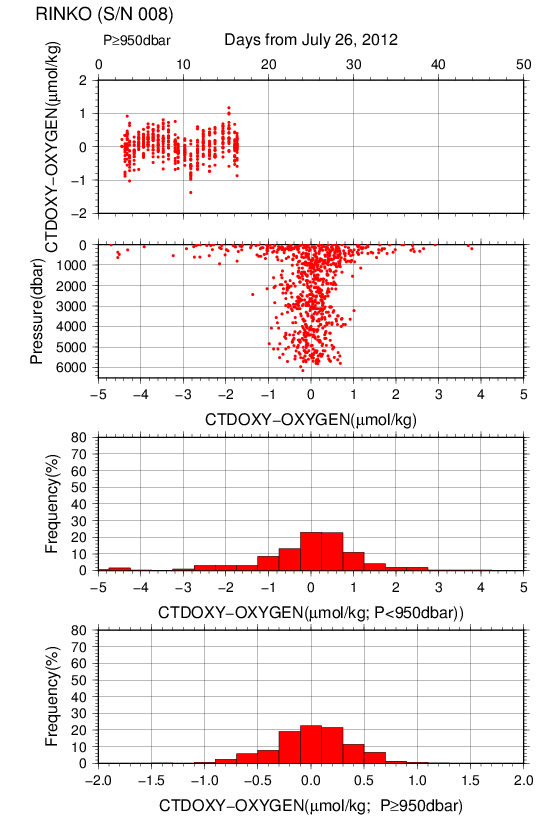


Figure C.1.5. Difference between the CTD oxygen (*S/N 008*) and bottle dissolved oxygen at Leg 1. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.

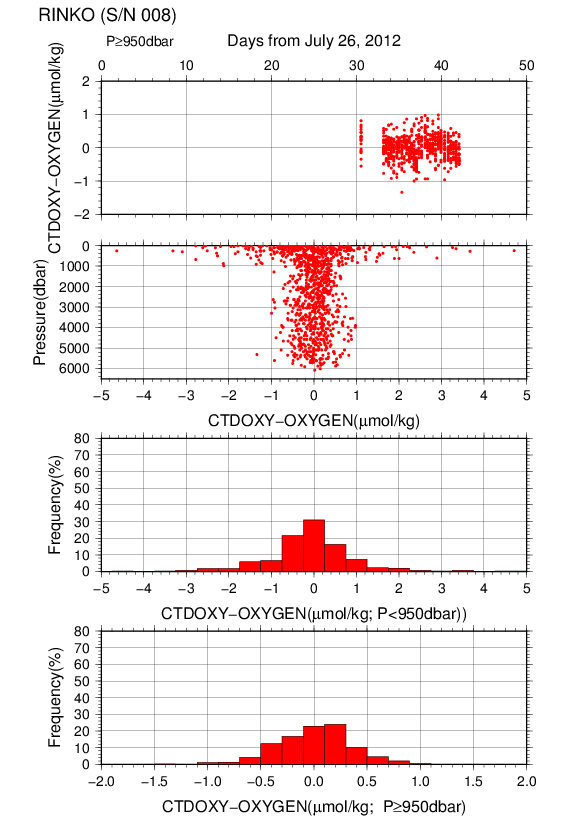


Figure C.1.6. Difference between the CTD oxygen (*S/N 008*) and bottle dissolved oxygen at Leg 2. Red dots in upper two panels indicate the result of calibration. Lower two panels show histogram of the difference between calibrated oxygen and bottle oxygen.

#### (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.1.8.

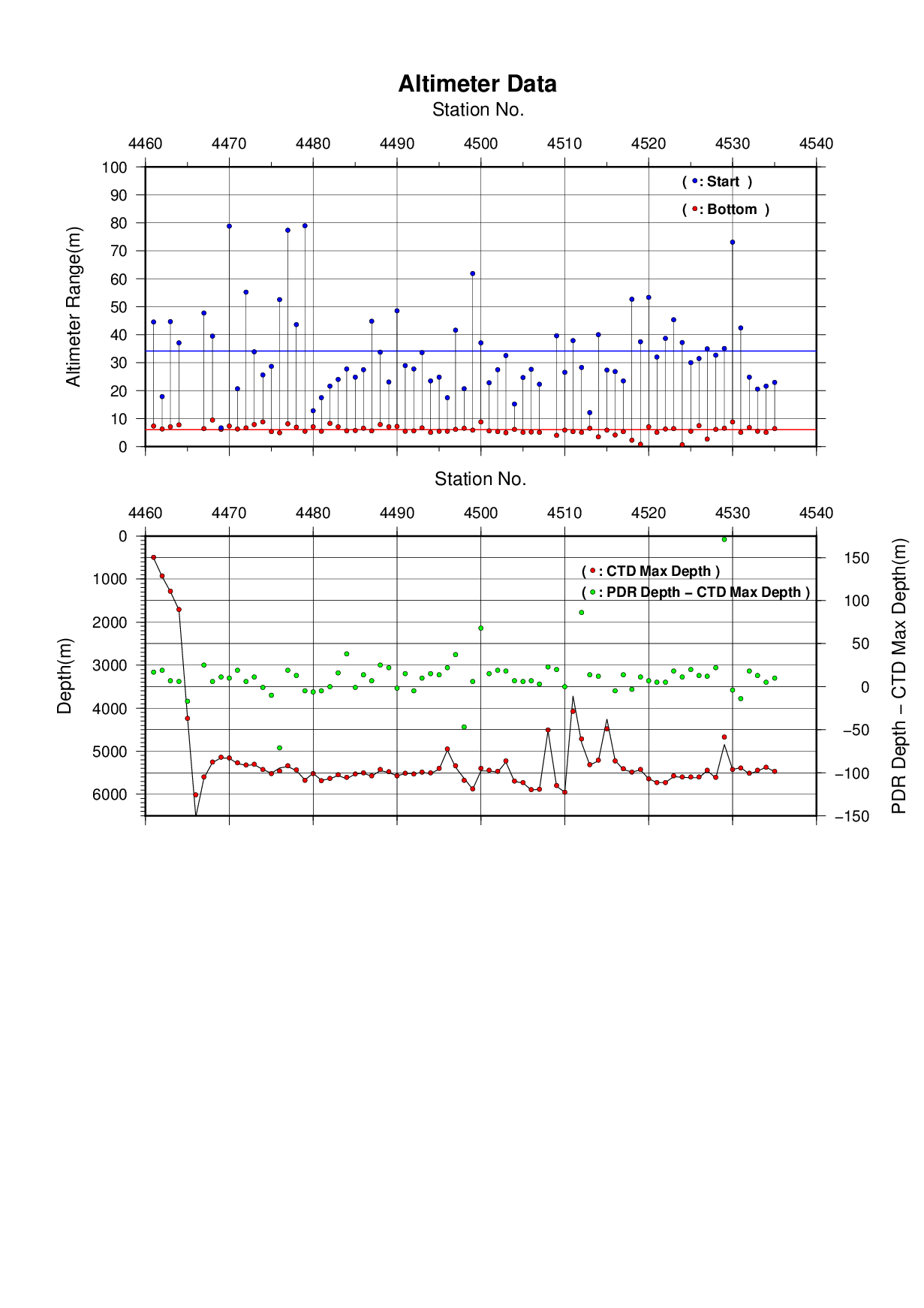
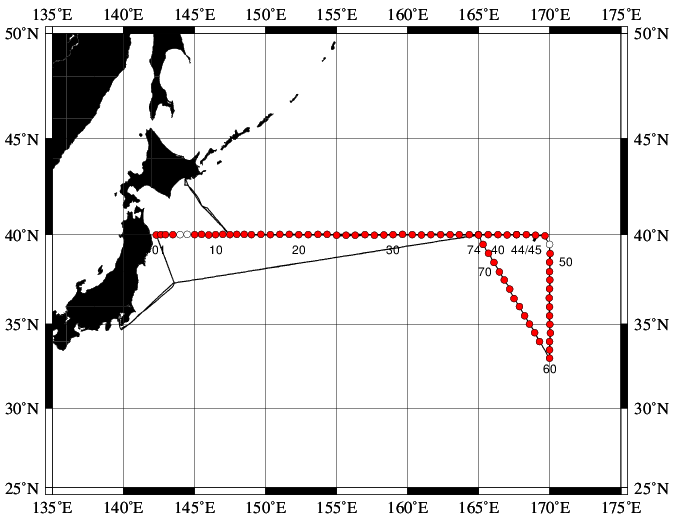


Figure C.1.7. The summary of detection of PSA-916D. The left panel shows the stations of detection, the right panel shows the relationship among PSA-916D, bathymetry and CTD depth. In the left panel, closed and open circles indicate react and no-react stations, respectively.

***References***

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

Garcìa, 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-based oxygen sensors. *J. Atmos. Oceanic Technol.,* ***25****, 2271–2281*.

## Salinity

### Personnel

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Koichi WADA (GEMD/JMA)

Yasunori SASAKI (GEMD/JMA)

### 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 (K15=0.99990)

### 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.

### Station occupied

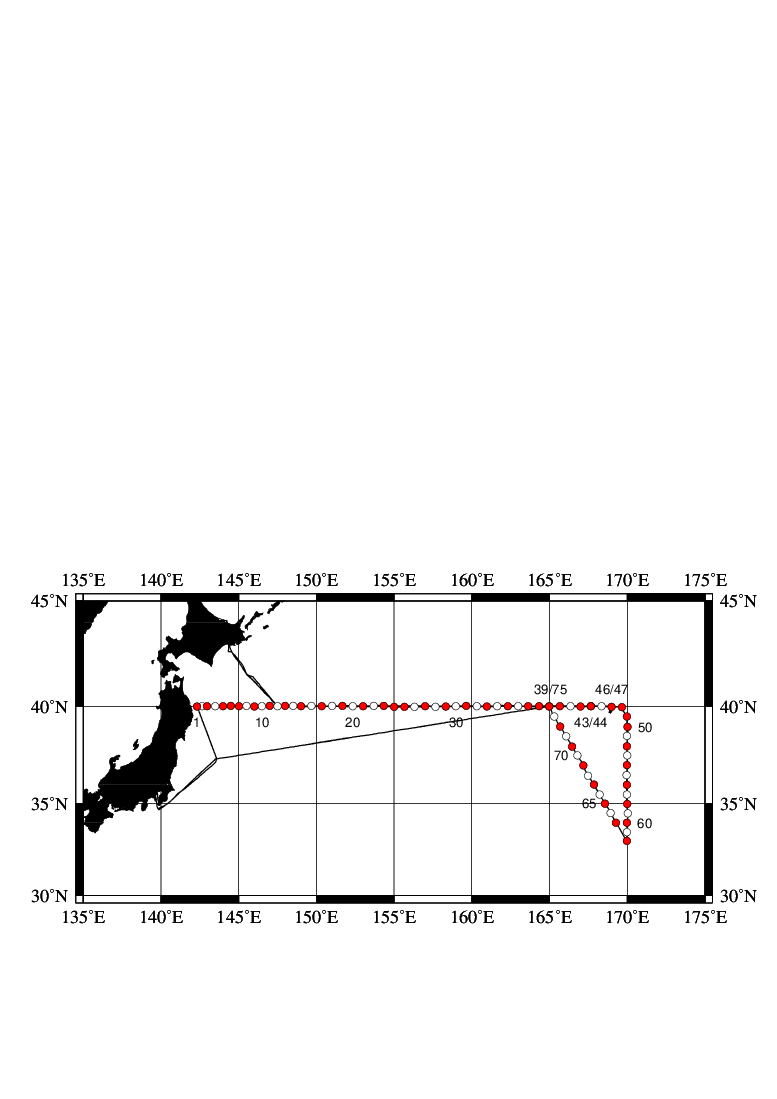


Figure C.2.1. Location of observation stations of bottle salinity. Closed and open circles indicate sampling and no-sampling station, respectively.

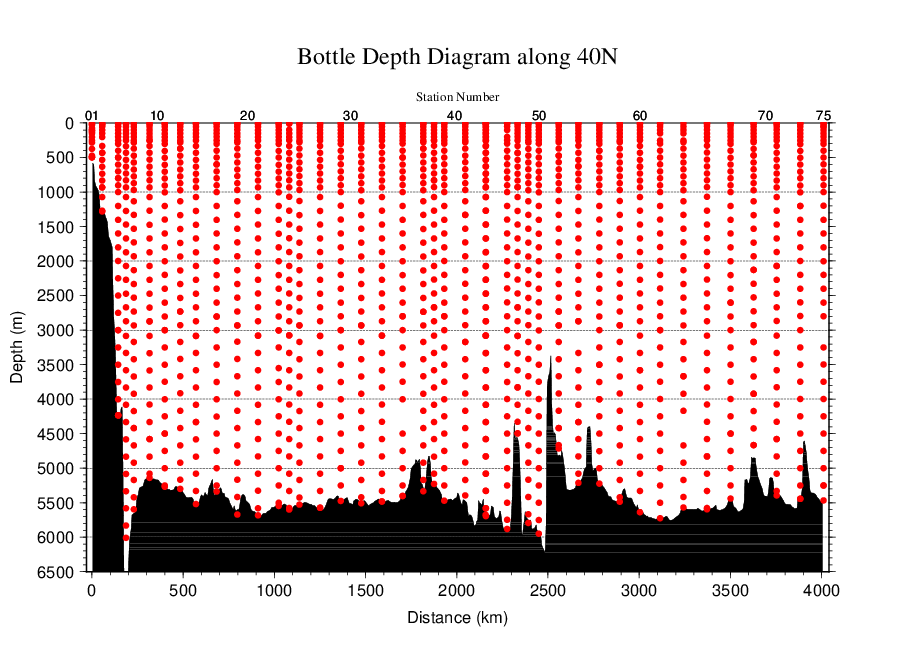


Figure C.2.2. Distance-depth distribution of sampling layers of bottle salinity.

### Result

#### (5.1) Ambient temperature, bath temperature and SSW measurements

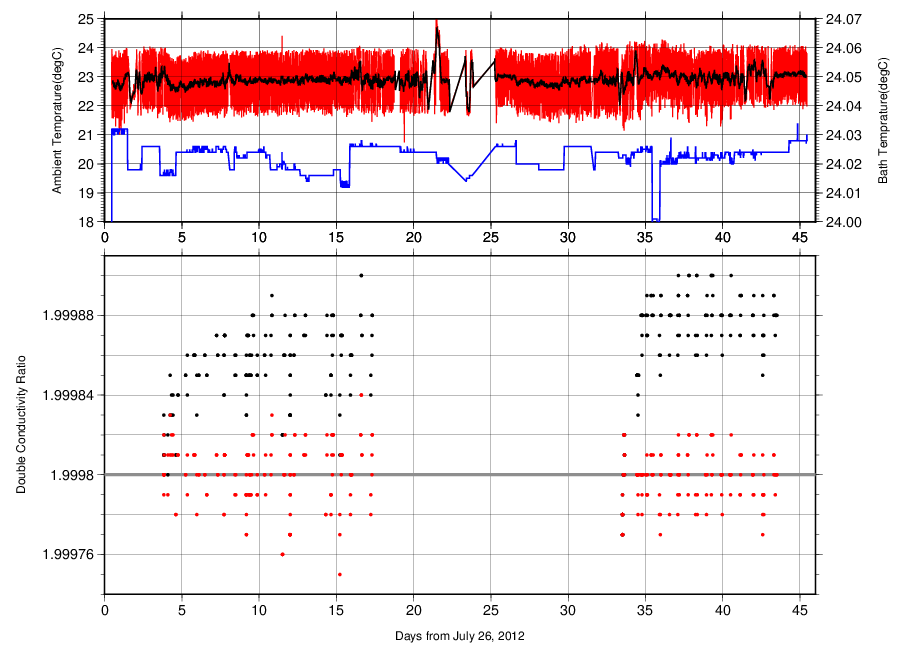


Figure C.2.3. The upper panel, red line, black line and blue line indicate time-series of ambient temperature, ambient temperature average and bath temperature during cruise. The lower panel, black dots and red dots indicate raw and corrected time-series of the double conductivity ratio of the standard 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. ± S.D.** |
| Replicate | 0.0005±0.0005 (N=100) |
| Duplicate | 0.0007±0.0007 (N=67) |

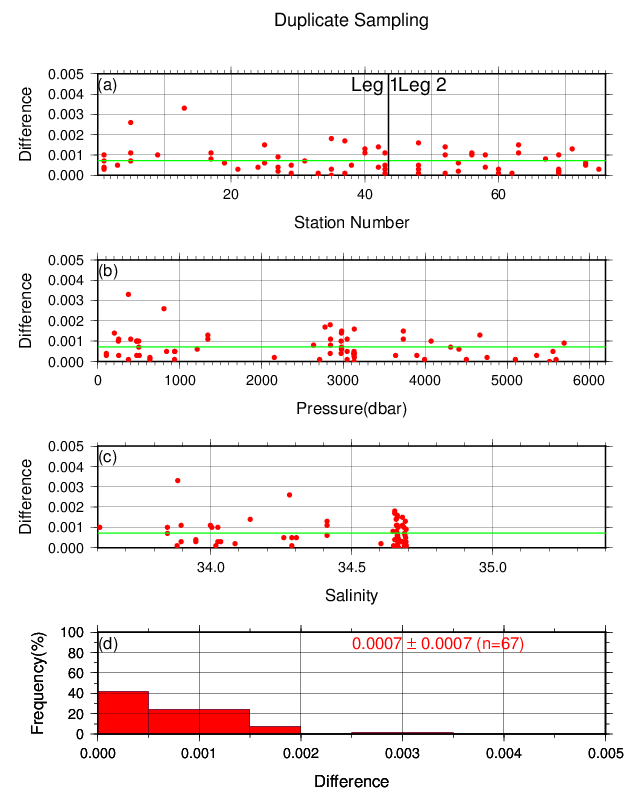
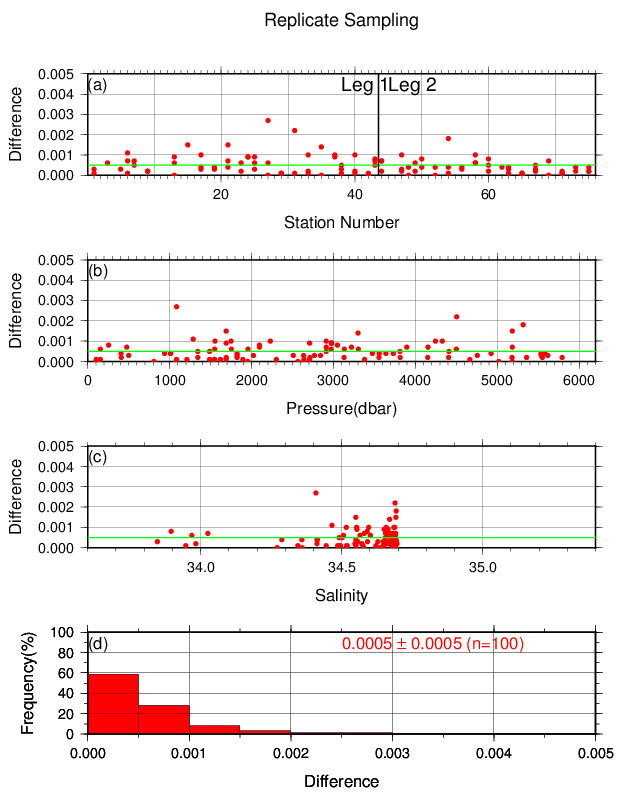


Figure C.2.4. Result of (left) replicate and (right) duplicate analyses during the cruise against (a) station number, (b) pressure and (c) salinity, and (d) histogram of the measurements. Green line indicates the mean of the differences of salinity of replicate/duplicate.

#### (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.*

## Bottle Oxygen

### Personnel

Chihiro KAWAMURA (GEMD/JMA)

Sho HIBINO (GEMD/JMA)

Hiroki SHIOZURU (GEMD/JMA)

### Station 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.

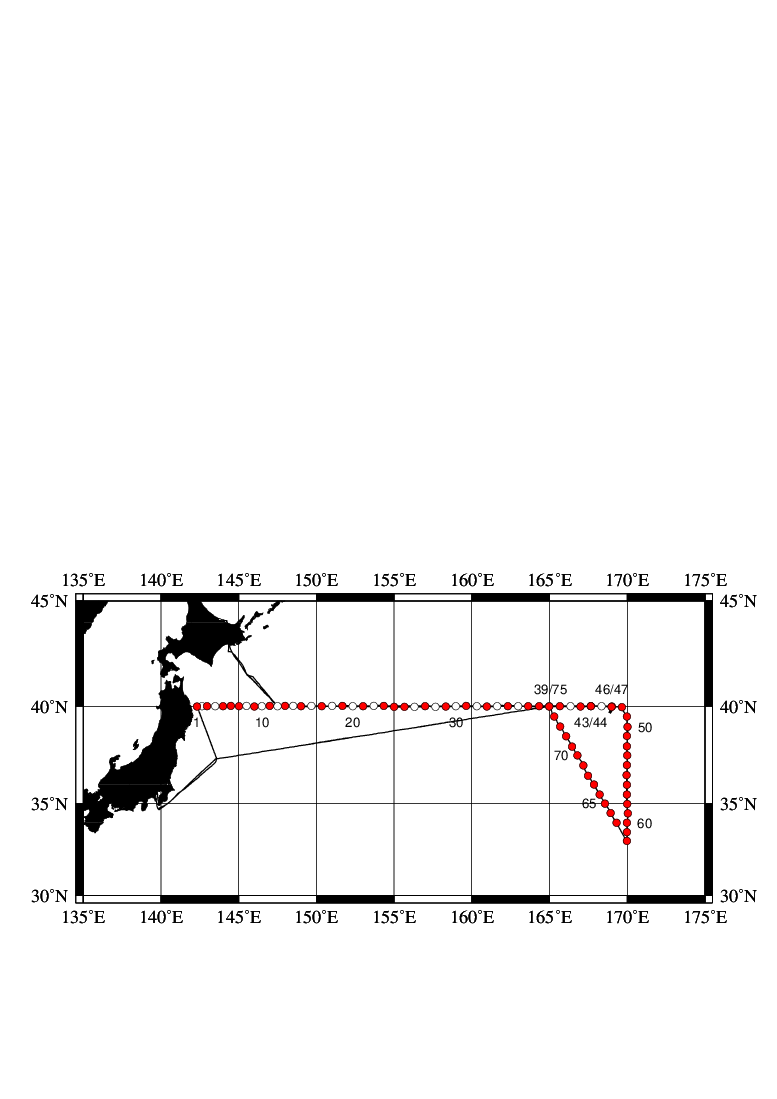


Figure C.3.1. Location of observation stations of bottle oxygen. Closed and open circles indicate sampling and no-sampling stations, respectively.

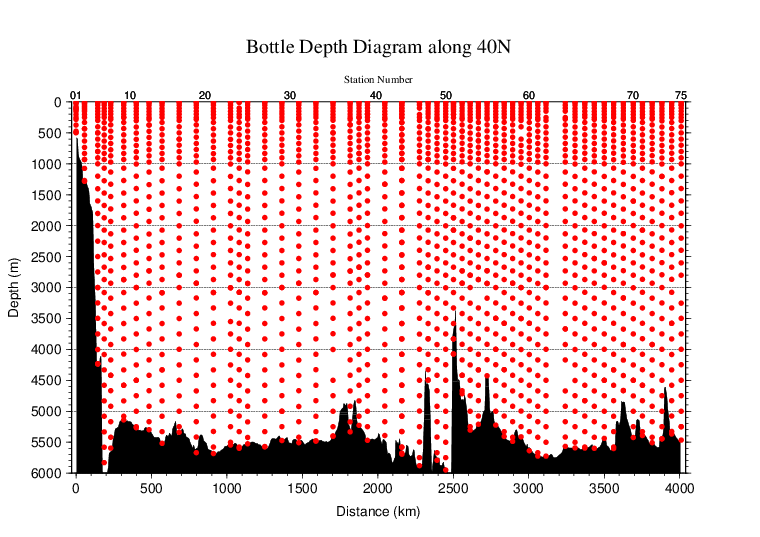


Figure C.3.2. Distance-depth distribution of sampling layers of bottle oxygen.

### Instrument

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

Burette: APB-510 (Kyoto Electronic, Japan)

### 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 KIO3 solutions were prepared gravimetrically using the highest purity standard substance KIO3 (Lot. No. 92404G, Merck KGaA, Germany). Batch list of prepared standard KIO3 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 KIO3 solutions.

|  |  |  |
| --- | --- | --- |
| **KIO3 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 |

### Standardization

Concentration of Na2S2O3 titrant was determined with the standard KIO3 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.

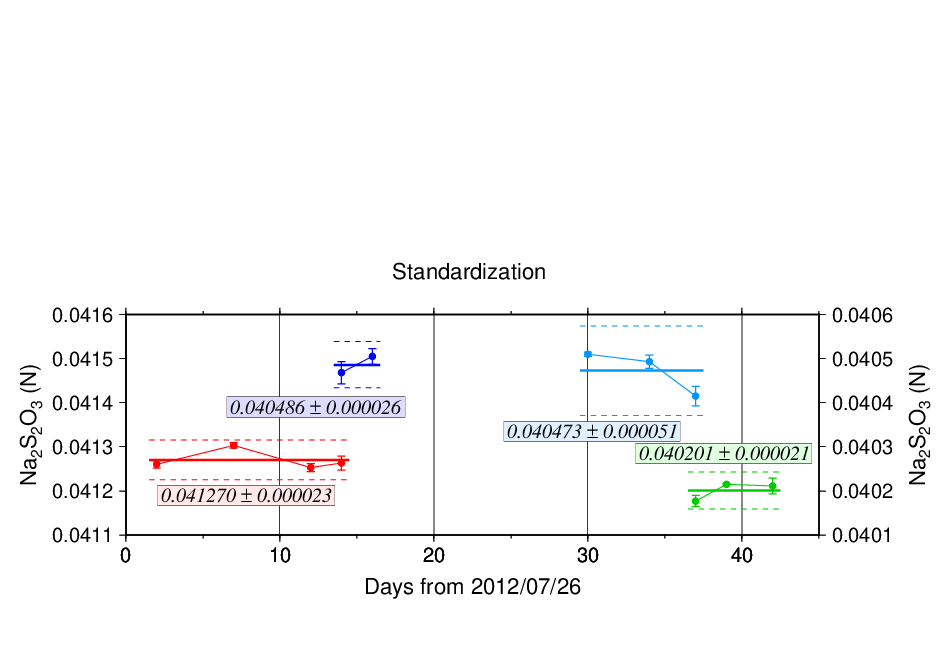


Figure C.3.3. Calculated concentration of Na2S2O3 solution at 20 °C in standardization during the cruise. Different colors of plots indicate different batches of Na2S2O3 solution; red (blue, light blue, and green) plots correspond to the left (right) y-axis. Error bars of plots show standard deviation of concentration of Na2S2O3 in the measurement. Thick and dashed lines denote the mean and 2 times of standard deviations for the batch measurements, respectively.

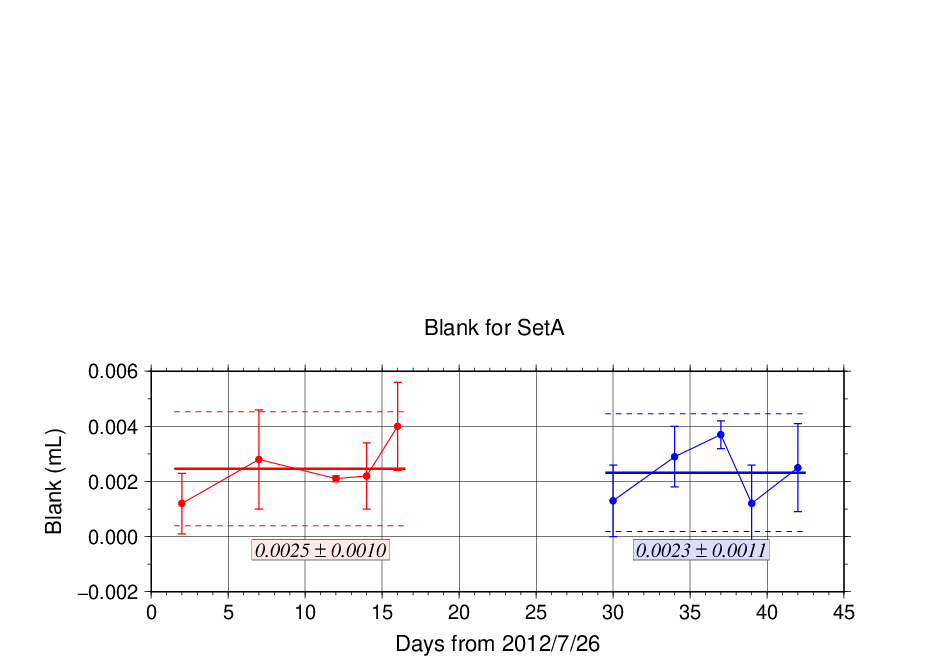
### Blank

#### (6.1) Reagent blank

Blank in oxygen measurement (reagent blank; Vblk, dw) can be represented as follows;

Vblk, dw = Vblk, ep + Vblk, reg (C3.1)

where Vblk, ep represents a blank due to differences between the measured end-point and the equivalence point, and Vblk, reg a blank associated with oxidants or reductants in the reagent. The reagent blank Vblk, 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).



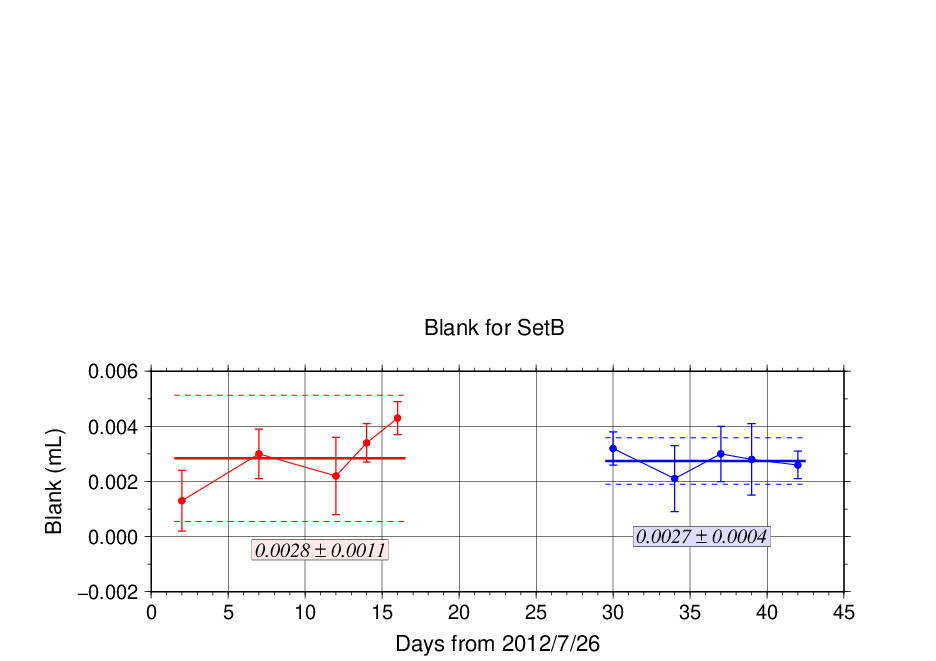


Figure C.3.4. Reagent blank (Vblk, dw) determination for set A (top) and set B (bottom). Error bars of plots show standard deviation of the measurement. Thick and dashed lines denote the mean and 2 times of standard deviations for the batch measurement, respectively.

#### (6.2) Other blanks

We also determined another blanks related to oxygen measurement; the blank Vblk, reg. Details are described in Appendix A3.

### 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. ± S.D. (mol kg−1)** |
| Replicate | 0.22±0.21 (N=213) |
| Duplicate | 0.35±0.33 (N=87) |

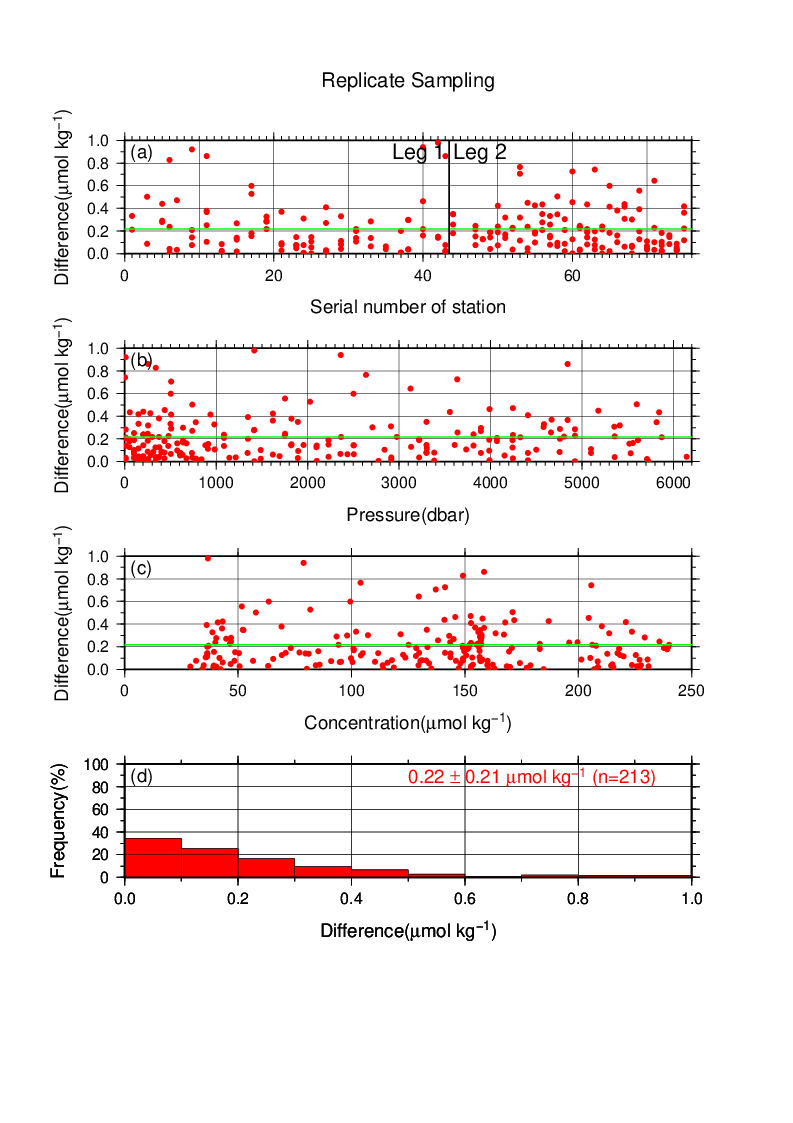
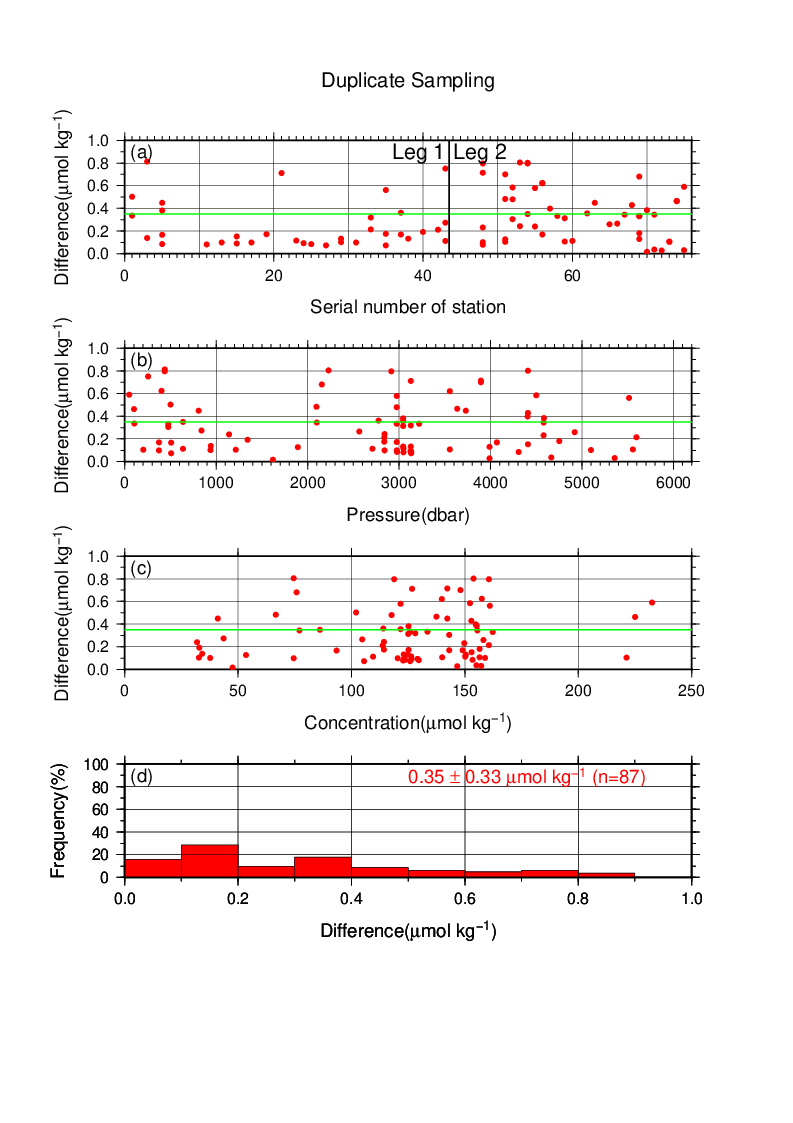
 

Figure C.3.5. Results of (left) replicate and (right) duplicate analyses during the cruise against (a) station number, (b) pressure and (c) concentration of dissolved oxygen. Green line denotes the average of the measurements. Bottom panels (d) show histogram of the measurements.

#### (7.2) Mutual comparison between each standard KIO3 solution

During the cruise, mutual comparison between different lots of standard KIO3 solution was performed to confirm the accuracy of our oxygen measurement and the bias of a standard KIO3 solution. A concentration of the standard KIO3 solution “20120404-2” was determined using Na2S2O3 solution standardized with the KIO3 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).

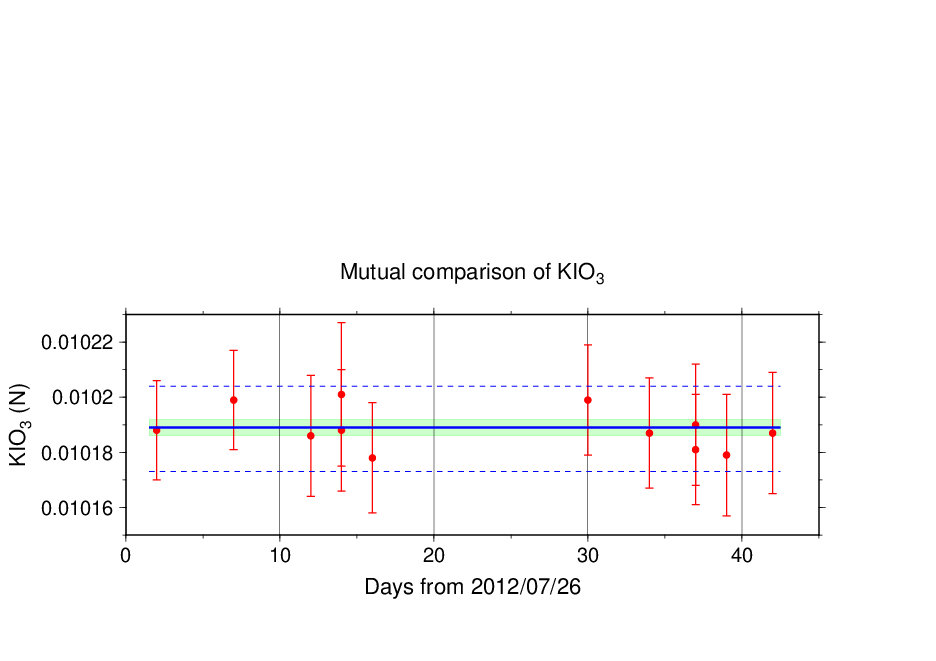


Figure C.3.6. Result of mutual comparison of standard KIO3 solutions during the cruise. Circles and error bars show mean of the measurement value and its uncertainty (k=2), respectively. Thick and dashed lines in blue denote the mean and 2 times of standard deviations, respectively, for the measurement. Green thin line and light green thick line denote nominal concentration and its uncertainty (k=2) of standard KIO3 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 |

### 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 Na2S2O3 solution, and uncertainty of KIO3 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.

|  |  |
| --- | --- |
| O2 conc. (μmol kg−1) | Uncertainty (μmol 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 H2SO4 solution and a magnetic stirrer bar into the sample glass, samples were titrated with Na2S2O3 solution whose molarity was determined with KIO3 solution. During the titration, the absorbance of iodine in the solution was monitored using a detector. Also, temperature of Na2S2O3 solution during the titration was recorded using a thermometer. Dissolved oxygen concentration (mol kg−1) was calculated from sample temperature at the fixation, CTD salinity, glass volume, and titrated volume of the Na2S2O3 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 molL−1)

Dissolve 600 g of MnCl2·4H2O in DW, then dilute the solution with DW to a final volume of 1 L.

Pickling reagent-II; Sodium hydroxide (8 molL−1) / sodium iodide solution (4 molL−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.

H2SO4 solution; Sulfuric acid solution (5 molL−1)

Slowly add 280 mL concentrated H2SO4 to roughly 500 mL of DW. After cooling the final volume should be 1 L.

Na2S2O3 solution; Sodium thiosulfate solution (0.04 molL−1)

Dissolve 50 g of Na2S2O3·5H2O and 0.4 g of Na2CO3 in DW, then dilute the solution with DW to a final volume of 5 L.

KIO3 solution; Potassium iodate solution (0.001667 mol L−1)

Dry high purity KIO3 for two hours in an oven at 130 °C. After weight out accurately KIO3, 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 Vblk, reg, associated with oxidants or reductants in the reagent, was determined as follows. Using a calibrated pipette, 1 mL of the standard KIO3 solution and 100 mL of DW were added to two glasses each. Then, 1 mL H2SO4 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 H2SO4 solution, pickling reagent-II and I each) into the second one. After that, the sample was titrated to the end-point with Na2S2O3 solution. Vblk, reg was determined with difference of titrated volume of Na2S2O3 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.

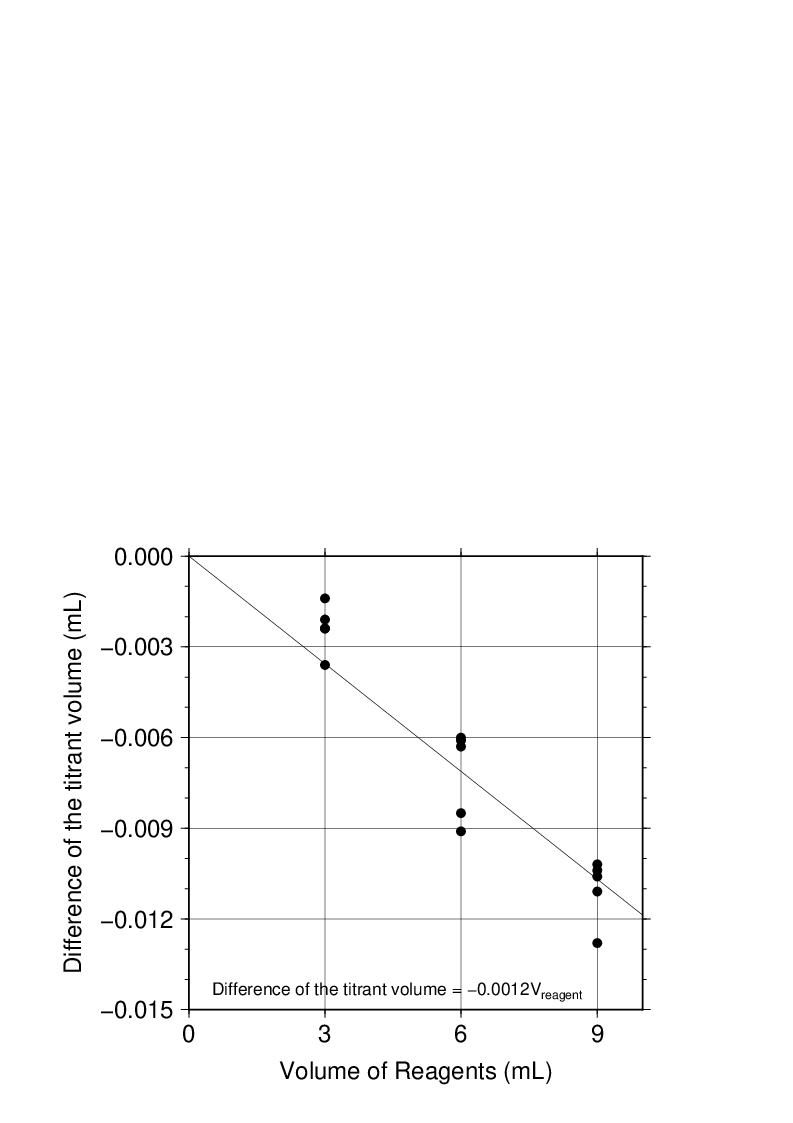


Figure C.3.A1. Blank (mL) due to redox species other than oxygen in the reagents.

The relation between difference of the titrant volume and the reagents of the volume (Vreg) is expressed as follows;

Difference of the titrant volume = –0.0012 Vreg. (C3.A1)

Therefore, Vblk, reg was estimated to be +0.004 mL.

***Reference***

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*.

## Nutrients

### Personnel

Kazuhiro SAITO (GEMD/JMA)

Hiroyuki FUJIWARA (GEMD/JMA)

(Leg 1) Minoru HAMANA (GEMD/JMA)

(Leg 2) Takashi MIYAO (GEMD/JMA)

### Station 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.

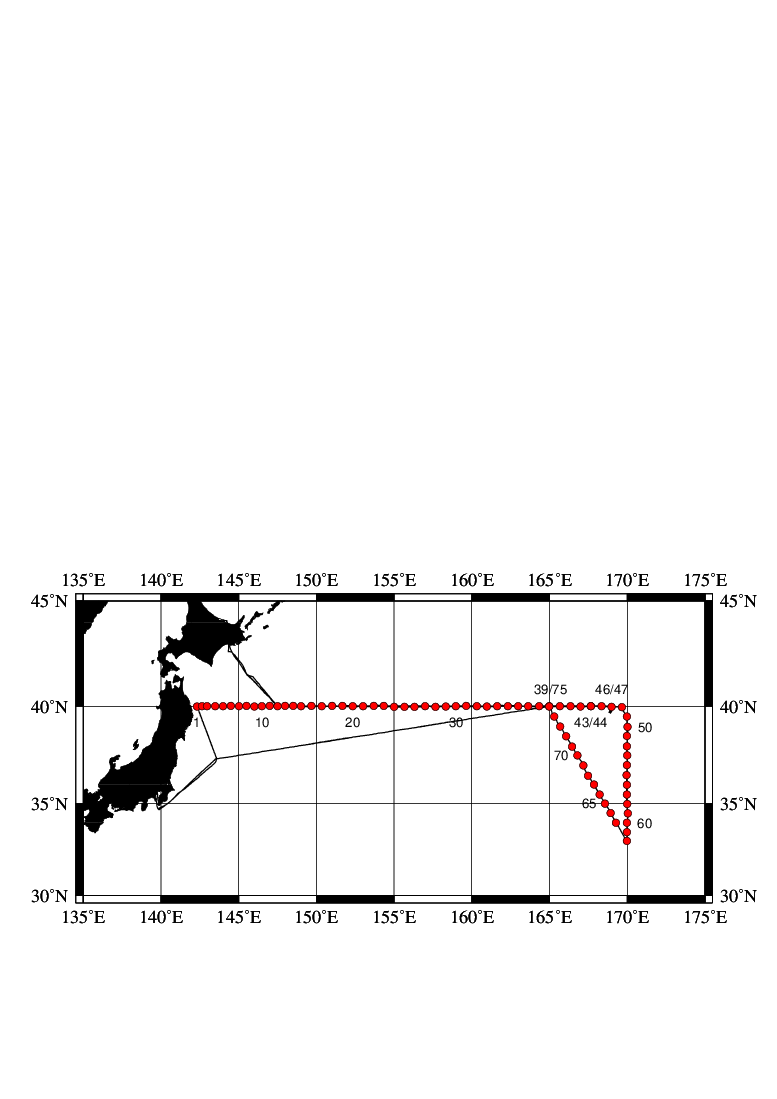


Figure C.4.1. Location of observation stations of nutrients. Closed and open circles indicate sampling and no-sampling stations, respectively.

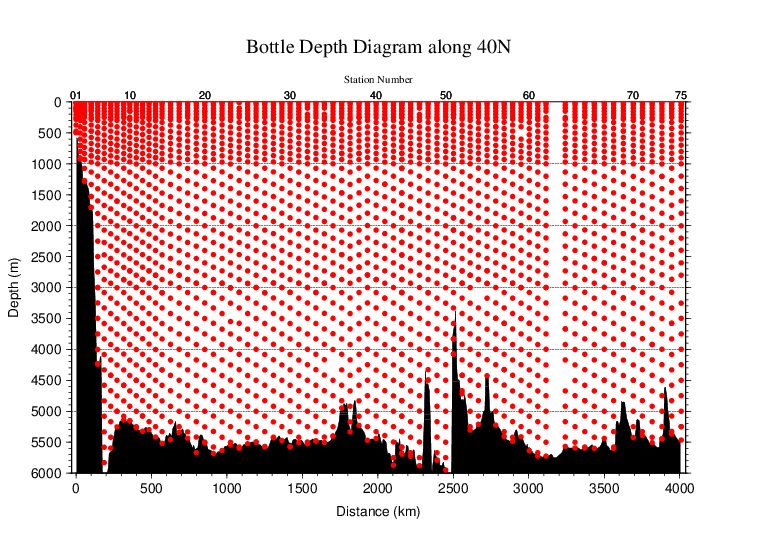


Figure C.4.2. Distance-depth distributions of sampling layers of nutrients.

### 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.

### 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.

### 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  35680 | 2300  2310 | 183.9  184.2 |

|  |  |
| --- | --- |
| Table C.4.3. Schedule of renewal of in-house standards. | |
| Standard | Renewal |
| A-1 std. (NO3) | No renewal |
| A-2 std. (NO2) | No renewal |
| A-3 std. (PO4) | 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 |

### Certified reference material

Certified reference material (CRM) and reference material (RM) for nutrients in seawater, which were prepared by the General Environmental Technos (KANSO 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 μmol 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.

### 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 μmol 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) |

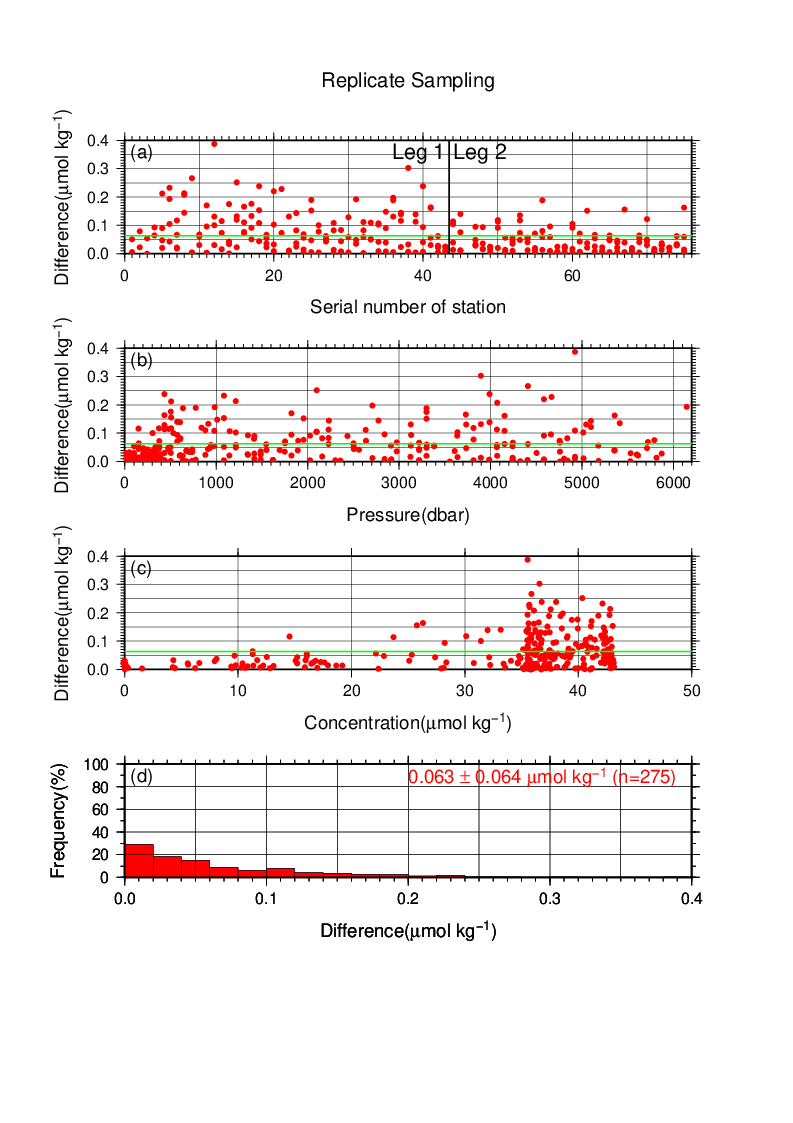
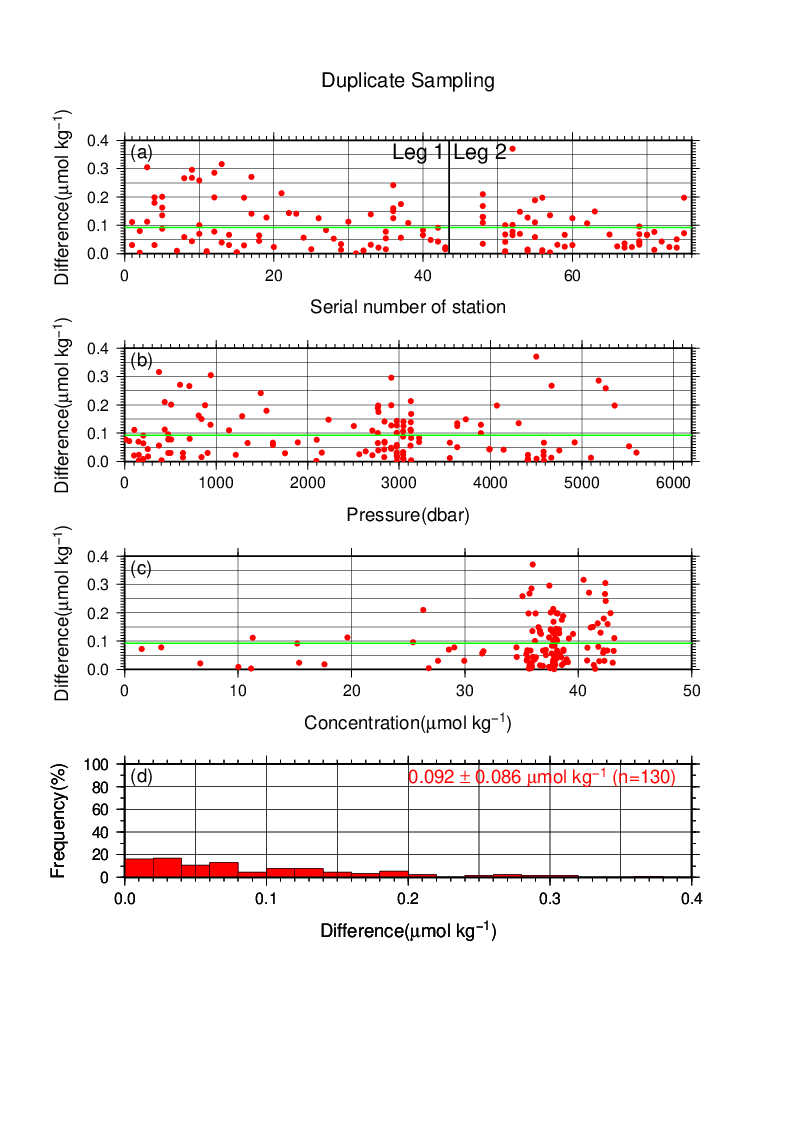
 

Figure C.4.3. Result of (left) replicate and (right) duplicate analyses of nitrate+nitrite through the cruise versus (a) station number, (b) sampling pressure, (c) concentration, and (d) histogram of the measurements. Green line indicates the mean of the differences of concentration of replicate/duplicate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

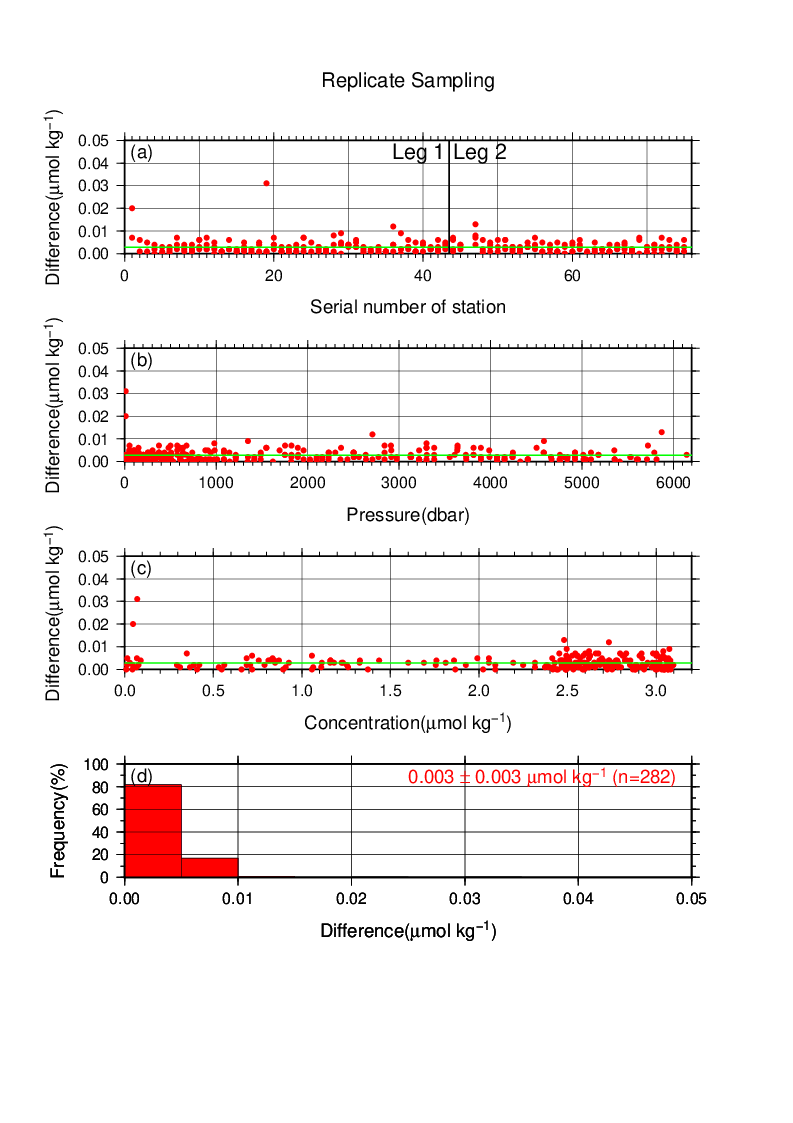
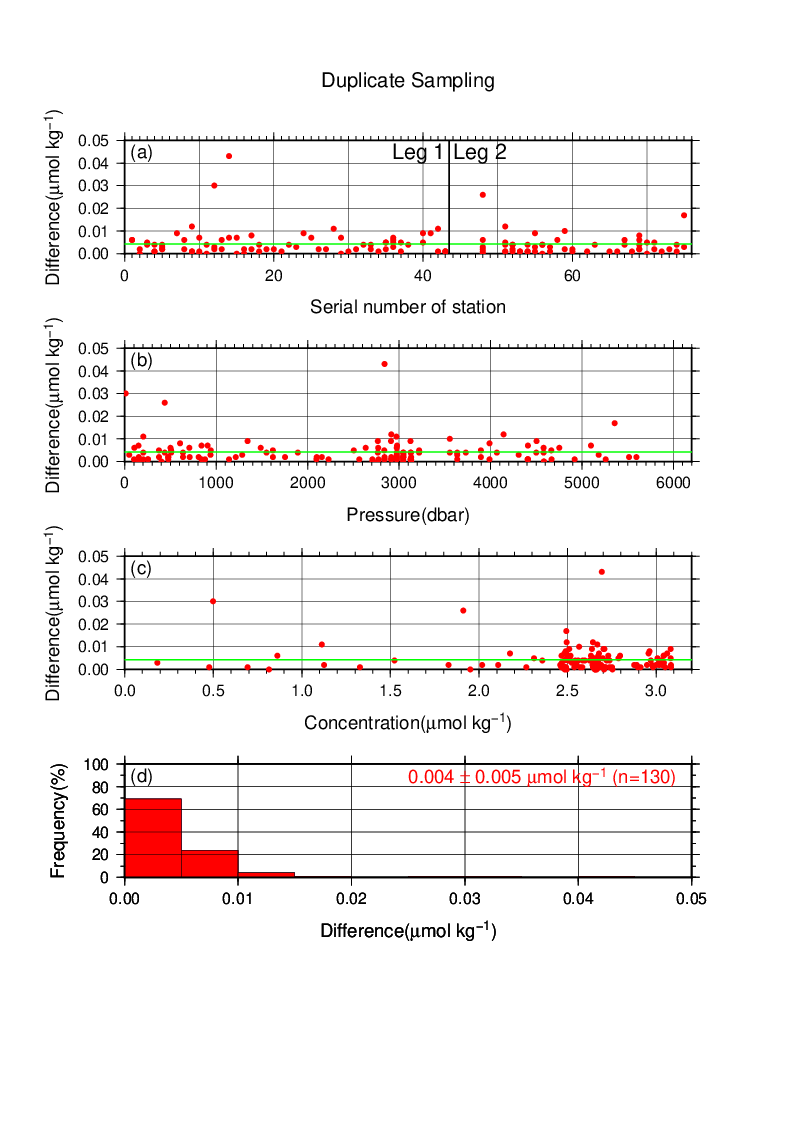
 

Figure C.4.4. Same as Figure C.4.3 but for phosphate.

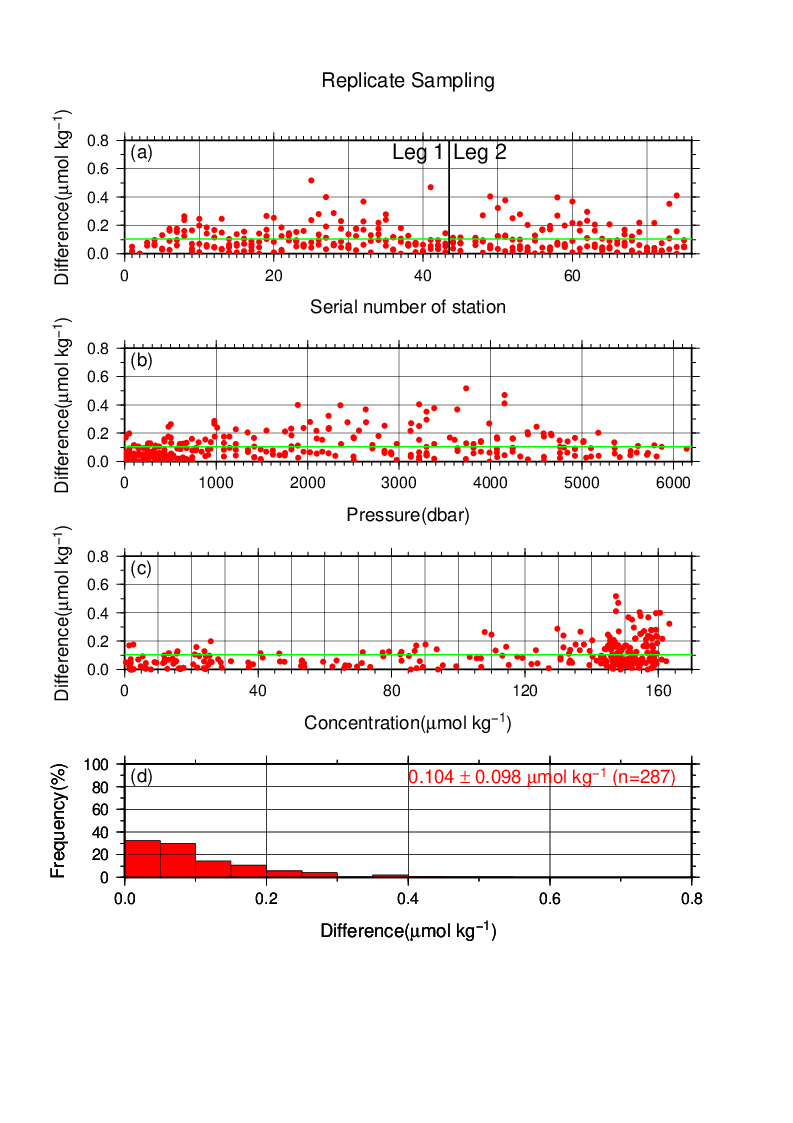
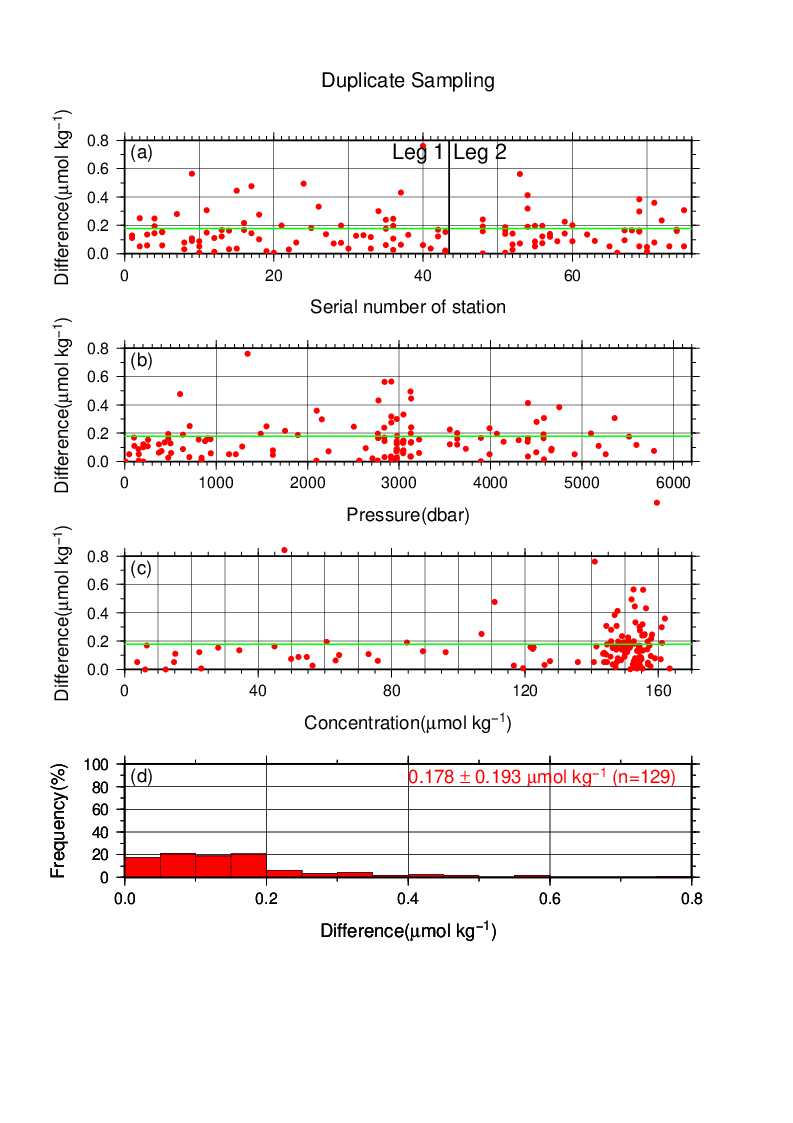
 

Figure C.4.5. Same as Figure C.4.3 but for silicate.

#### (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: μmol 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 | 0.074±0.038  51.71%  (N=147) | 0.013±0.004  28.83%  (N=144) | 0.029±0.006  21.47%  (N=147) | 1.74±0.10  5.90%  (N=147) |
| RM-BT | 18.64±0.07  0.40%  (N=112) | 0.046±0.026  5.70%  (N=112) | 1.29±0.01  0.74%  (N=112) | 40.96±0.15  0.38%  (N=112) |
| CRM-BV | 35.40±0.10  0.29%  (N=147) | 0.040±0.005  11.32%  (N=146) | 2.50±0.01  0.45%  (N=147) | 99.71±0.28  0.28%  (N=147) |
| RM-BF | 41.39±0.11  0.27%  (N=112) | 0.017±0.003  17.67%  (N=112) | 2.79±0.01  0.38%  (N=112) | 149.90±0.38  0.26%  (N=112) |

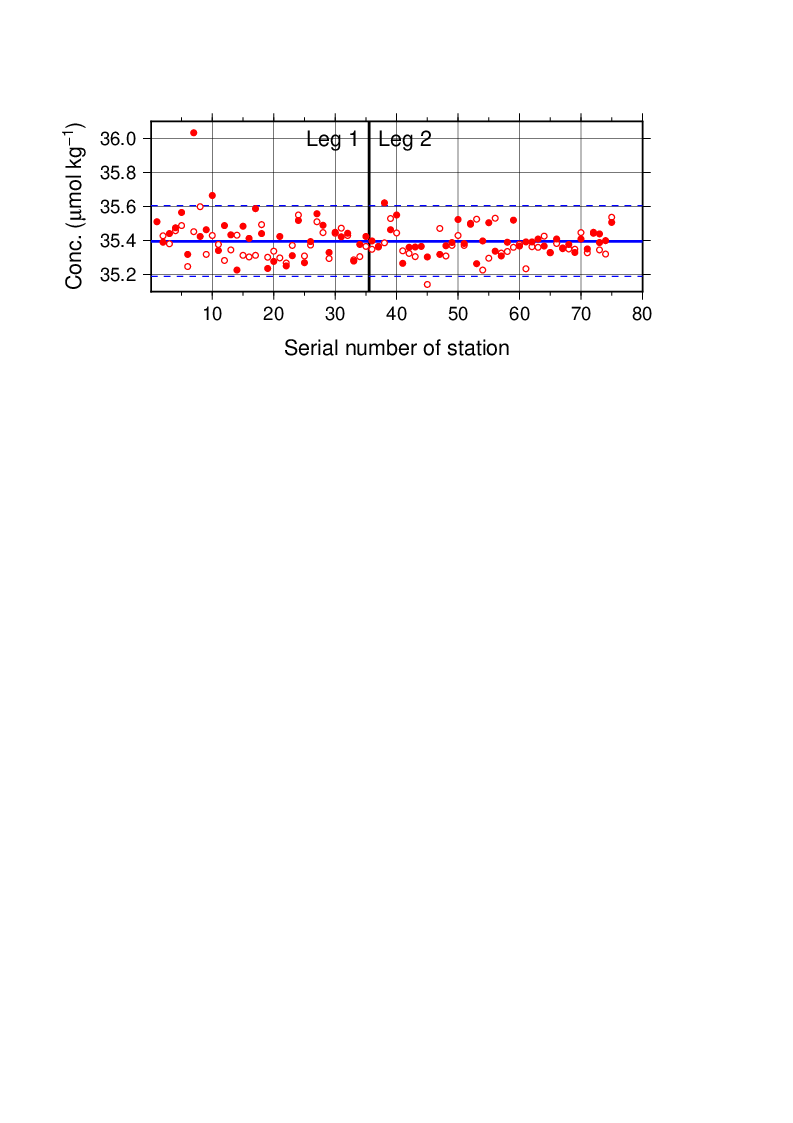


Figure C.4.6. Time-series of measured concentration of nitrate+nitrite of CRM-BV through the cruise. Closed and open circles indicate the newly and previously opened bottle, respectively. Thick and dashed lines denote the mean and 2 times of standard deviations of the measurements through the cruise,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

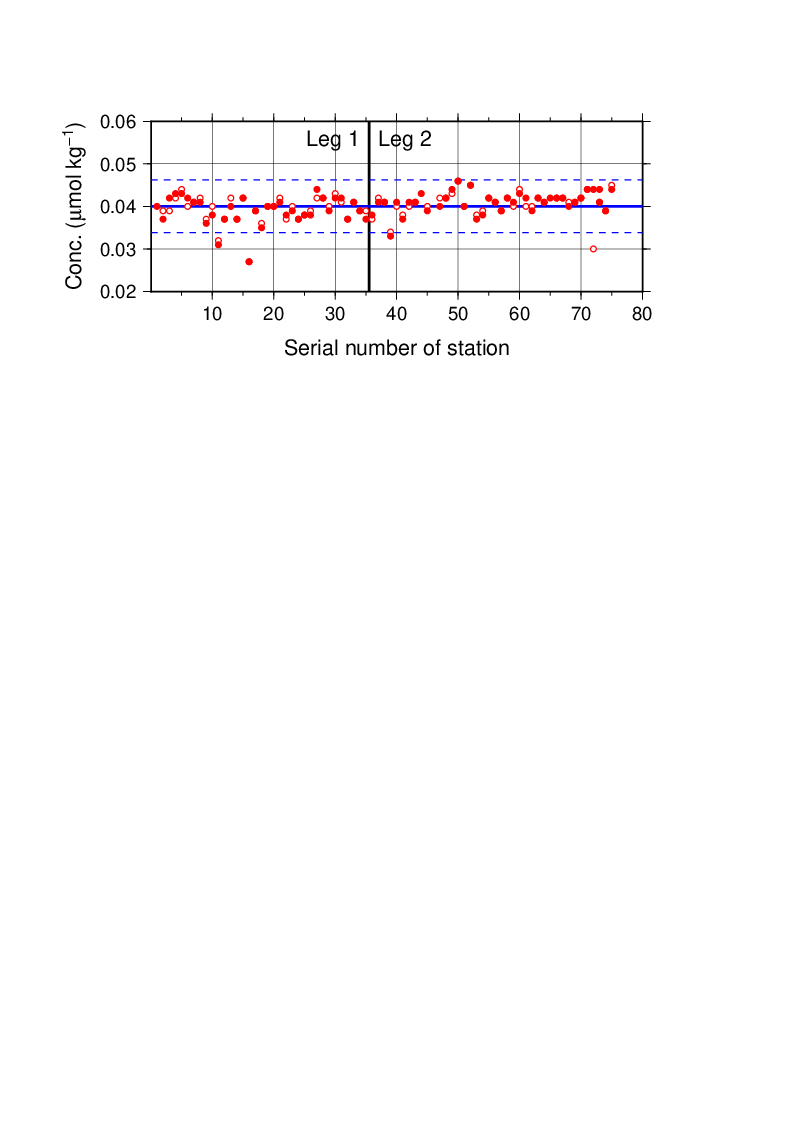


Figure C.4.7. Same as Figure C.4.6 but for nitrite.

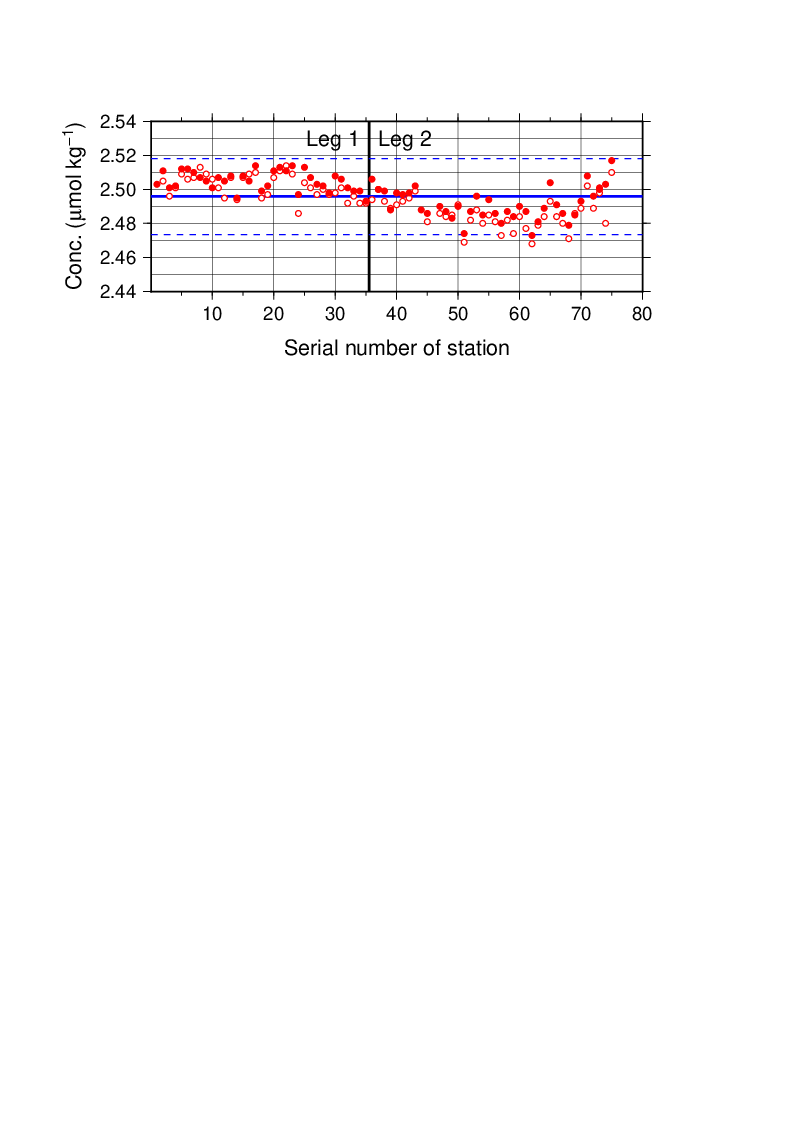


Figure C.4.8. Same as Figure C.4.6 but for phosphate.

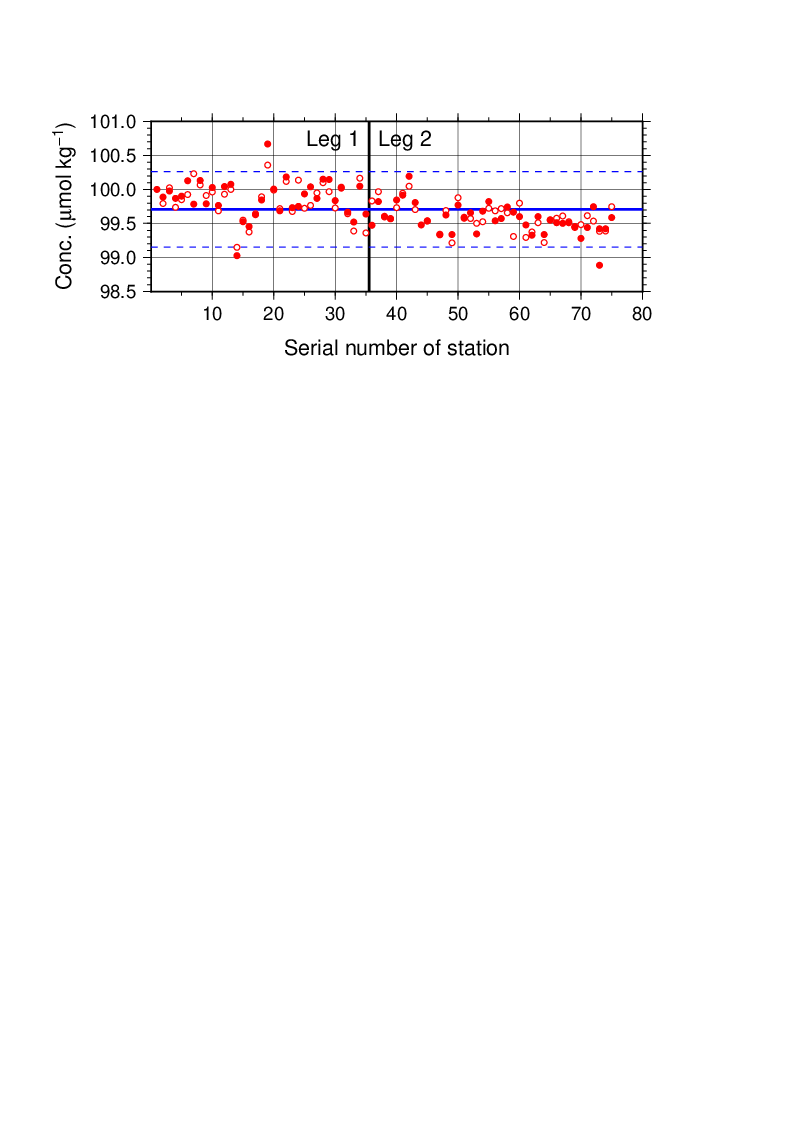


Figure C.4.9. Same as Figure C.4.6 but for silicate.

#### (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.

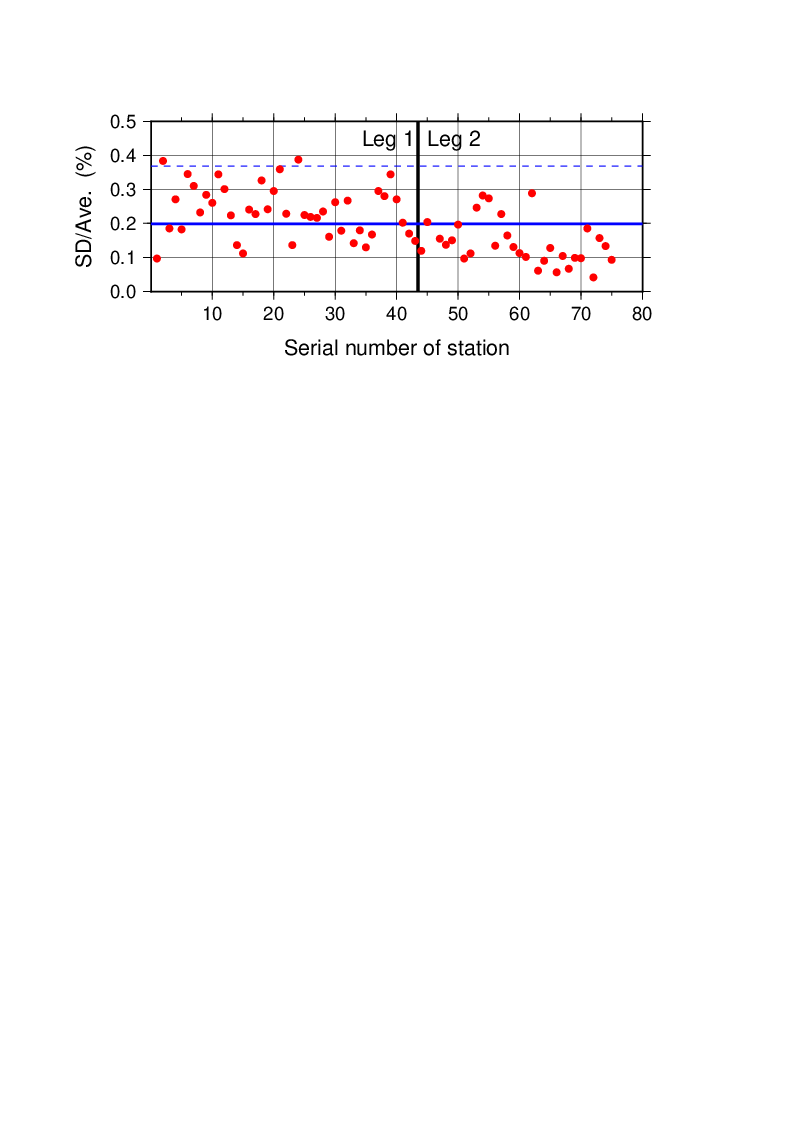


Figure C.4.10. Time-series of coefficient of variation of “check standard” measurement of nitrate+nitrite through the cruise. Thick and dashed lines denote the mean and 2 times of standard deviations of the measurements through the cruise, respectively.

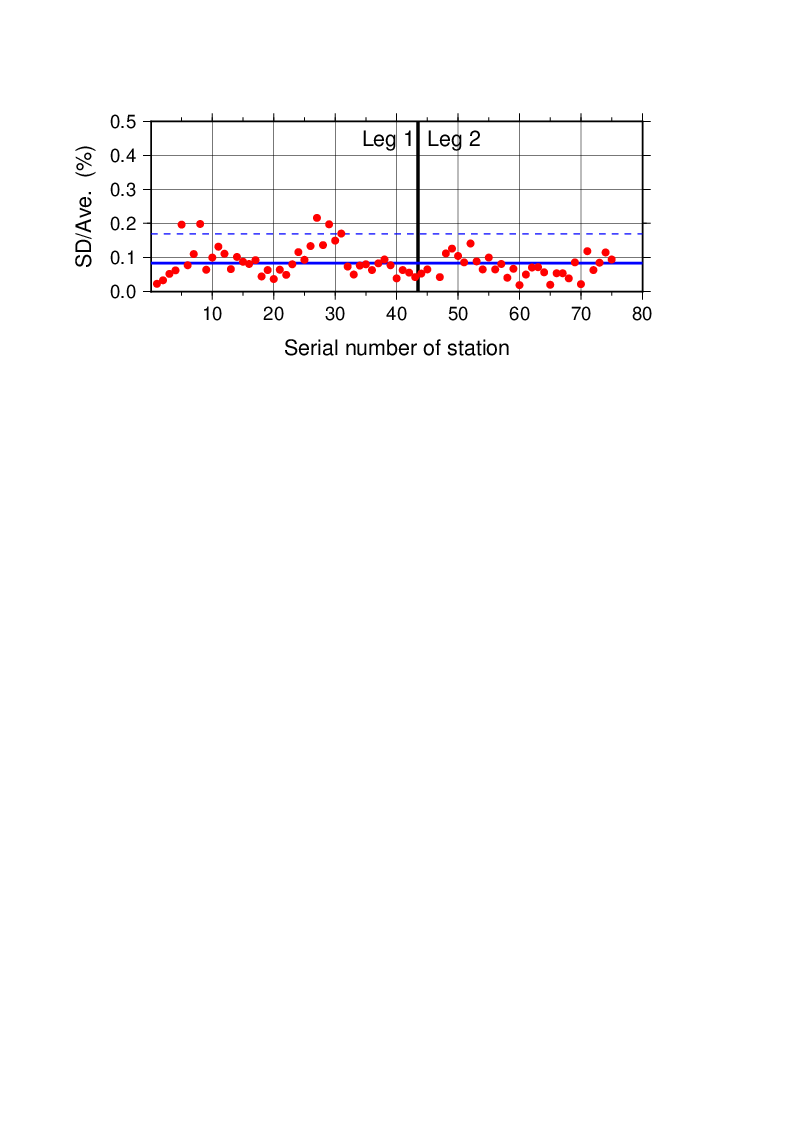


Figure C.4.11. Same as Figure C.4.10 but for nitrite.

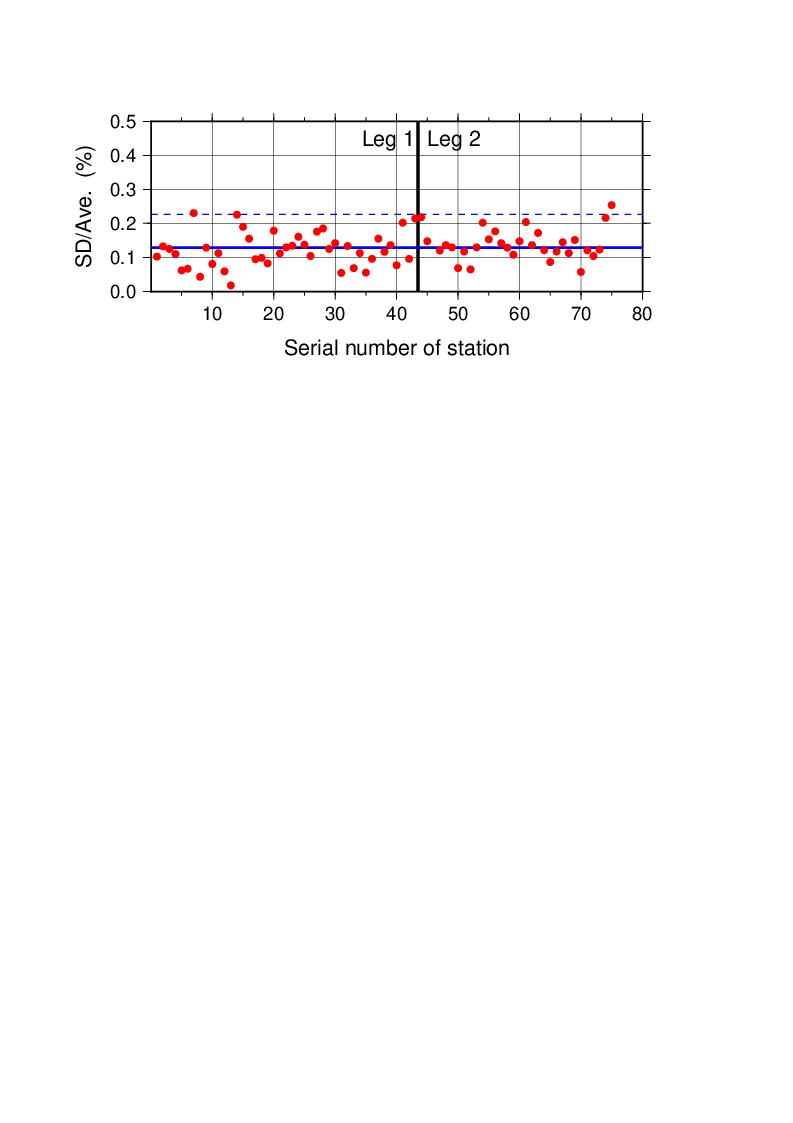


Figure C.4.12. Same as Figure C.4.10 but for phosphate.

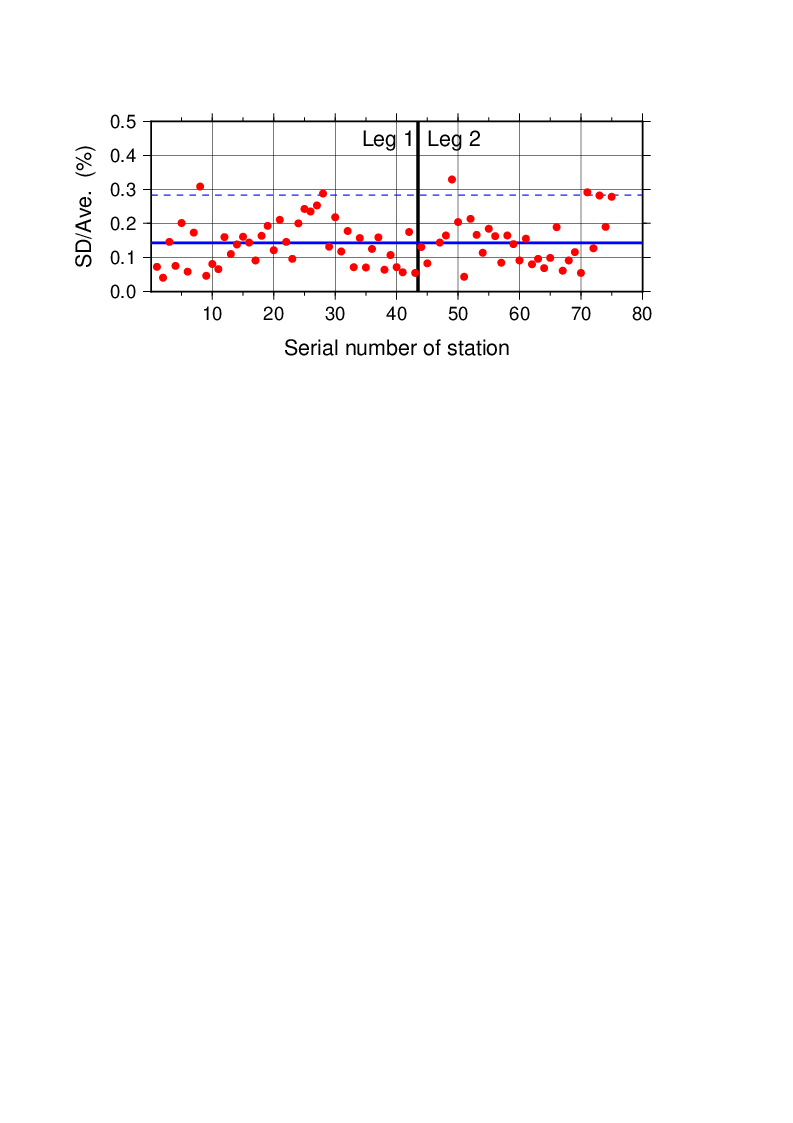


Figure C.4.13. Same as Figure C.4.10 but for silicate.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 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 μmol 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 |

### Uncertainty

#### (8.1) Uncertainty of analysis between runs

Uncertainty of analysis between runs was evaluated from coefficient of variation of measured concentration of CRM-BV throughout cruise as shown in subsection (7.2).

#### (8.2) Uncertainty of analysis in a run

Uncertainty of analysis in a run was evaluated from coefficient of variation of repeated measurements of “check standard” solution as shown in subsection (7.3).

#### (8.3) Uncertainty associated with concentration level

Uncertainty of nutrient measurement associated with concentrations level (*Uc*) was empirically represented as follows;

*Uc* (%) = *a* + *b* (1/*Cx*) + *c* (1/ *Cx*)2 (C4.1)

where *Cx* is concentration of sample for parameter X.

Using coefficient of variation of CRM measurement through the cruise and CRM concentration, uncertainty associated with concentration level for nitrate+nitrite, phosphate, and silicate were determined as follows;

*Uc* (%) = 0.115 + 2.417 × (1/*Cn*) + 0.024 × (1/*Cn*)2 (C4.2)

*Uc* (%) = −0.143 + 0.709 × (1/*Cp*) − 0.022 × (1/*Cp*)2(C4.3)

*Uc* (%) = 0.081 + 3.291 × (1/*Cs*) + 14.971 × (1/*Cs*)2, (C4.4)

where *Cn*, *Cp*, and *Cs* represent concentrations of nitrate+nitrite, phosphate, and silicate, respectively, in μmol kg−1. The determined uncertainty was also represented as graphs in Appendix A5.

#### (8.4) Combined relative standard uncertainty

Combined relative standard uncertainty (*U*) is calculated as follows:

*U*= (C4.5)

where *Ur* is uncertainty of CRM concentration, *Us* is uncertainty of in-house standard, *Ua* is uncertainty of analysis, and *Uc* is uncertainty according to concentration level. Here, as representative, the uncertainties obtained from CRM measurement were shown Table C.4.10.

|  |  |  |  |
| --- | --- | --- | --- |
| Table C.4.10. Result of concentration and expanded uncertainty (k=2) determined for CRM and RM measurements. Unit is μmol kg−1. | | | |
|  | Nitrate+nitrite | Phosphate | Silicate |
| RM-BS | 0.07±0.06 | 0.029±0.001 | 1.78±0.24 |
| RM-BT | 18.64±0.20 | 1.29±0.02 | 42.00±0.37 |
| CRM-BV | 35.39±0.36 | 2.50±0.02 | 102.26±0.87 |
| RM-BF | 41.38±0.42 | 2.79±0.03 | 153.73±1.30 |

### 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.

ORN/WHT N-1-naphtylethylene-diamine (0.23)

ORN/WHT sample or ASW (0.23)

5T

10T

20T

WHT/WHT debubble (0.60 cc min−1)

YEL/YEL ammonium chloride (buffer) (1.20)

BLK/BLK air (0.32)

BLK/BLK air (0.32)

ORN/WHT sulfanilamide (0.23)

Waste

Waste

Colorimeter

1.5 mm (I.D.) × 15 mm flow cell

530 nm

Cd tube

10T

Waste

GRY/GRY waste (1.00)

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

GRY/GRY sample or ASW (1.00)

ORN/WHT sulfanilamide (0.23)

ORN/WHT N-1-naphtylethylene-diamine (0.23)

Waste

Colorimeter

1.5 mm (I.D.) × 50 mm flow cell

530 nm

10T

20T

10T

Waste

RED/RED waste (0.80)

Waste

WHT/WHT debubble (0.60)

BLK/BLK air (0.32 cc min−1)

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.

Waste

ORN/ORN debubble (0.42)

BLK/BLK ammonium molybdate (0.32)

YEL/BLU sample or ASW (1.40)

BLK/BLK air (0.32 cc min−1)

ORN/WHT ascolbic acid (0.23)

Waste

Colorimeter

1.5 mm (I.D.) × 50 mm flow cell

880 nm

10T

Waste

RED/RED waste (0.80)

10T

Heating bath

37°C

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.

WHT/WHT ammonium molybdate (0.60)

ORN/YEL sample or ASW (0.16)

BLK/BLK air (0.32 cc min−1)

ORN/ORN oxalic acid (0.42)

Waste

Colorimeter

1.5 mm (I.D.) × 15 mm flow cell

820 nm

Heating bath

37°C

10T

Waste

YEL/YEL waste (1.20)

WHT/WHT ascolbic acid (0.60)

10T

10T

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;

1. Check the shape of each peak and position of peak values taken, and then change the positions of peak values taken if necessary.
2. Baseline correction was done basically using liner regression.
3. Reagent blank correction was done basically using liner regression.
4. Carryover correction was applied to peak heights of each sample.
5. Sensitivity correction was applied to peak heights of each sample.
6. Refraction error correction was applied to peak heights of each seawater sample.
7. Calibration curves to get nutrients concentration were assumed quadratic expression.
8. Concentrations were converted from μmol L−1 to μmol kg−1 using seawater density.

**A4. Reagents recipes**

**(A4.1) Nitrate+nitrite**

Ammonium chloride (buffer), 0.7 μmol L−1 (0.04 % w/v);

Dissolve 190 g ammonium chloride, NH4Cl, in ca. 5 L of DW, add about 5 mL ammonia(aq) to adjust pH of 8.2–8.5.

Sulfanilamide, 0.06 μmol L −1 (1 % w/v);

Dissolve 5 g sulfanilamide, 4-NH2C6H4SO3H, 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 μmol L −1 (0.1 % w/v);

Dissolve 0.5 g NEDA, C10H7NH2CH2CH2NH2·2HCl, in 500 mL DW.

**(A4.2) Nitrite**

Sulfanilamide, 0.06 μmol L −1 (1 % w/v); Shared from nitrate reagent.

N-1-naphtylethylene-diamine dihydrochloride (NEDA), 0.004 μmol L −1 (0.1 % w/v); Shared from nitrate reagent.

**(A4.3) Phosphate**

Ammonium molybdate, 0.005 μmol L−1 (0.6 % w/v);

Dissolve 3 g ammonium molybdate(VI) tetrahydrate, (NH4)6Mo7O24·4H2O, and 0.05 g potassium antimonyl tartrate, C8H4K2O12Sb2·3H2O, in 400 mL DW and add 40 mL concentrated H2SO4. 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 μmol L−1 (1.5 % w/v);

Dissolve 4.5 g L(+)-ascorbic acid, C6H8O6, in 300 mL DW. After mixing, add 10 mL acetone. This reagent was freshly prepared before every measurement.

**(A4.4) Silicate**

Ammonium molydate, 0.005 μmol L−1 (0.6 % w/v);

Dissolve 3 g ammonium molybdate(VI) tetrahydrate, (NH4)6Mo7O24·4H2O, in 500 mL DW and added concentrated 2 mL H2SO4. After mixing, add 2 mL sodium dodecyl sulfate (15 % solution in water).

Oxalic acid, 0.4 μmol L−1 (5 % w/v);

Dissolve 25 g oxalic acid dihydrate, (COOH)2·2H2O, in 500 mL DW.

L(+)-ascorbic acid, 0.08 μmol 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, MgSO4·7H2O, and 0.84 g sodium hydrogen carbonate, NaHCO3, in 5 L DW.

**A5. Uncertainty associated with concentration level**

Uncertainty associated with concentration level given by eqs. (C4.2)–(C4.4) are shown in Figures C.4.A5–C.4.A7, respectively.

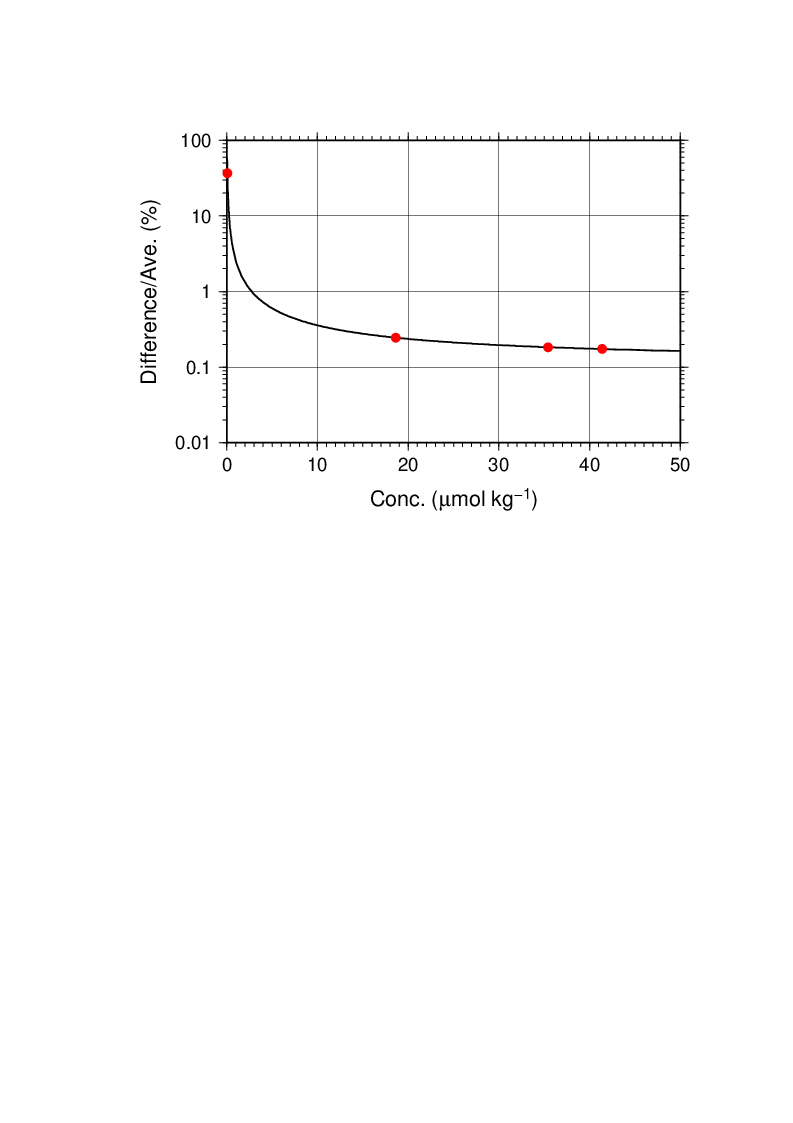


Figure C.4.A5. Uncertainty of nitrate+nitrite associated with concentration level.

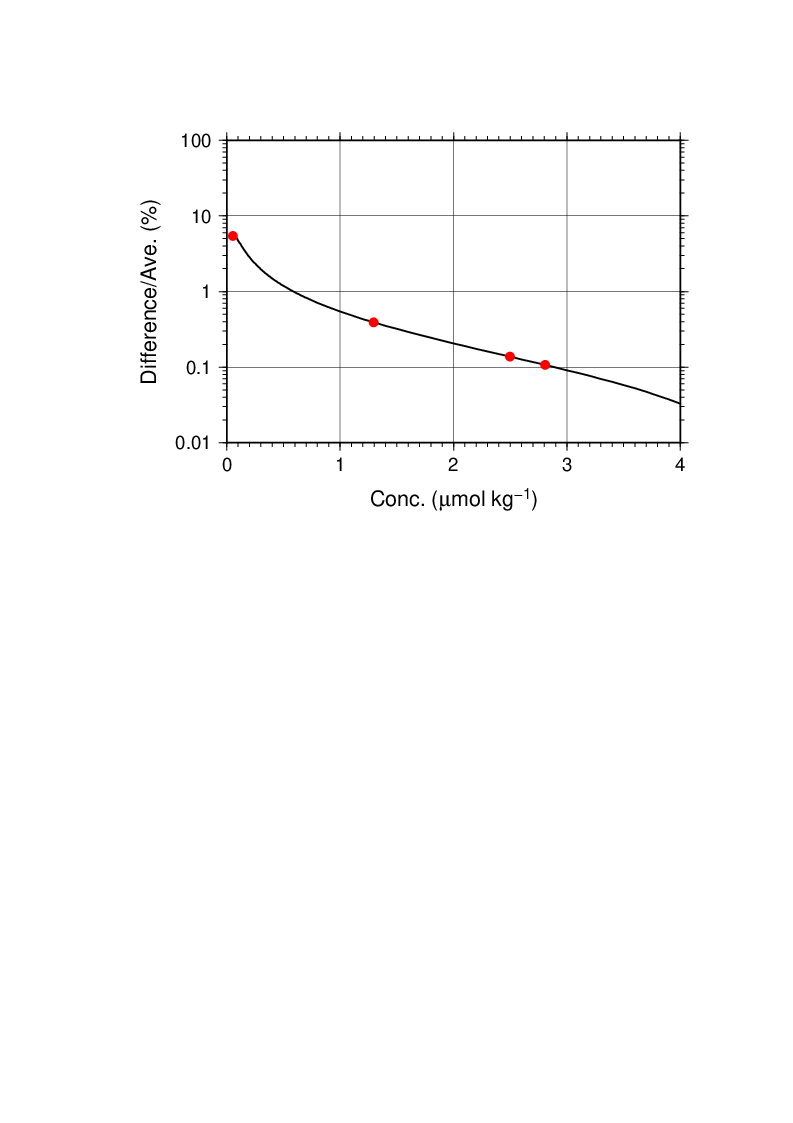


Figure C.4.A6. Same as Figure C.4.A5 but for phosphate.

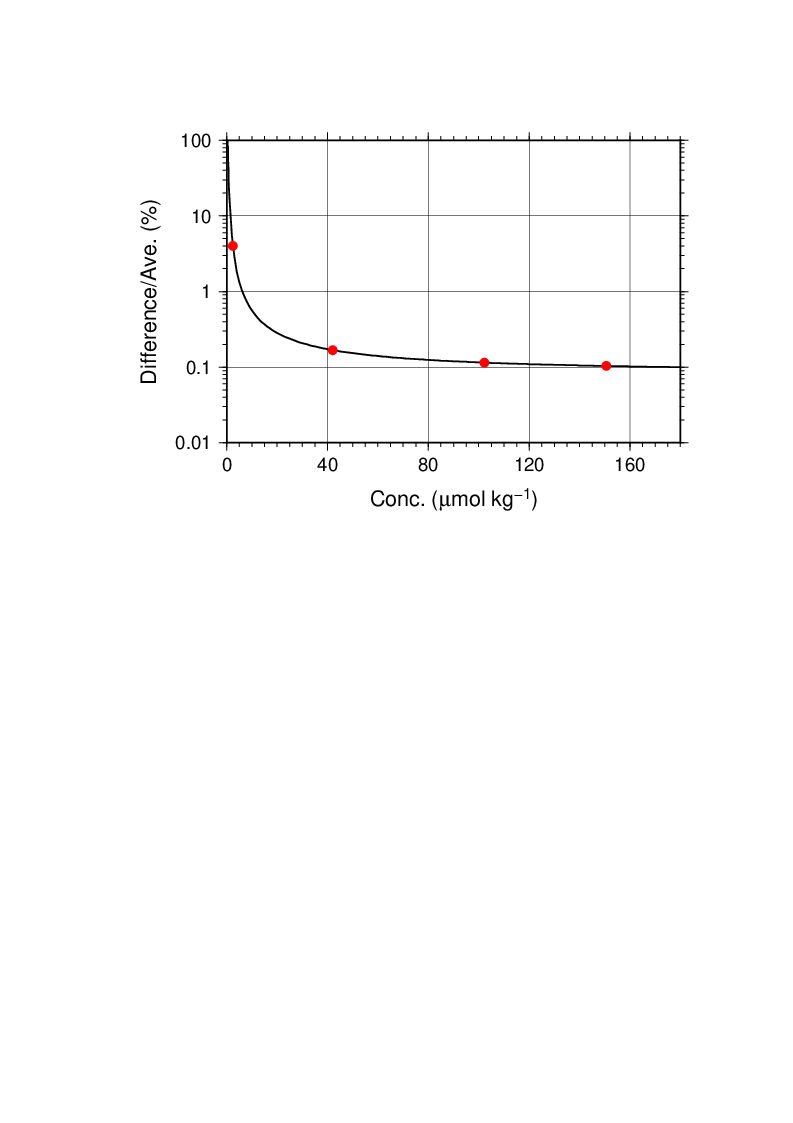


Figure C.4.A7. Same as Figure C.4.A5 but for silicate.

***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*.

## Phytopigments (chlorophyll-a and phaeopigment)

### Personnel

Chihiro KAWAMURA (GEMD/JMA)

Takashi MIYAO (GEMD/JMA)

### Station 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.

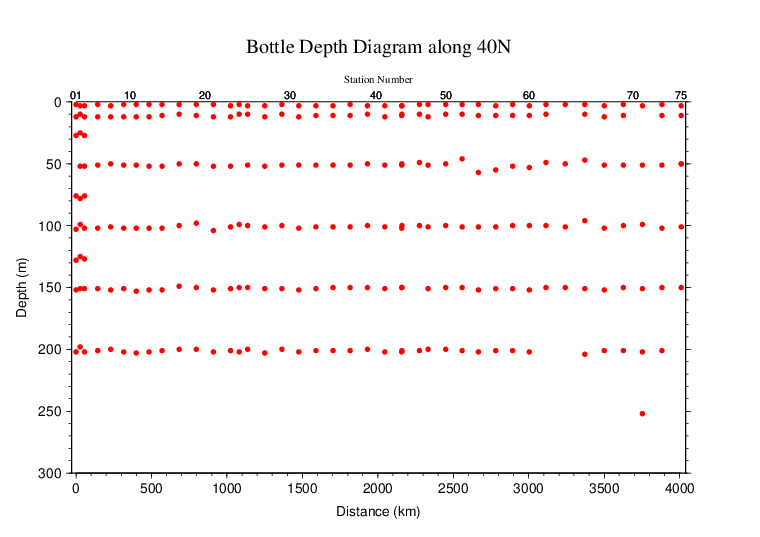


Figure C.5.2. Distance-depth distribution of sampling layers of chlorophyll-*a*.

### 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)

### Instruments

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

Spectrophotometer: UV-1800 (Shimadzu, Japan)

### 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:

chl *a* concentration (g mL−1) = Achl / a\*phy (C5.1)

where Achl 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 fph

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 mol L−1 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 (fph) of the fluorometer was calculated as the slope of the acidified reading against chlorophyll-*a* concentration. The R and fph in the cruise are shown in Table C.5.1.

Table C.5.1. R and fph in the cruise.

|  |  |
| --- | --- |
| Acidification coefficient (R) | 1.764 |
| Linear calibration factor (fph) | 7.8333 |

### 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 mol L−1 HCl. Chlorophyll-*a* and phaeopigment concentrations (g mL−1) in the sample are calculated as follows:

 (C5.2)

 (C5.3)

F0: reading before acidification

Fa: reading after acidification

R: acidification coefficient (F0/Fa) for pure chlorophyll-*a*

fph: linear calibration factor

v: extraction volume

V: sample volume.

### 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 *a* | 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 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.*