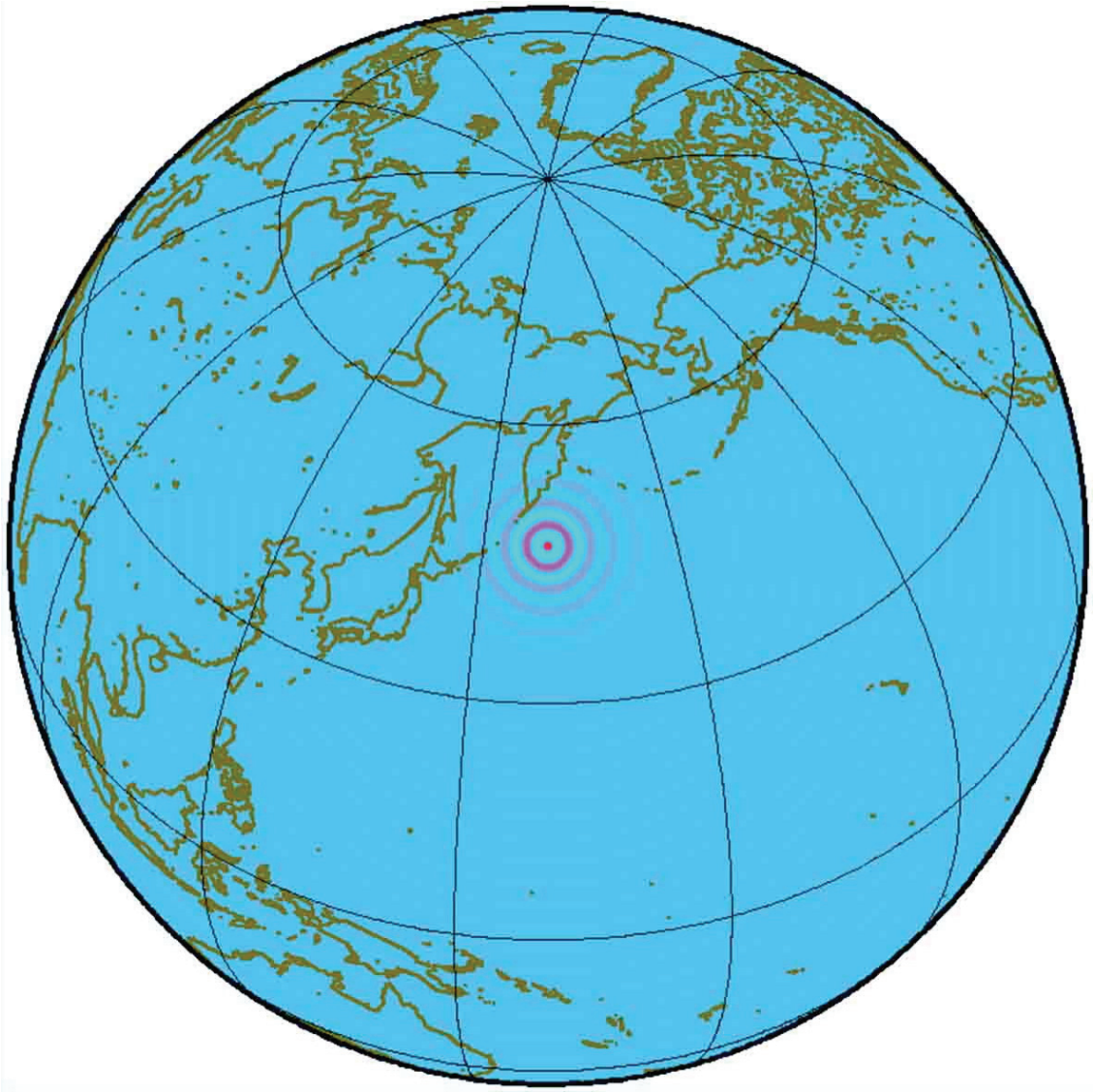
Hydrograhic Data at Station K2 between 2001 and 2006

Version 20070112



January 2007

Mutsu Institute for Oceanography
Japan Agency for Marine-Earth Science and Technology

Contents

1. Introduction 2

2. List of Investigators 3

3. Cruises and hydrocasts for observations 4

4. Sampling and analytical methods 6
   4.1 CTD and water bottle
   4.2 Salinity
   4.3 Dissolved oxygen (DO)
   4.4 Nutrients
   4.5 Dissolved inorganic carbon (DIC)
   4.6 Total alkalinity (TALK)

5. Correction of data between cruises 27

6. Future update of data and contact persons 29

7. Acknowledgements 30

Appendix
(1) Vertical profiles for respective months in the upper 200 dbar
(2) Time series data for respective components in the upper 200 dbar during MR06-03 cruise (18 May – 25 July 2006)

Cover sheet was designed by Mr. Suguru Okamoto from Hokkaido University, who was a cruise participant of MR06-03 cruise, with wish that his oceanographic data at station K2 will be useful and helpful for many scientists in the world and for his Ph.D thesis.

1. Introduction

The global warming and climate change has been great concern in the world and importance of the global ocean observation has been requested strongly in order to predict the future earth and propose appropriate countermeasures.

It is no doubt that time-series observation is important to understand the carbon cycle and biogeochemical change in the ocean precisely. Since 2001, Mutsu Institute for Oceanography (MIO) has been conducted a time-series observation for biogeochemistry in the northwestern North Pacific. Several stations were decided as time-series stations in the Western Subarctic Gyre and biogeochemical observation has been conducted with mooring systems that consist of various sensors and automatic samplers. In addition, hydrographic observation has been conducted by research vessels, mainly R/V MIRAI, in order to measure dissolved chemical components and verify its seasonal and interannual variability. Among time-series stations, station K2 (47°N / 160°E) was a principal station and a lot of data has been accumulated.

We herewith wrap up seasonal oceanographic data (routine data) obtained by hydrocasts / chemical analysis during MIO research-related cruises. Chemical data quality was not excellent before year of 2000. However, after 2003 when the JAMSTEC BEAGLE cruise was conducted in the southern ocean as a part of World Ocean Circulation Experiment (WOCE) revisit expedition, sampling and analytical techniques have been improved and systematic data quality control has been established thanks to great efforts of marine technicians from Marine Works Japan Co.

We hope these data will be useful and helpful for users' science after users' own data arrangements.

January 2007

Mutsu Institute for Oceanography (MIO)
Japan Agency for Marine-Earth Science and technology (JAMSTEC)

2. List of Investigators

Tetsuichi Fujiki (MIO/JAMSTEC)

Makio Honda (MIO/JAMSTEC)

Hajime Kawakami (MIO/JAMSTEC)

Yuichiro Kumamoto (Institute of Observational Research for Global Change (IORGC)/ JAMSTEC)

Kazuhiko Matsumoto (MIO/JAMSTEC)

Akihiko Murata (IORGC/JAMSTEC)

Yoshiyuki Nakano (MIO/JAMSTEC)

Kenichi Sasaki (MIO/JAMSTEC)

Masahide Wakita (MIO/JAMSTEC)

Shuichi Watanabe (MIO/JAMSTEC)

3. Cruise and hydrocasts for routine observations

Between June 2001 and July 2006, more than ten scientific cruises associating MIO time-series observation had been conducted by JAMSTEC fleets, mainly R/V MIRAI (Fig. 3.1).

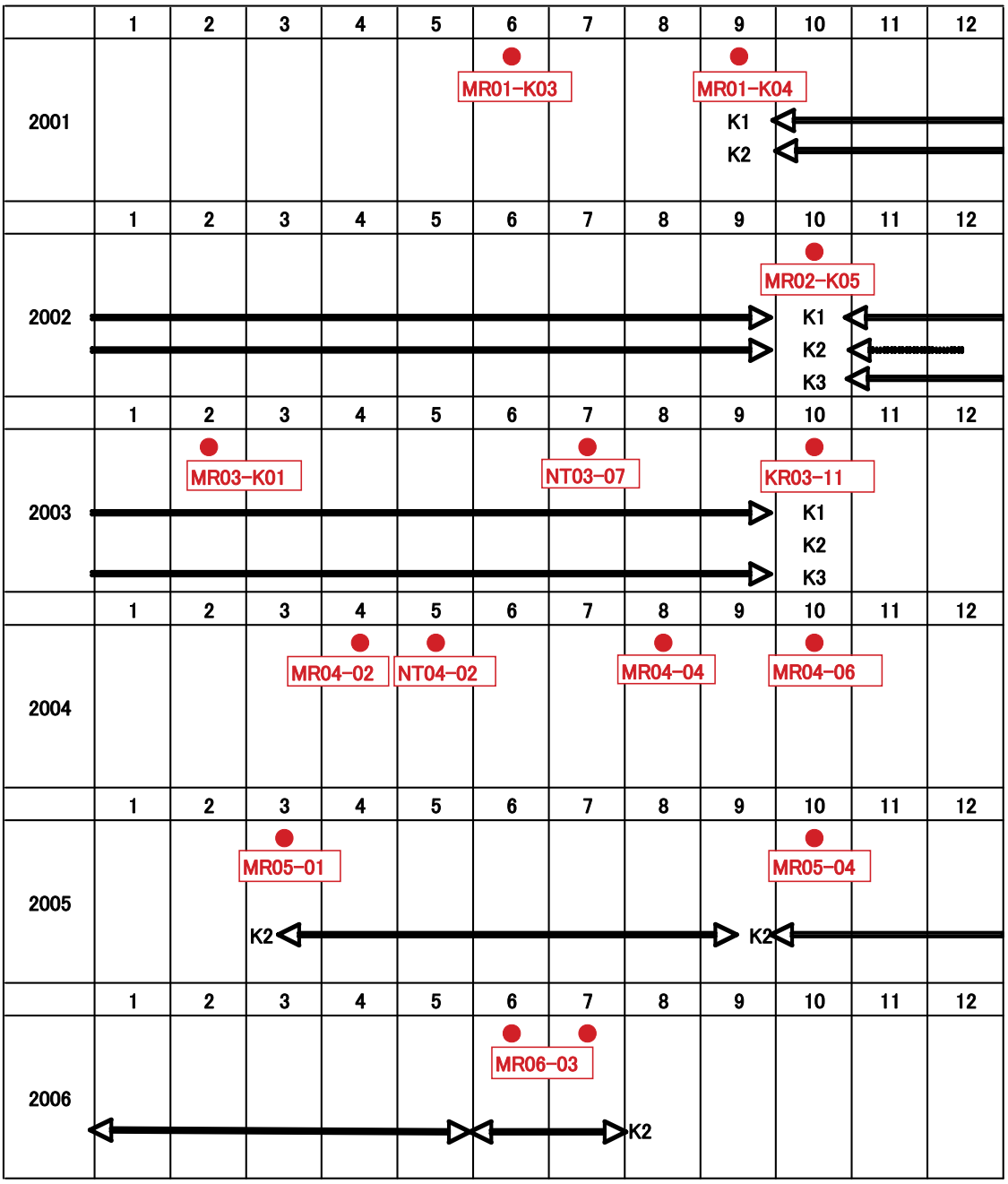


Fig. 3.1 Scientific cruises associating with MIO project. Red circles show cruises and arrows show mooring period for respective stations. MR: R/V *MIRAI*, NT: R/V *NATSUSHIMA*, KR: R/V *KAIREI*

During above cruises, hydrocasts for routine observation at station K2 are conducted once or several times. Table 3.1 shows list of hydrocasts and measured chemical components in this data set.

Table 3.1 List of hydrocasts at station K2 and measured chemical components

No.	Cruise name	R/V	Date	Maximum pressure	DO	Silicate	Nitrate	Nitrite	Phosphate	DIC	TA	Ammonium
1	MR01-K03	Mirai	2001.6.10	5260.3	○	○	○	○	○	○	○	○
2	MR01-K04	Mirai	2001.9.7	5204.2	○	○	○	○	○	○	○	
3	MR02-K05	Mirai	2002.10.21	5235.4	○	○	○	○	○	○	○	○
4	MR03-K01	Mirai	2003.2.25	5233.8	○	○	○	○	○	○	○	
5	NT03-07	Natsushima	2003.7.11	3557.7	○	○	○	○	○	○	○	
6	KR03-11	Kairei	2003.10.4	202.6	○	○	○	○	○	○	○	
7	MR04-02	Mirai	2004.4.7	3048.6	○	○	○	○	○	○	○	○
8	NT04-07	Natsushima	2004.5.27	3506.9	○	○	○	○	○	○		
9	MR04-04	Mirai	2004.8.17	5303.4	○	○	○	○	○	○	○	
10	MR04-06	Mirai	2004.10.20	5301.4	○	○	○	○	○	○		
11	MR05-01	Mirai	2005.3.4	5239.6	○	○	○	○	○	○	○	
12	MR05-04	Mirai	2005.9.24	5277.9	○	○	○	○	○	○	○	
13	MR06-03(1-1)	Mirai	2006.6.3	202.8	○	○	○	○	○	○	○	○
14	MR06-03(1-2)	Mirai	2006.6.3	5246.5	○	○	○	○	○	○	○	
15	MR06-03(2)	Mirai	2006.6.12	202.1	○	○	○	○	○	○	○	○
16	MR06-03(3-1)	Mirai	2006.6.22	5292.8	○	○	○	○	○	○	○	○
17	MR06-03(3-2)	Mirai	2006.6.25	201.3	○	○	○	○	○	○	○	○
18	MR06-03(4)	Mirai	2006.7.1	203.0	○	○	○	○	○	○	○	○
18	MR06-03(5-1)	Mirai	2006.7.8	203.0	○	○	○	○	○	○	○	○
19	MR06-03(5-2)	Mirai	2006.7.10	202.3	○	○	○	○	○	○	○	○
20	MR06-03(6-1)	Mirai	2006.7.14	5307.8	○	○	○	○	○	○	○	○
21	MR06-03(6-2)	Mirai	2006.7.16	201.7	○	○	○	○	○	○	○	○

* In case of cruises of R/V NATSUSHIMA and KAIREI, seawater samples for nutrients analysis were kept in freezer and those for analysis of carbon species were preserved with saturated $HgCl_2$ solution, and transferred to the land laboratory. Concentrations of nutrients and carbon species were measured at National Institute of Environmental Science (NIES) and Institute of Advanced Industrial Science and Technology (AIST), respectively (courtesy of Dr. Nojiri and Dr. Tsurushima)

4. Sampling and analytical methods

CTD / water sampling system and analytical methods on R/Vs MIRAI, NATSUSHIMA and KAIREI have been changed gradually during the last 5 years. However general CTD / water sampling system and principle of analytical methods are identical. Followings are sampling and analytical methods and precision or accuracy of routine data analysis during MR06-03 cruise: updates of water sampling system and analytical methods quoted from MR06-03 preliminary cruise report. Those during other R/V MIRAI cruises are obtained from JAMSTEC web site (http://www.jamstec.go.jp/mirai/all_year/index.html).

4.1 CTD and water bottle

The CTD system, SBE 911plus system (Sea-Bird Electronics, Inc., USA), is a real time data system with the CTD data transmitted from a SBE 9plus underwater unit via a conducting cable to the SBE 11plus deck unit. The SBE 11plus deck unit is a rack-mountable interface which supplies DC power to the underwater unit, decodes the serial data stream, formats the data under microprocessor control, and passes the data to a companion computer. The serial data from the underwater unit is sent to the deck unit in RS-232 NRZ format using a 34560 Hz carrier-modulated differential-phase-shift-keying (DPSK) telemetry link. The deck unit decodes the serial data and sends them to a personal computer (Hewlett Packard Vectra VL, Intel™ Celeron™, Microsoft Windows98 2nd edition) to display, at the same time, to storage in a disk file using SBE SEASOFT software.

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

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

4.2 Salinity

(1) Sample collection

Seawater samples were collected with 12 liter Niskin-X bottles, bucket, and an underway sea surface observation system (EPCS). The salinity sample bottle of the 250 ml brown grass bottle with screw cap was used to collect the sample water. Each bottle was rinsed three times with the sample water, and was filled with sample water to the bottle shoulder. Its cap was also thoroughly rinsed. The bottle was stored more than 12 hours in the laboratory before the salinity measurement. The kind and number of samples during MR06-03 cruise are shown as follows ;

Table 4.2.1 Kind and number of samples

Kind of Samples	Number of Samples
Samples for CTD and Bucket	1,674
Samples for EPCS	96
Total	1,770

(2) Instruments and method

The salinity analysis was carried out on R/V MIRAI during the cruise of MR06-03 using the salinometer (Model 8400B "AUTOSAL" ; Guildline Instruments Ltd.: S/N 62556, 62827) with additional peristaltic-type intake pump (Ocean Scientific International, Ltd.). We also used two pairs of precision digital thermometers (Model 9540 ; Guildline Instruments Ltd.). One thermometer monitored an ambient temperature and the other monitored a bath temperature. The specifications of AUTOSAL salinometer and thermometer are shown as follows ;

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

Measurement Range: 0.005 to 42 (PSU)

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

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

Thermometer (Model 9540; Guildline Instruments Ltd.)

Measurement Range: -180 to +240 °C

Resolution: 0.001

Limits of error ±°C: 0.01 (24 hours @ 23 °C ± 1 °C)

Repeatability: ±2 least significant digits

The measurement system was almost same as Aoyama *et al.* (2002). The salinometer was operated in the air-conditioned ship's laboratory at a bath temperature of 24 °C. An ambient temperature varied from approximately 19 °C to 24 °C, while a bath temperature is very stable

and varied within ± 0.002 deg C on rare occasion. The measurement for each sample was done with a double conductivity ratio that is defined as median of 31 times reading of the salinometer. Data collection was started in 5 seconds after filling sample to the cell and it took about 10 seconds when S/N62556 was used, and 20 second after filling sample to the cell and it took about 15 second when serial number (S/N) 62827 was used to collect 31 readings by a personal computer. Data were taken for the sixth and seventh filling of the cell. In case the difference between the double conductivity ratio of these two fillings is smaller than 0.00002, the average value of these double conductivity ratio was used to calculate the bottle salinity with the algorithm for practical salinity scale, 1978 (UNESCO, 1981). If the difference was greater than or equal to 0.0003, we measured eighth filling of the cell. In case the double conductivity ratio of eighth filling did not satisfy the criteria above, we measured ninth and tenth filling of the cell and the median of the double conductivity ratios of five fillings are used to calculate the bottle salinity.

During MR06-03 cruise, the measurement was conducted about 12hours per day (typically from 8:00 to 20:00 in Leg1, from 15:00 to 03:00 in Leg2) and the cell was cleaned with soap or thin-ethanol or both after the measurement of the day. We measured 1,674 samples in total.

(3) Standard Seawater

Standardization control of the salinometer with S/N 62556 was set to 480 and all the measurements were done by this setting STANDBY of 62556 was 5502 ± 0001 and ZERO was 0.0 ± 0001. We used IAPSO Standard Seawater batch P146 which conductivity ratio was 0.99979 (double conductivity ratio is 1.99958) as the standard for salinity. We measured 73 bottles of P146.

Standardization control of the salinometer with S/N 62827 was set to 400 and all the measurements were done by this setting STANDBY of 62827 was 5530 ± 0001 and ZERO was 0.0 ± 0000. We used IAPSO Standard Seawater batch P146 as the standard for salinity. We measured 31 bottles of P146.

Fig. 4.2.1 shows the history of double conductivity ratio of the Standard Seawater batch P146. The average of double conductivity ratio of S/N 62556 and 62827 were 1.99957 and 1.99952, respectively, and the standard deviation were 0.00002 and 0.00003, which is equivalent to 0.0004 and 0.0006 in salinity, respectively.

We added a value to data among two value of standard seawater that were measured about every 40 sample to correct nearly equal the determinate value of standard seawater.

Fig. 4.2.2 shows the history of double conductivity ratio of the Standard Seawater batch P146 after correct.

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

Standard seawater (SSW)

Batch:	P146
Conductivity ratio:	0.99979
Salinity:	34.992
Preparation date:	12 May. 2005

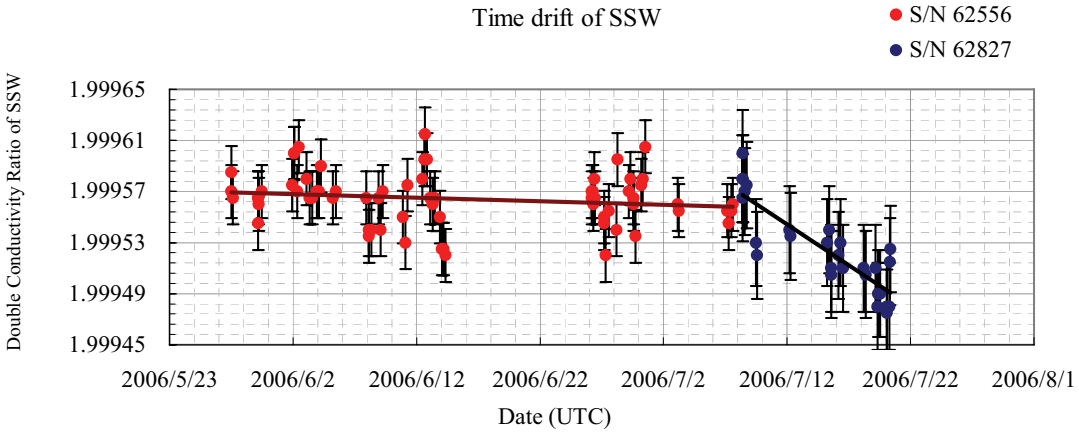


Fig. 4.2.1 History of double conductivity ratio of the Standard Seawater batch P146 of S/N 62556 and 62827

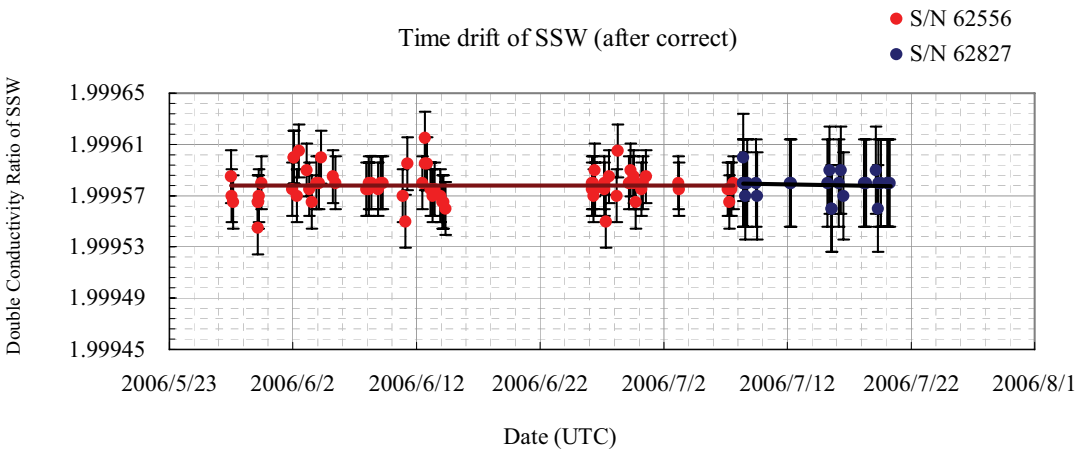


Fig. 4.2.2 History of double conductivity ratio of the Standard Seawater batch P146 of S/N 62556 and 62827 (after correct)

(4) Sub-Standard Seawater

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

(5) Replicate Samples

We took 219 pairs of replicate samples during MR06-03 cruise. Fig.4.2.3 shows the histogram of the absolute difference between replicate samples, respectively. There were 9 questionable measurement of replicate samples. The standard deviation of the absolute deference of replicate samples was 0.0002 in salinity.

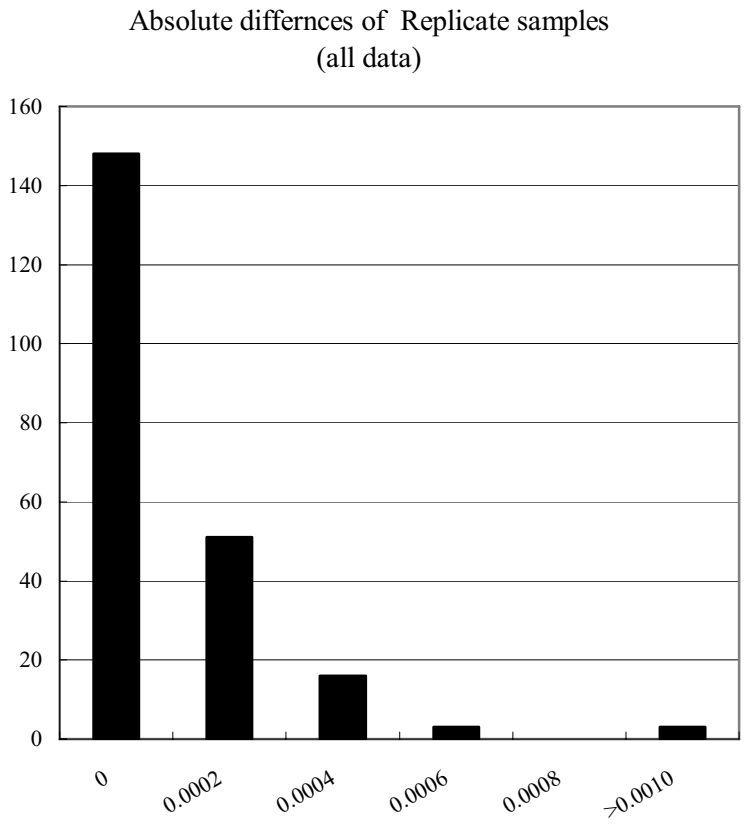


Fig. 4.2.3 the histogram of the difference between replicate samples (include bad sample)

Reference

Aoyama, M., T. Joyce, T. Kawano and Y. Takatsuki (2002) Standard seawater comparison up to P129. Deep-Sea Research, I, Vol. 49, 1103-1114.

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

4.3 DO

(1) Reagents:

Pickling Reagent I: Manganous chloride solution (3M)
Pickling Reagent II: Sodium hydroxide (8M) / sodium iodide solution (4M)
Sulfuric acid solution (5M)
Sodium thiosulfate (0.025M)
Potassium iodate (0.001667M)

(2) Instruments:

Burette for sodium thiosulfate;
APB-510 manufactured by Kyoto Electronic Co. Ltd. / 10 cm^3 of titration vessel
Burette for potassium iodate;
APB-410 manufactured by Kyoto Electronic Co. Ltd. / 20 cm^3 of titration vessel
Detector and Software; Automatic photometric titrator manufactured by Kimoto Electronic Co. Ltd.

(3) Sampling

Following procedure is based on the WHP Operations and Methods (Dickson, 1996).

Seawater samples were collected with Niskin bottle attached to the CTD-system. Seawater for oxygen measurement was transferred from Niskin sampler bottle to a volume calibrated flask (*ca.* 100 cm^3). Seawater of three times volume of the flask was overflowed. Temperature was measured by digital thermometer during the overflowing. Then two reagent solutions (Reagent I, II) of 0.5 cm^3 each were added immediately into the sample flask and the stopper was inserted carefully into the flask. The sample flask was then shaken vigorously to mix the contents and to disperse the precipitate finely throughout. After the precipitate has settled at least halfway down the flask, the flask was shaken again vigorously to disperse the precipitate. The sample flasks containing pickled samples were stored in a laboratory until they were titrated.

(4) Sample measurement

At least two hours after the re-shaking, the pickled samples were measured on board. A magnetic stirrer bar and 1 cm^3 sulfuric acid solution were added into the sample flask and stirring began. Samples were titrated by sodium thiosulfate solution whose morality was determined by potassium iodate solution. Temperature of sodium thiosulfate during titration was recorded by a digital thermometer. During this cruise we measured dissolved oxygen concentration using two sets of the titration apparatus (DOT-1 and DOT-2). Dissolved oxygen concentration (μmol kg^{-1}) was calculated by sample temperature during seawater sampling, salinity of the sample, and titrated volume of sodium thiosulfate solution without the blank.

(5) Standardization and determination of the blank

Concentration of sodium thiosulfate titrant (*ca.* 0.025M) was determined by potassium iodate solution. Pure potassium iodate was dried in an oven at 130°C. 1.7835 g potassium iodate weighed out accurately was dissolved in deionized water and diluted to final volume of 5 dm^3 in a calibrated volumetric flask (0.001667M). 10 cm^3 of the standard potassium iodate solution was added to a flask using a calibrated dispenser. Then 90 cm^3 of deionized water, 1 cm^3 of sulfuric acid solution, and 0.5 cm^3 of pickling reagent solution II and I were added into the flask in order. Amount of sodium thiosulfate titrated gave the morality of sodium thiosulfate titrant.

The blank from the presence of redox species apart from oxygen in the reagents was determined as follows. 1 cm^3 of the standard potassium iodate solution was added to a flask using a calibrated dispenser. Then 100 cm^3 of deionized water, 1 cm^3 of sulfuric acid solution, and 0.5 cm^3 of pickling reagent solution II and I were added into the flask in order. Just after titration of the first potassium iodate, a further 1 cm^3 of standard potassium iodate was added and titrated. The blank was determined by difference between the first and second titrated volumes of the sodium thiosulfate. The oxygen in the pickling reagents I (0.5 cm^3) and II (0.5 cm^3) were assumed to be 3.8×10^{-8} mol (Dickson, 1996).

Table 4.3.1 shows results of the standardization and the blank determination during this cruise.

Table 4.3.1 Results of the standardization and the blank determinations during this cruise. E.P. is end point of titration.

Date	KIO_3		DOT-1 (cm^3)			DOT-3 (cm^3)			Samples
(UTC)	#	bottle	$Na_2S_2O_3$	E.P.	blank	$Na_2S_2O_3$	E.P.	blank	(Stations)
2006/05/29	1	20060419-02-02	20060514-3	3.960	-0.012	20060514-4	3.957	-0.011	M06001
2006/06/01		20060419-02-03	20060514-3	3.958	-0.011	20060514-4	3.955	-0.011	M06011,012,013,014,015
2006/06/03		20060419-02-04	20060514-3	3.953	-0.011	20060514-4	3.953	-0.012	M06002cast3,cast4
2006/06/06		20060419-02-05	20060528-1	3.955	-0.012	20060528-2	3.956	-0.014	M0616,017,018
2006/06/07		20060419-02-06	20060528-1	3.958	-0.014	20060528-2	3.957	-0.012	M06003,004
2006/06/09		20060419-02-07	20060528-1	3.955	-0.012	20060528-2	3.958	-0.009	M06010,009,008
2006/06/11		20060419-02-08	20060528-3	3.958	-0.013	20060528-4	3.959	-0.014	.M06007,006
2006/06/12	2	20060419-03-01	20060528-3	3.959	-0.012	20060528-4	3.957	-0.013	M06019
2006/06/22	2	20060419-03-04	20060614-1	3.966	-0.011	20060614-2	3.966	-0.012	M06020 cast2(deep),M06020
2006/06/26		20060419-03-05	20060614-1	3.966	-0.012	20060614-2	3.966	-0.009	M06021,022,023,024,025
2006/06/29		20060419-03-06	20060614-3	3.967	-	20060614-4	3.968	-	M06026 cast1,cast9
2006/07/04		20060419-03-07	20060614-3	3.966	-0.011	20060614-4	3.964	-0.009	M06031,030,029,028,027
2006/07/08		20060419-03-08	20060630-1	3.960	-0.011	20060630-2	3.960	-0.011	M06032 cast6, cast9
2006/07/13	3	20060419-04-01	20060630-1	3.961	-0.011	20060630-2	3.961	-0.010	M06037,036,035
2006/07/14		20060419-04-02	20060630-1	3.960	-0.011	20060630-2	3.960	-0.010	M06039 cast1, cast3
2006/07/17		20060419-04-03	20060630-3	3.958	-0.014	20060630-4	3.960	-0.013	M06033,034,038

Batch number of the KIO_3 standard solution.

(6) Reproducibility of sample measurement

Replicate samples were taken at every CTD cast; usually these were 5 - 10 % of seawater samples of each cast during this cruise. Results of the replicate samples were shown in Table 4.3.2 and this histogram shown in Fig. 4.3.1. The standard deviation was calculated by a procedure (SOP23) in DOE (1994).

Table 4.3.2 Results of the replicate sample measurements

Number of replicate sample pairs	Oxygen concentration (μmol/kg)
	Standard Deviation.
156	0.087

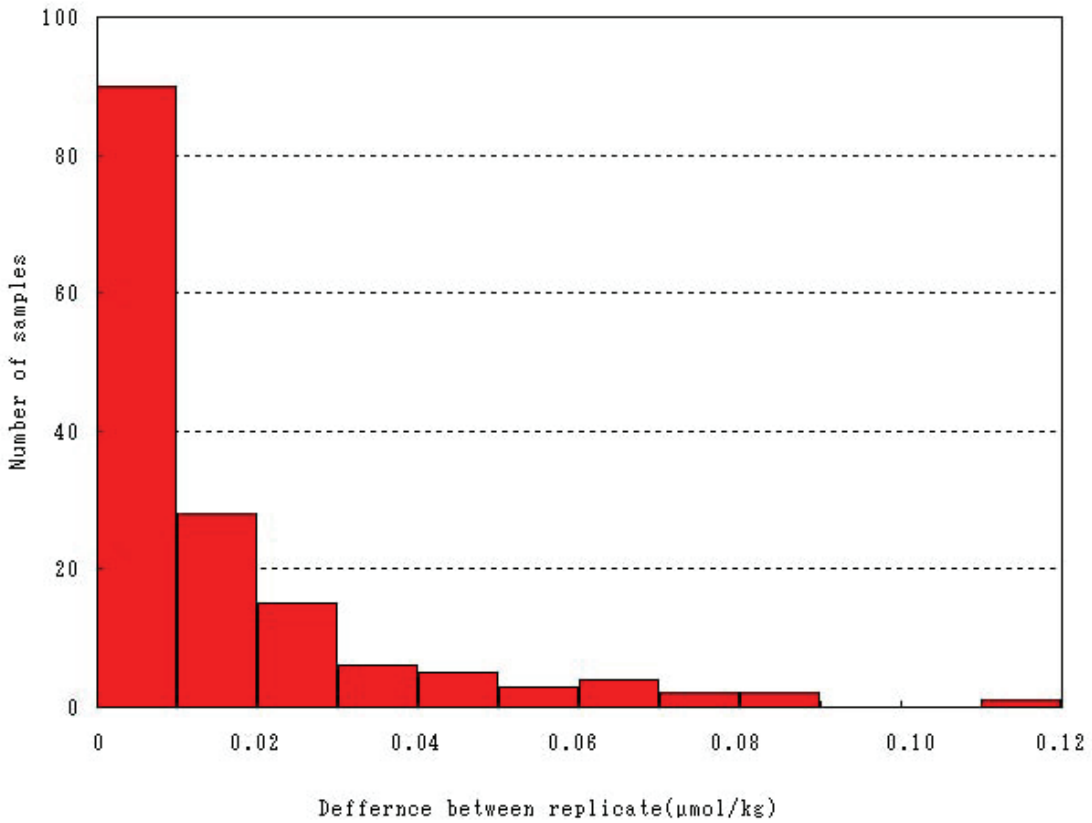


Fig. 4.3.1 Results of the replicate sample measurements

References:

Dickson, A. (1996) Dissolved Oxygen, in WHP Operations and Methods, Woods Hole, pp1-13.

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.

Emerson, S, S. Mecking and J.Abell (2001) The biological pump in the subtropical North Pacific Ocean: nutrient sources, redfield ratios, and recent changes. *Global Biogeochem. Cycles*, 15, 535-554.

Watanabe, Y. W., T. Ono, A. Shimamoto, T. Sugimoto, M. Wakita and S. Watanabe (2001) Probability of a reduction in the formation rate of subsurface water in the North Pacific during the 1980s and 1990s. *Geophys. Res. Letts*., 28, 3298-3292.

4.4 Nutrients

Nutrient analysis was performed on the BRAN+LUEBBE TRAACS 800 system. The laboratory temperature was maintained between 25 - 27 °C.

(1) Measured parameters

Nitrate + nitrite and nitrite are analyzed according to the modification method of Grasshoff (1970). The sample nitrate is reduced to nitrite in a cadmium tube inside of which is coated with metallic copper. The sample stream with its equivalent nitrite is treated with an acidic, sulfanilamide reagent and the nitrite forms nitrous acid, which reacts with the sulfanilamide to produce a diazonium ion. N1-Naphthylethylene-diamine added to the sample stream then couples with the diazonium ion to produce a red, azo dye. With reduction of the nitrate to nitrite, both nitrate and nitrite react and are measured; without reduction, only nitrite reacts. Thus, for the nitrite analysis, no reduction is performed and the alkaline buffer is not necessary. Nitrate is computed by difference. Absorbance of 550 nm by azo dye in analysis is measured using a 3 cm length cell for Nitrate and 5 cm length cell for Nitrite.

The silicate (Although silicic acid is correct, we use silicate because a term of silicate is widely used in oceanographic community) method is analogous to that described for phosphate. The method used is essentially that of Grasshoff et al. (1983), wherein silicomolybdic acid is first formed from the silicic acid in the sample and added molybdic acid; then the silicomolybdic acid is reduced to silicomolybdous acid, or "molybdenum blue," using ascorbic acid as the reductant. Absorbance of 630 nm by silicomolybdous acid in analysis is measured using a 3 cm length cell.

The phosphate analysis is a modification of the procedure of Murphy and Riley (1962). Molybdic acid is added to the seawater sample to form phosphomolybdic acid, which is in turn reduced to phosphomolybdous acid using ascorbic acid as the reductant. Absorbance of 880 nm by phosphomolybdous acid in analysis is measured using a 5 cm length cell.

Ammonia in seawater is mixed with an alkaline solution containing EDTA, ammonia as gas state is formed from seawater. The ammonia (gas) is absorbed in sulfuric acid solution by way of 0.5 µm pore size membrane filter (ADVANTEC PTFE) at the dialyzer attached to analytical system. The ammonia absorbed in acid solution is determined by coupling with phenol and hypochlorite solution to from an indophenol blue compound. Absorbance of 630 nm by indophenol blue compound in analysis is measured using a 3 cm length cell.

(2) Nutrients standard

Silicate standard solution, the silicate primary standard, was obtained from Merck, Ltd. This standard solution, traceable to SRM from NIST was 1000 mg per litter. Since this solution is alkaline solution of 0.5 M NaOH, an aliquot of 40ml solution were diluted to 500 ml together with an aliquot of 20 ml of 1M HCl. Primary standard for nitrate (KNO_3) and phosphate (KH_2PO_4) were obtained from Merck, Ltd. and nitrite ($NaNO_2$) and ammonia ($(NH_4)_2SO_4$) were obtained from Wako Pure Chemical Industries, Ltd. Detail information

about standard reagents in the previous cruises is shown in Table 4.4.1. The relative ratio between different types of standard reagent was evaluated based on the 6-9 measurements at the same concentration during a run. Summary of the ratios are shown in Table 4.4.2.

(3) Sampling procedures

Samples were drawn into virgin 10 ml polyacrylates vials that were rinsed three times before sampling without sample drawing tubes. Sets of 5 different concentrations for nitrate, nitrite, silicate, phosphate and 4 different concentrations for ammonia of the shipboard standards were analyzed at beginning and end of each group of analysis. The standard solutions of highest concentration were measured every 7 – 13 samples and were used to evaluate precision of nutrients analysis during the cruise. We also used three concentrations of reference material for nutrients in seawater, RMNS (KANSO Co., Ltd., lots AS, AT and AU), for all runs to secure comparability on nutrient analysis throughout the cruise.

(4) Low Nutrients Sea Water (LNSW)

Surface water having low nutrient concentration was taken and filtered using 0.45 µm pore size membrane filter. This water is stored in 20-liter cubitainer with paper box. The concentrations of nutrient of this water were measured carefully in April 2006.

(5) Precision

Analytical precisions were 0.07% (55 µM) for nitrate, 0.07% (1.2 µM) for nitrite, 0.07% (171 µM) for silicate, 0.09% (3.6 µM) for phosphate and 0.25% (4.0 µM) for ammonia in terms of median of precision, respectively.

Results of RMNS analysis are shown in Tables 4.4.3 - 4.4.5 for the station's comparability, and in Table 4.4.6 for the cruise's comparability.

Reference

Grasshoff, K. (1970) Technicon paper, 691-57.

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 chim. Acta 27, 31-36.

Table 4.4.1 Summary of standard reagents.

	NO_3		NO_2		SiO_2		PO_4		NH_4	
Cruise	Maker	Batch	Maker	Batch	Maker	Batch	Maker	Batch	Maker	Batch
M06-03	Merck	B267665016	Wako	KSF7907 KSE7907*	Merck	OC551722	Merck	B781508550	Wako	CKR2895
M05-04	Wako	KSL4956	Wako	KSF7907	Kanto Chemical	609F9157	Wako	KSK5677	Wako	CKR2895
MR04-04 MR05-01	Wako	KSL4956	Wako	KSF7907	Kanto Chemical	507F9205	Wako	KSK5677	---	---

* Stn.M06039_3, M06033, M06034, M06038 used

NO_3: Merck, Potassium Nitrate 99,995 Suprapur
Wako, Potassium Nitrate, Analytical Grade
NO_2: Wako, Sodium Nitrite, Analytical Grade
SiO_2: Merck, Silicon standard solution traceable to SRM from NIST, SiO2 in NaOH 0.5 mol/l 1000mg/l Si CertiPUR
Kanto Chemical, Silicon standard solution for ICP analysis, SiO2 in KOH 0.5 mol/l
PO_4: Merck, Potassoim Dihydrogen Phosphate Anhydrous 99,995 Suprapur
Wako, Potassoim Dihydrogen Phosphate Anhydrous, Analytical Grade
NH_4: Wako, Ammonium Sulfate , Analytical Grade

Table 4.4.2 The relative ratio between different types of standard reagent.

NO_3	Batch or Serial	factor	count
Merck	B267665016	1.003±0.001	9
Wako	KSL4956	1.002±0.001	9

	SiO_2	Batch or Serial	factor	count
M06-03	Merck	OC551722	1.001±0.001	9
M05-04	Kanto Chemical	609F9157	0.975±0.001	9

	SiO_2	Batch or Serial	factor	count
M05-04	Kanto Chemical	609F9157	0.999±0.001	9
M04-04, MR05-01	Kanto Chemical	507F9205	1.002±0.001	9

PO_4	Batch or Serial	factor	count
Merck	B781508550	1.002±0.001	6
Wako	KSK5677	1.002±0.001	9

Table 4.4.3 Results of RMNS Lot.AS analysis in MR06-03 cruise.

μmol/kg

	serial	Stn.	NO_3	NO_2	SiO_2	PO_4	NH_4
RM-AS	461	M06001	0.09	0.01	1.69	0.065	---
RM-AS	322	M06011	0.08	0.02	1.69	0.060	---
RM-AS	322	M06012	0.09	0.02	1.68	0.055	---
RM-AS	468	M06013	0.08	0.01	1.71	0.059	---
RM-AS	468	M06014	0.09	0.01	1.68	0.074	---
RM-AS	468	M06015	---	0.02	1.56	0.065	---
RM-AS	777	M06015	0.07	0.01	---	---	---
RM-AS	777	M06002_3	0.10	0.01	1.68	0.071	0.89
RM-AS	777	M06002_4	0.09	0.01	1.70	0.073	---
RM-AS	378	M06016	0.13	0.01	1.78	0.071	---
RM-AS	378	M06017	0.12	0.01	1.68	0.076	---
RM-AS	270	M06018	0.09	0.01	1.68	0.080	---
RM-AS	270	M06003	0.08	0.01	1.69	0.081	---
RM-AS	270	M06004	0.09	0.02	1.67	0.079	---
RM-AS	779	M06010	0.11	0.02	1.78	0.079	---
RM-AS	779	M06009	0.07	0.02	1.56	0.059	---
RM-AS	383	M06008	0.10	0.02	1.67	0.064	---
RM-AS	505	M06007	0.10	0.02	1.71	0.057	---
RM-AS	505	M06006	0.11	0.02	1.56	0.064	---
RM-AS	866	M06005	0.11	0.01	1.64	0.056	0.80
RM-AS	22	M06019	0.09	0.01	1.62	0.065	---
RM-AS	125	M06020_2	0.07	0.02	1.57	0.063	0.84
RM-AS	747	M06020_8	0.09	0.01	1.65	0.071	0.87
RM-AS	747	RAS1	0.09	0.02	1.61	0.064	---
RM-AS	500	M06021	0.10	0.01	1.61	0.070	---
RM-AS	203	M06022	0.09	0.02	1.63	0.071	---
RM-AS	203	M06023	0.10	0.02	1.54	0.060	---
RM-AS	587	M06024	0.11	0.01	1.68	0.061	---
RM-AS	587	M06025	0.10	0.01	1.62	0.064	---
RM-AS	939	M06026_1	0.09	0.01	1.64	0.067	0.86
RM-AS	661	M06026_9	0.10	0.02	1.67	0.072	0.89
RM-AS	466	M06031	0.07	0.02	1.69	0.066	---
RM-AS	466	M06030	0.10	0.01	1.61	0.070	---
RM-AS	10	M06029	0.09	0.01	1.55	0.057	---
RM-AS	10	M06028	0.09	0.02	1.64	0.069	---
RM-AS	10	M06027	0.11	0.02	1.77	0.069	---
RM-AS	966	M06032_6	0.11	0.01	1.70	0.077	0.84
RM-AS	603	M06032_9	0.13	0.01	1.71	0.063	0.85
RM-AS	792	M06037	0.09	0.01	1.62	0.056	---
RM-AS	792	M06036	0.10	0.01	1.62	0.052	---
RM-AS	792	M06035	0.11	0.02	1.66	0.056	---
RM-AS	868	M06039_1	0.11	0.01	1.83	0.060	0.82
RM-AS	791	M06039_3	0.08	0.02	1.52	0.058	0.83
RM-AS	103	M06033	0.11	0.02	1.69	0.080	---
RM-AS	103	M06034	0.09	0.02	1.58	0.071	---
RM-AS	996	RAS2	0.10	0.02	1.67	0.068	---
RM-AS	996	M06038	0.10	0.01	1.57	0.069	---

Table 4.4.4 Results of RMNS Lot.AT analysis in MR06-03 cruise.

μmol/kg

	serial	Stn.	NO_3	NO_2	SiO_2	PO_4	NH_4
RM-AT	125	M06001	7.47	0.02	17.93	0.573	---
RM-AT	981	M06011	7.51	0.02	17.95	0.571	---
RM-AT	981	M06012	7.47	0.02	17.97	0.563	---
RM-AT	406	M06013	7.53	0.02	17.94	0.568	---
RM-AT	406	M06014	7.47	0.02	17.99	0.584	---
RM-AT	406	M06015	---	0.02	17.88	0.576	---
RM-AT	523	M06015	7.39	0.02	---	---	---
RM-AT	523	M06002_3	7.46	0.02	17.98	0.582	0.72
RM-AT	523	M06002_4	7.45	0.02	18.04	0.577	---
RM-AT	298	M06016	7.52	0.02	18.08	0.581	---
RM-AT	298	M06017	7.50	0.02	18.00	0.589	---
RM-AT	287	M06018	7.45	0.02	17.92	0.584	---
RM-AT	287	M06003	7.56	0.02	18.01	0.595	---
RM-AT	287	M06004	7.52	0.02	17.93	0.589	---
RM-AT	884	M06010	7.50	0.02	17.98	0.581	---
RM-AT	884	M06009	7.44	0.02	17.92	0.571	---
RM-AT	209	M06008	7.47	0.02	17.91	0.579	---
RM-AT	209	M06007	7.47	0.02	17.89	0.574	---
RM-AT	209	M06006	7.48	0.02	17.82	0.568	---
RM-AT	600	M06005	7.43	0.02	17.95	0.559	---
RM-AT	600	M06019	7.48	0.02	17.98	0.566	0.72
RM-AT	66	M06020_2	7.49	0.02	17.94	0.577	0.77
RM-AT	873	M06020_8	7.45	0.02	18.03	0.578	0.73
RM-AT	873	RAS1	7.47	0.02	17.98	0.573	---
RM-AT	724	M06021	7.48	0.01	17.97	0.587	---
RM-AT	766	M06022	7.46	0.02	17.93	0.586	---
RM-AT	766	M06023	7.45	0.02	17.84	0.571	---
RM-AT	598	M06024	7.51	0.02	17.92	0.570	---
RM-AT	598	M06025	7.47	0.02	18.01	0.572	---
RM-AT	779	M06026_1	7.46	0.01	17.99	0.576	0.73
RM-AT	813	M06026_9	7.45	0.02	18.01	0.582	0.76
RM-AT	937	M06031	7.44	0.02	18.04	0.578	---
RM-AT	937	M06030	7.52	0.02	17.93	0.580	---
RM-AT	417	M06029	7.48	0.01	17.87	0.568	---
RM-AT	417	M06028	7.49	0.02	17.88	0.572	---
RM-AT	417	M06027	7.51	0.02	18.09	0.572	---
RM-AT	973	M06032_6	7.50	0.02	18.02	0.583	0.76
RM-AT	801	M06032_9	7.55	0.02	18.04	0.570	0.77
RM-AT	845	M06037	7.45	0.02	17.97	0.570	---
RM-AT	845	M06036	7.46	0.02	17.91	0.563	---
RM-AT	845	M06035	7.49	0.02	17.89	0.565	---
RM-AT	59	M06039_1	7.42	0.02	17.98	0.576	0.76
RM-AT	651	M06039_3	7.47	0.02	17.94	0.569	0.76
RM-AT	888	M06033	7.47	0.03	17.99	0.581	---
RM-AT	888	M06034	7.50	0.02	17.96	0.580	---
RM-AT	207	RAS2	7.49	0.02	17.99	0.577	---
RM-AT	207	M06038	7.48	0.02	17.87	0.579	---

Table 4.4.5 Results of RMNS Lot.AU analysis in MR06-03 cruise.

μmol/kg

	serial	Stn.	NO_3	NO_2	SiO_2	PO_4	NH_4
RM-AU	6	M06001	29.86	0.01	66.39	2.179	---
RM-AU	450	M06011	30.07	0.02	66.59	2.162	---
RM-AU	6	M06011	30.02	0.02	66.51	2.163	---
RM-AU	450	M06012	29.93	0.02	66.39	2.162	---
RM-AU	6	M06012	29.90	0.02	66.44	2.169	---
RM-AU	458	M06013	30.01	0.02	66.55	2.173	---
RM-AU	450	M06013	30.03	0.01	66.48	2.175	---
RM-AU	458	M06014	29.85	0.01	66.48	2.173	---
RM-AU	450	M06014	29.81	0.01	66.54	2.177	---
RM-AU	458	M06015	---	0.01	66.41	2.173	---
RM-AU	450	M06015	---	0.01	66.52	2.180	---
RM-AU	604	M06015	29.82	0.01	---	---	---
RM-AU	458	M06015	29.81	0.01	---	---	---
RM-AU	604	M06002_3	29.82	0.01	66.52	2.169	0.58
RM-AU	458	M06002_3	29.84	0.01	66.46	2.179	---
RM-AU	604	M06002_4	29.86	0.01	66.57	2.170	---
RM-AU	458	M06002_4	29.86	0.01	66.50	2.179	---
RM-AU	988	M06016	29.91	0.01	66.67	2.171	---
RM-AU	604	M06016	29.95	0.01	66.67	2.178	---
RM-AU	988	M06017	29.97	0.01	66.62	2.181	---
RM-AU	604	M06017	30.03	0.01	66.65	2.184	---
RM-AU	495	M06018	29.95	0.01	66.36	2.179	---
RM-AU	988	M06018	29.90	0.02	66.36	2.183	---
RM-AU	495	M06003	30.05	0.01	66.70	2.187	---
RM-AU	988	M06003	30.07	0.01	66.77	2.186	---
RM-AU	495	M06004	29.89	0.01	66.44	2.185	---
RM-AU	988	M06004	30.03	0.02	66.44	2.185	---
RM-AU	288	M06010	29.84	0.01	66.49	2.165	---
RM-AU	495	M06010	29.86	0.02	66.51	2.170	---
RM-AU	288	M06009	29.85	0.02	66.53	2.163	---
RM-AU	495	M06009	29.83	0.02	66.58	2.169	---
RM-AU	505	M06008	29.86	0.02	66.41	2.167	---
RM-AU	288	M06008	29.90	0.02	66.41	2.170	---
RM-AU	505	M06007	29.90	0.02	66.37	2.171	---
RM-AU	288	M06007	29.86	0.02	66.28	2.173	---
RM-AU	505	M06006	30.00	0.02	66.26	2.160	---
RM-AU	288	M06006	30.00	0.02	66.33	2.160	---
RM-AU	866	M06005	29.99	0.02	66.50	2.160	---
RM-AU	505	M06005	29.97	0.01	66.55	2.163	---
RM-AU	866	M06019	29.91	0.02	66.66	2.158	0.55
RM-AU	505	M06019	29.83	0.02	66.68	2.164	0.55
RM-AU	119	M06020_2	29.93	0.02	66.60	2.179	0.55
RM-AU	50	M06020_2	29.97	0.02	66.54	2.185	---
RM-AU	514	M06020_8	29.85	0.01	66.74	2.175	0.57
RM-AU	119	M06020_8	29.88	0.02	66.77	2.185	---
RM-AU	514	RAS1	29.93	0.02	66.63	2.181	---
RM-AU	119	RAS1	29.93	0.02	66.80	2.182	---

RM-AU	998	M06021	29.86	0.00	66.49	2.186	---
RM-AU	514	M06021	29.94	0.01	66.54	2.193	---
RM-AU	35	M06022	29.91	0.01	66.44	2.181	---
RM-AU	998	M06022	29.84	0.01	66.40	2.185	---
RM-AU	35	M06023	29.91	0.02	66.38	2.172	---
RM-AU	998	M06023	29.81	0.02	66.54	2.177	---
RM-AU	672	M06024	30.00	0.01	66.49	2.169	---
RM-AU	35	M06024	30.03	0.01	66.53	2.170	---
RM-AU	672	M06025	29.85	0.01	66.56	2.174	---
RM-AU	35	M06025	29.91	0.01	66.64	2.176	---
RM-AU	43	M06026_1	29.85	0.02	66.58	2.19	0.55
RM-AU	672	M06026_1	29.87	0.01	66.70	2.192	---
RM-AU	650	M06026_9	29.83	0.02	66.53	2.177	0.55
RM-AU	43	M06026_9	29.86	0.02	66.62	2.181	---
RM-AU	525	M06031	29.91	0.01	66.61	2.172	---
RM-AU	650	M06031	29.93	0.01	66.69	2.177	---
RM-AU	525	M06030	29.95	0.01	66.48	2.180	---
RM-AU	650	M06030	30.04	0.01	66.51	2.181	---
RM-AU	110	M06029	29.87	0.01	66.47	2.181	---
RM-AU	525	M06029	29.86	0.01	66.54	2.174	---
RM-AU	110	M06028	29.83	0.02	66.36	2.176	---
RM-AU	525	M06028	29.89	0.02	66.48	2.179	---
RM-AU	110	M06027	29.88	0.02	66.69	2.175	---
RM-AU	525	M06027	29.87	0.02	66.63	2.171	---
RM-AU	986	M06032_6	29.97	0.01	66.57	2.176	0.56
RM-AU	272	M06032_6	29.99	0.01	66.65	2.187	---
RM-AU	23	M06032_9	29.86	0.01	66.61	2.167	0.56
RM-AU	986	M06032_9	29.88	0.01	66.70	2.165	---
RM-AU	430	M06037	29.85	0.01	66.61	2.171	---
RM-AU	23	M06037	29.86	0.02	66.62	2.175	---
RM-AU	430	M06036	29.90	0.01	66.48	2.165	---
RM-AU	23	M06036	29.88	0.01	66.44	2.167	---
RM-AU	430	M06035	29.94	0.02	66.55	2.169	---
RM-AU	23	M06035	29.91	0.02	66.54	2.168	---
RM-AU	626	M06039_1	29.79	0.01	66.55	2.180	0.56
RM-AU	430	M06039_1	29.81	0.01	66.57	2.187	---
RM-AU	682	M06039_3	29.84	0.01	66.66	2.160	0.58
RM-AU	626	M06039_3	29.91	0.01	66.90	2.165	---
RM-AU	277	M06033	29.92	0.02	66.56	2.167	---
RM-AU	682	M06033	29.95	0.02	66.49	2.169	---
RM-AU	277	M06034	29.93	0.02	66.45	2.165	---
RM-AU	682	M06034	29.91	0.02	66.46	2.169	---
RM-AU	863	RAS2	29.92	0.02	66.46	2.176	---
RM-AU	277	RAS2	29.94	0.02	66.53	2.179	---
RM-AU	863	M06038	29.89	0.01	66.53	2.170	---
RM-AU	277	M06038	29.90	0.01	66.52	2.167	---

Table 4.4.6 Summary of RMNS Lot.AS, AT, AU analysis in MR04-04, MR05-05, MR05-04, and MR06-03 cruise.

μmol/kg

RM-AS		NO_3	NO_2	SiO_2	PO_4	NH_4
MR06-03	median	0.10	0.01	1.67	0.065	0.84
	stdev	0.01	0.00	0.07	0.008	0.03
	n=	49	50	49	49	12
MR05-04	median	0.14	0.01	1.68	0.078	0.82
	stdev	0.02	0.00	0.04	0.011	0.02
	n=	15	15	16	15	14
MR05-01	median	0.09	0.01	1.65	0.077	ND
	stdev	0.03	0.00	0.06	0.005	ND
	n=	16	16	16	16	ND
MR04-04	median	0.11	0.01	1.63	0.072	ND
	stdev	0.02	0.00	0.10	0.014	ND
	n=	41	41	42	41	ND

μmol/kg

RM-AT		NO_3	NO_2	SiO_2	PO_4	NH_4
MR06-03	median	7.47	0.02	17.97	0.576	0.76
	stdev	0.03	0.00	0.06	0.008	0.02
	n=	49	50	49	49	12
MR05-04	median	7.49	0.02	18.40	0.591	0.71
	stdev	0.03	0.00	0.05	0.011	0.02
	n=	15	15	16	15	14
MR05-01	median	7.49	0.02	18.31	0.587	ND
	stdev	0.06	0.00	0.07	0.005	ND
	n=	16	16	16	16	ND
MR04-04	median	7.47	0.01	18.32	0.582	ND
	stdev	0.04	0.00	0.10	0.012	ND
	n=	41	41	42	41	ND

μmol/kg

RM-AU		NO_3	NO_2	SiO_2	PO_4	NH_4
MR06-03	median	29.90	0.01	66.53	2.174	0.56
	stdev	0.07	0.00	0.12	0.008	0.01
	n=	94	96	94	94	12
MR05-04	median	29.99	0.01	68.25	2.186	0.52
	stdev	0.06	0.00	0.15	0.011	0.02
	n=	28	28	30	28	13
MR05-01	median	29.97	0.01	67.92	2.191	ND
	stdev	0.09	0.00	0.21	0.007	ND
	n=	28	28	28	28	ND
MR04-04	median	29.94	0.01	68.00	2.176	ND
	stdev	0.08	0.00	0.17	0.012	ND
	n=	102	102	104	102	ND

4.5 Dissolved inorganic carbon (DIC)

(1) Seawater sampling

Seawater samples were collected by 12L Niskin bottles at 38 stations during MR06-03. Seawater was sampled in a 300ml glass bottle that was previously soaked in 5% non-phosphoric acid detergent (pH13) solution at least 3 hours and was cleaned by fresh water for 5 times and Milli-Q deionized water for 3 times. A sampling tube was connected to the Niskin bottle when the sampling was carried out. The glass bottles were filled from the bottom, without rinsing, and were overflowed for 20 seconds with care not to leave any bubbles in the bottle. After collecting the samples on the deck, the glass bottles were transferred to the lab to be measured. Prior to the analysis, 3ml of the sample (1% of the bottle volume) was removed from the glass bottle in order to make a headspace. The samples were then poisoned with 100μl of over saturated solution of mercury chloride within one hour from the sampling point. After poisoning, the samples were sealed using grease (Apiezon M grease) and a stopper-clip. The samples were stored in a refrigerator at approximately 5 °C until analyzed.

(2) Seawater analysis

Measurements of DIC was made with two total CO_2 measuring systems (systems A and B and C; Nippon ANS, Inc.), which are slightly different from each other. The systems comprise of a sea water dispensing system, a CO_2 extraction system and a coulometer (Model 5012, UIC Inc.).

The seawater dispensing system has an auto-sampler (6 ports), which takes seawater into a glass bottle and dispenses the seawater to a pipette of nominal 20 ml (system A and C) and 16ml (system B) volume by PC control. The pipette was kept at 20 °C by a water jacket, in which water from a water bath set at 20 °C is circulated.

CO_2 dissolved in a seawater sample is extracted in a stripping chamber of the CO_2 extraction system by adding phosphoric acid (10% v/v). The stripping chamber is made approx. 25 cm long and has a fine frit at the bottom. To degas CO_2 as quickly as possible, a heating wire kept at 40 °C (system A and B) is rolled from the bottom to a 1/3 height of the stripping chamber. The acid is added to the stripping chamber from the bottom of the chamber by pressurizing an acid bottle for a given time to push out the right amount of acid. The pressurizing is made with nitrogen gas (99.9999 %). After the acid is transferred to the stripping chamber, a seawater sample kept in a pipette is introduced to the stripping chamber by the same method as that for adding an acid. The seawater reacted with phosphoric acid is stripped of CO_2 by bubbling the nitrogen gas through a fine frit at the bottom of the stripping chamber. The CO_2 stripped in the chamber is carried by the nitrogen gas (flow rates of 140ml min^{-1}) to the coulometer through a dehydrating module. For system A, the module consists of two electric dehumidifiers (kept at 1 - 2 °C) and a chemical desiccant ($Mg(ClO_4)_2$). For system B, it consists of three electric dehumidifiers with a chemical desiccant. For system C, the module consists of two electric dehumidifiers (kept at 1 - 2 °C).

The measurement sequence such as 2 % CO_2 gas in a nitrogen base, system blank (phosphoric acid blank), and seawater samples (6) was programmed to repeat. The measurement of 2 % CO_2 gas was made to monitor response of coulometer solutions (from UIC, Inc.).

(5) Precision

During the cruise, 1529 samples were analyzed for DIC. A replicate analysis was made on every forth seawater sample and the difference between each pair of analyses was plotted on a range control chart (see Fig. 4.5.1). The average of the differences was 1.3 μmol/kg (n=140). The standard deviation was 1.2 μmol/kg, which indicates that the analysis was accurate enough according to DOE (1994).

Reference

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 & C. Goyet, Eds., ORNS/CDIAC-74

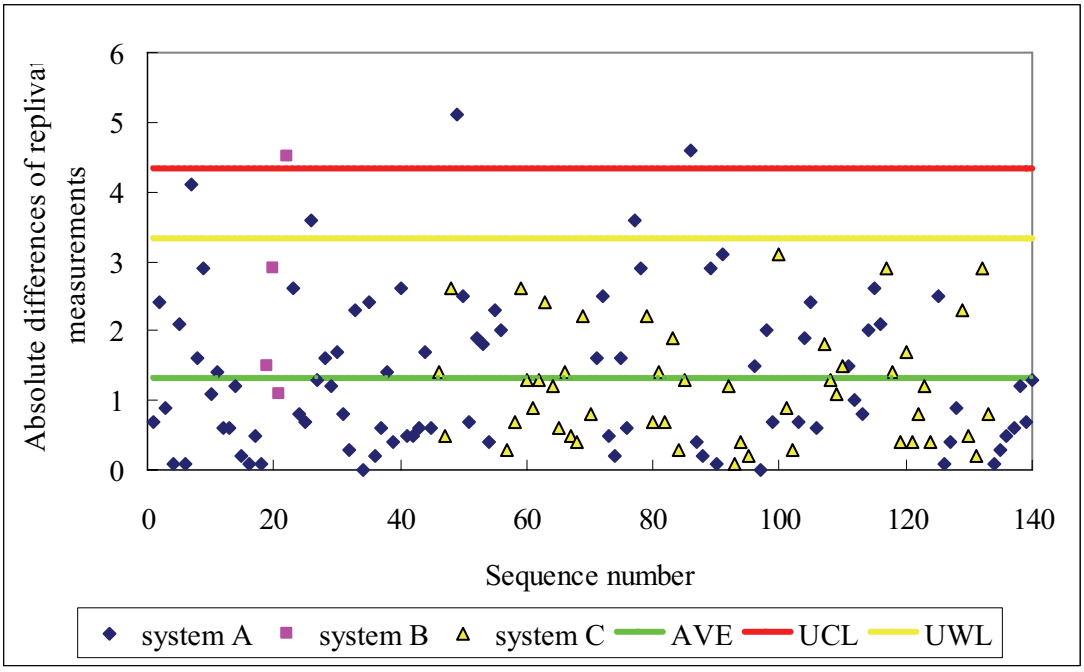


Fig. 4.5.1 Range control chart of the absolute differences of replicate measurements carried out in the analysis of DIC during MR06-03 cruise.

4.6 Total alkalinity (TALK)

(1) Seawater sampling

Seawater samples were collected by 12L Niskin bottles at 39 stations. Seawater was sampled in a 125 ml glass bottle (SCHOTT DURAN) that was previously soaked in 5% non-phosphoric acid detergent (pH13) solution for at least 2 hours and was cleaned by fresh water and Milli-Q deionized water for 3 times each. A sampling tube was connected to the Niskin bottle when the sampling was carried out. The glass bottles were filled from the bottom, without rinsing, and were overflowed for 10 seconds with care not to leave any bubbles in the bottle. After collecting the samples on the deck, the glass bottles were removed to the lab to be analyzed. The bottles were put in the water bath kept about 25℃ before the measurement.

(2) Seawater analysis

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

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

Calibration of the acid titrant was made by measuring TA of 6 solutions of Na_2CO_3 in 0.7 M NaCl solutions. The computed TAs were approx. 0, 500, 1000, 1500, 2000 and 2500 μmol kg^{-1}. The measured values of TA (calculated by assuming 0.05 M) should be a linear function of the TA contributed by the Na_2CO_3. The line was fitted by the method of least squares. Theoretically, the slope should be unity. If the measured slope is not equal to one, the acid normality should be adjusted by dividing initial normality by the slope, and the whole set of calculations is repeated until the slope = 1

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

(3) Precision

A few replicate samples were taken on every station and the difference between each pair of analyses was plotted on a range control chart (see Fig. 4.6.1). The average of the difference was 1.3 μmol/kg (n= 133). The standard deviation was 1.1 μmol/kg, which indicates that the analysis was accurate enough according to DOE (1994).

Reference

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 & C. Goyet, Eds., ORNS/CDIAC-74

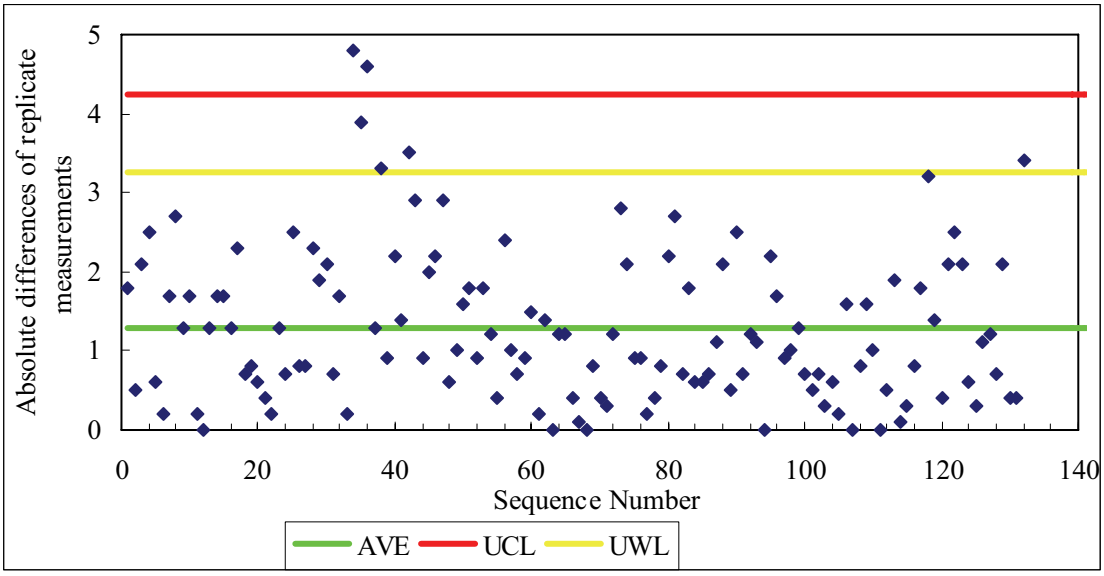


Fig. 4.6.1 Range control chart of the absolute differences of replicate measurements carried out in the analysis of TA during MR06-03 cruise.

5. Correction of data between cruises

Though sampling technique and analytical method between cruises were identical, there should be differences in condition of analytical instruments and quality of standard solution and so on between cruises. In order to compare data obtained from different cruises and detect a tiny, but crucial changes by natural or anthropogenic forces, data quality should be unified. Assuming no change in chemical composition in the deep seawater, we corrected data collected for the last 5 years as follows:

(1) The North Pacific Deep Water (NPDW) was defined as seawater with density (sigma theta) of between 27.69 and 27.77 because chlorofluorocarbon (CFC) 11 and 12 were not detected below layers with density > 27.69 (Watanabe et al., Geophys. Res. Letts. 28, 3289-3292, 2001) and seawater with density > 27.7 were defined as "bottom water" with different properties from those of the NPDW (Johnson et al., J. Mar. Res., 52, 177–196, 1994)

(2) Standard isopychnal layers (σ_θ = 27.69, 27.70, 27.71, 27.72, 27.73, 27.74, 27.75, 27.76, 27.77) were selected and averages of chemical components along these layers were calculated with data obtained from MR04-04, MR04-06, MR05-01, MR05-04, and MR06-03 cruise. In the case of total alkalinity, values obtained during MR06-03 cruise were decided as a standard value.

(3) Mean deviations from the above standard values at respective layers were estimated for respective cruises and data were corrected assuming that estimated deviation were systematic error attributable to condition of analytical instruments and quality of standard solution.Results of data correction are summarized in Table 5.1.

Table 5.1 Factors (for DO, silicate, and nitrate) and values (for DIC and TA) of the corrections

No.	Cruise name	DO µmol/kg	Silicate µmol/kg	Nitrate µmol/kg	Phosphate µmol/kg	DIC µmol/kg	TA µmol/kg
1	MR01-K03	—	0.977	—	—	—	—
2	MR01-K04	—	1.017	1.020	0.980	3.1	—
3	MR02-K05	—	0.994	—	1.027	—	—
4	MR03-K01	—	0.987**	—	1.020	—	—
5	NT03-07	0.926	1.026	1.021	1.023	4.5	-7.3
6	KR03-11	—*	—*	—*	—*	—*	—*
7	MR04-02	—	0.987**	—	1.014	—	7.9
8	NT04-07	—	—	1.015	1.018	—	no data
9	MR04-04	—	0.975**	—	—	—	-5.7
10	MR04-06	—	0.975**	—	—	—	no data
11	MR05-01	—	0.975**	—	—	—	-4.8
12	MR05-04	—	0.975**	—	—	—	3.9
13	MR06-03(1-1)	—	—	—	—	—	—
14	MR06-03(1-2)	—	—	—	—	—	—
15	MR06-03(2)	—	—	—	—	—	—
16	MR06-03(3-1)	—	—	—	—	—	—
17	MR06-03(3-2)	—	—	—	—	—	—
18	MR06-03(4)	—	—	—	—	—	—
18	MR06-03(5-1)	—	—	—	—	—	—
19	MR06-03(5-2)	—	—	—	—	—	—
20	MR06-03(6-1)	—	—	—	—	—	—
21	MR06-03(6-2)	—	—	—	—	—	—

— : not corrected
—* : not corrected because of no deep data
** : to see text

It was noted that silicate data in R/V MIRAI cruises, MR03-K01, MR04-02, MR04-04, MR04-06, MR05-01 and MR05-04 was measured based on standard solution made by Kanto Kagaku Ltd. Deviation between “batch of standard solution” was found to be larger than requested precision. Standard solution made by Merck Ltd. was used in 2006 cruise. Silicate data before 2006 were corrected to Merck silicate standard solution volume.

Data obtained from cruises and corrected based on standard values for respective chemical composition were electrically compileds as an excel file “K2 data.xls”. Data for respective cruises are filed as “book style”. Example is as follows.

Ship name	Mirai
Cruise name	MR01-K03
Date	2001/6/10
Station	K2
Latitude	47.0 °N
Longitude	160.0 °E
Depth	5188.0 m

QF (Quality Flag)
0 : Good
1 : Unknown
2 : Data corrected systematic error (cf. Table 5.1 Factors (for DO, silicate, and nitrate) and values (for DIC and TA) of the corrections.)
4 : Questionable
8 : Bad
9 : No data

CTD data						Bottle data																	
Pressure db	Depth m	Temp. °C	θ °C	Salinity PSS-78	sigma-θ	Salinity PSS-78	QF	DO µmol/kg	QF	Silicate µmol/kg	QF	Nitrate µmol/kg	QF	Nitrite µmol/kg	QF	Phosphate µmol/kg	QF	DIC µmol/kg	QF	TA µmol/kg	QF	Ammonium µmol/kg	QF
10.1	10.0	3.2274	3.2268	32.9980	26.264	32.9946	0	374.3	0	16.9	2	13.7	0	0.18	0	1.21	0	2052.4	0	2241.4	0	0.28	0
19.7	19.5	2.9648	2.9637	32.9969	26.290	32.9972	0	375.3	0	15.8	2	13.9	0	0.17	0	1.21	0	2058.7	0	2240.1	0	0.30	0
29.5	29.3	2.6493	2.6477	33.0032	26.320	33.0015	0	360.9	0	18.7	2	15.3	0	0.18	0	1.32	0	2068.3	0	2241.4	0	0.56	0
51.1	50.6	1.5591	1.5568	33.0499	26.442	33.0508	0	345.2	0	27.8	2	20.4	0	0.25	0	1.79	0	2109.5	0	2238.3	0	0.69	0
76.2	75.5	0.7406	0.7376	33.1335	26.564	33.1382	0	336.7	0	44.2	2	26.5	0	0.35	0	2.06	0	2138.3	0	2239.5	0	0.31	0
101.1	100.2	0.6129	0.6090	33.1707	26.604	33.1788	0	329.1	0	46.3	2	27.5	0	0.20	0	2.10	0	2147.1	0	2239.6	0	0.00	0
125.9	124.8	1.1431	1.1376	33.3202	26.668	33.2979	0	276.6	0	53.7	2	30.6	0	0.05	0	2.29	0	2179.9	0	2249.8	0	-0.02	0
151.2	149.9	2.8092	2.8004	33.6299	26.831	33.6576	0	117.7	0	77.4	2	38.7	0	0.05	0	2.79	0	2270.1	0	2278.5	0	0.00	0
203.7	201.9	3.4963	3.4832	33.8565	26.925	33.8531	0	51.9	0	90.3	2	42.6	0	0.02	0	3.06	0	2318.2	0	2295.0	0	0.02	0
302.8	300.0	3.5181	3.4982	34.0292	27.061	34.0257	0	21.9	0	104.0	2	44.3	0	0.01	0	3.14	0	2348.1	0	2316.1	0	0.02	0
403.6	399.8	3.4025	3.3760	34.1421	27.164	34.1397	0	17.7	0	114.6	2	44.2	0	0.01	0	3.17	0	2357.3	0	2333.3	0	0.03	0
504.3	499.5	3.2388	3.2058	34.2274	27.247	34.2242	0	15.3	0	124.1	2	44.2	0	0.01	0	3.18	0	2369.1	0	2346.8	0	0.03	0
756.9	749.3	2.7983	2.7497	34.3683	27.398	34.3623	0	17.8	0	141.8	2	44.0	0	0.02	0	3.14	0	2383.3	0	2369.5	0	0.04	0
1010.5	999.7	2.4654	2.4010	34.4585	27.501	34.4536	0	27.9	0	152.2	2	43.5	0	0.02	0	3.12	0	2387.9	0	2390.5	0	0.03	0
1264.0	1249.7	2.1968	2.1162	34.5210	27.575	34.5170	0	39.2	0	160.1	2	42.9	0	0.01	0	3.07	0	2390.8	0	2397.7	0		9
1517.9	1499.8	2.0207	1.9228	34.5660	27.625	34.5602	0	53.8	0	162.3	2	42.1	0	0.01	0	3.01	0	2386.3	0	2405.8	0		9
2026.5	2000.0	1.7599	1.6250	34.6225	27.695	34.6185	0	83.9	0	163.8	2	40.5	0	0.01	0	2.88	0	2371.2	0	2414.8	0		9
2535.7	2499.6	1.6001	1.4241	34.6550	27.734	34.6490	0	111.9	0	158.9	2	38.9	0	0.02	0	2.76	0	2355.6	0	2416.7	0		9
3046.6	2999.7	1.5042	1.2829	34.6741	27.758	34.6660	0	133.2	0	152.4	2	37.6	0	0.01	0	2.64	0	2340.6	0	2415.7	0		9
3558.5	3499.5	1.4612	1.1900	34.6845	27.774	34.6779	0	145.6	0	150.3	2	37.0	0	0.01	0	2.59	0	2333.6	0	2414.9	0		9
4071.9	3999.8	1.4482	1.1228	34.6914	27.784	34.6848	0	154.5	0	147.9	2	36.3	0	0.01	0	2.53	0	2324.7	0	2412.8	0		9
4585.4	4498.9	1.4709	1.0869	34.6952	27.790	34.6899	0	159.4	0	147.1	2	36.0	0	0.01	0	2.49	0	2322.7	0	2412.8	0		9
5101.6	4999.7	1.5195	1.0721	34.6972	27.791	34.6893	0	161.6	0	145.9	2	36.0	0	0.01	0	2.49	0	2321.1	0	2416.0	4		9
5260.3	5153.3	1.5374	1.0697	34.6974	27.792	34.6908	0	161.5	0		8	35.7	0	0.01	0		8	2322.5	0	2413.5	0		9

6. Future update of data and contact persons

We will continue to correction and update K2 time-series observation data. These update data will be opened on the MIO web site in future.

Contact Persons

Shuichi Watanabe (E-mail: swata@jamstec.go.jp)

Makio Honda (E-mail: hondam@jamstec.go.jp)

Masahide Wakita (E-mail: mwakita@jamstec.go.jp)

Mutsu Institute for Oceanography

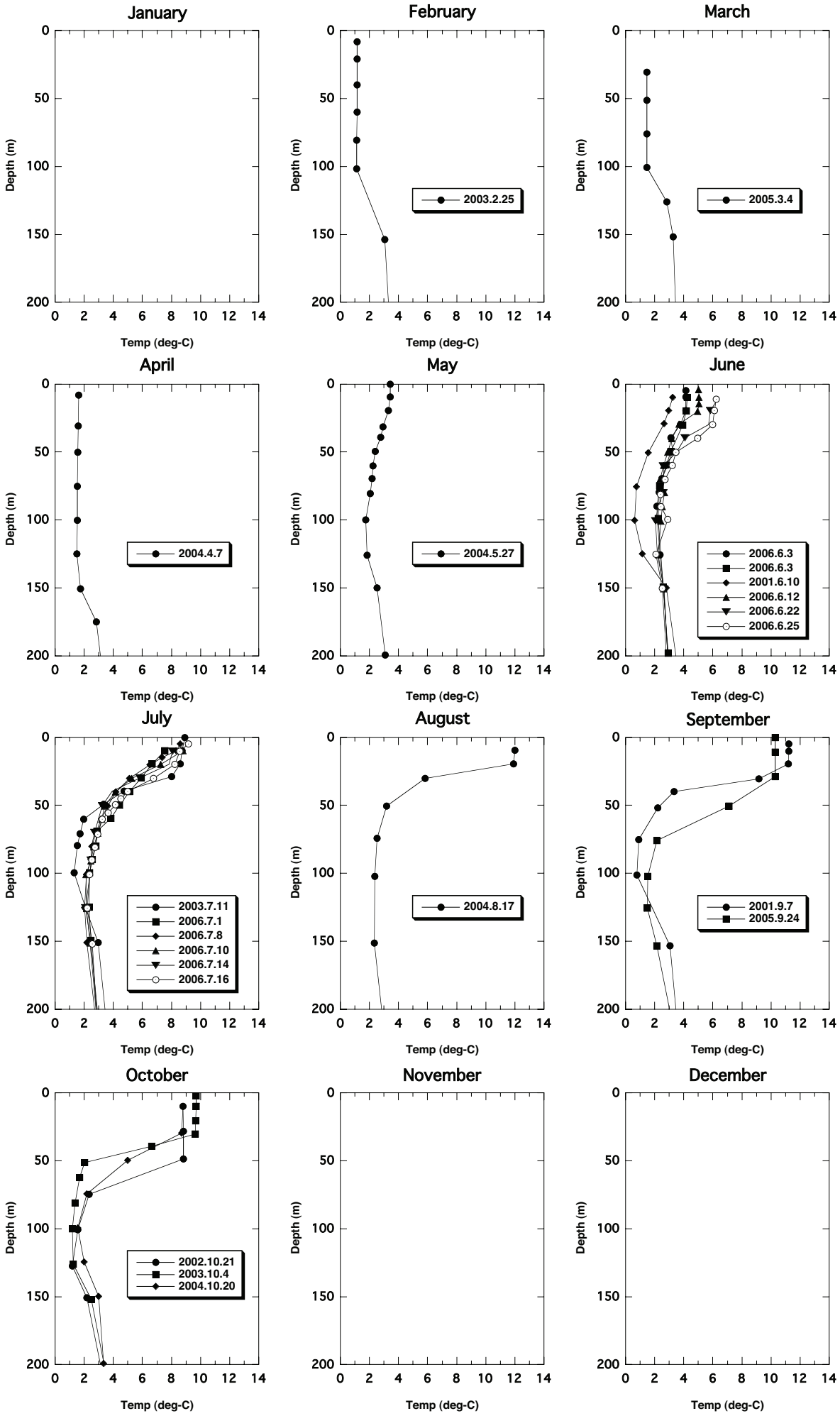
Japan Agency for Marine-Earth Science and Technology

690 Kitasekine, Sekine, Mutsu-city, Aomori 035-0022

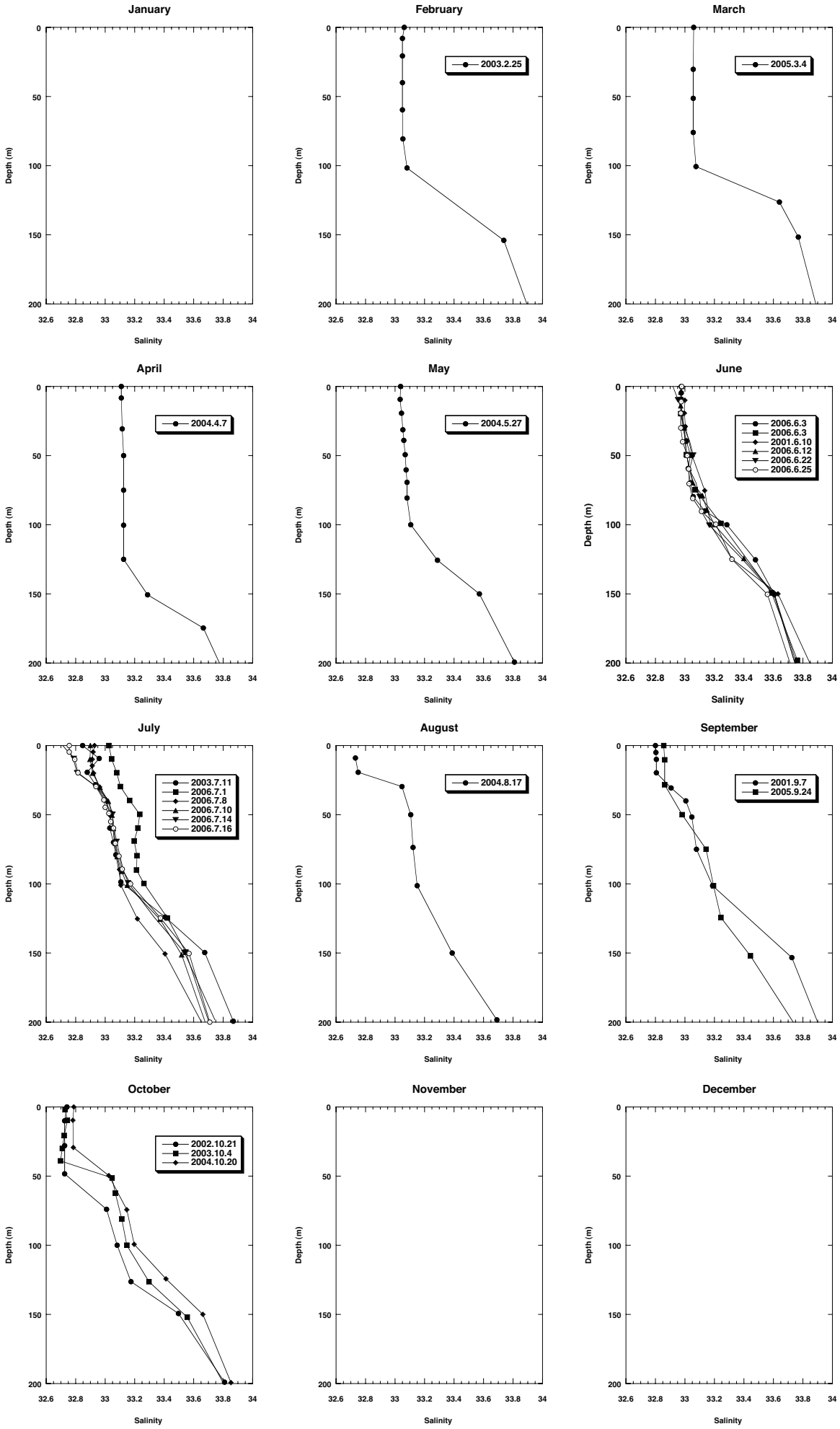
7. Acknowledgements

We would like to thank the captains, officers, crews of the R/Vs MIRAI, NATSUSHIMA, KAIREI, JAMSTEC for their help. We are grateful to Dr. H. Sako, Mr. K. Hayashi, Mr T. Idai, Mr. K. Yoshida, scientists and technicians for the kind cooperation in sampling and on board measurements.

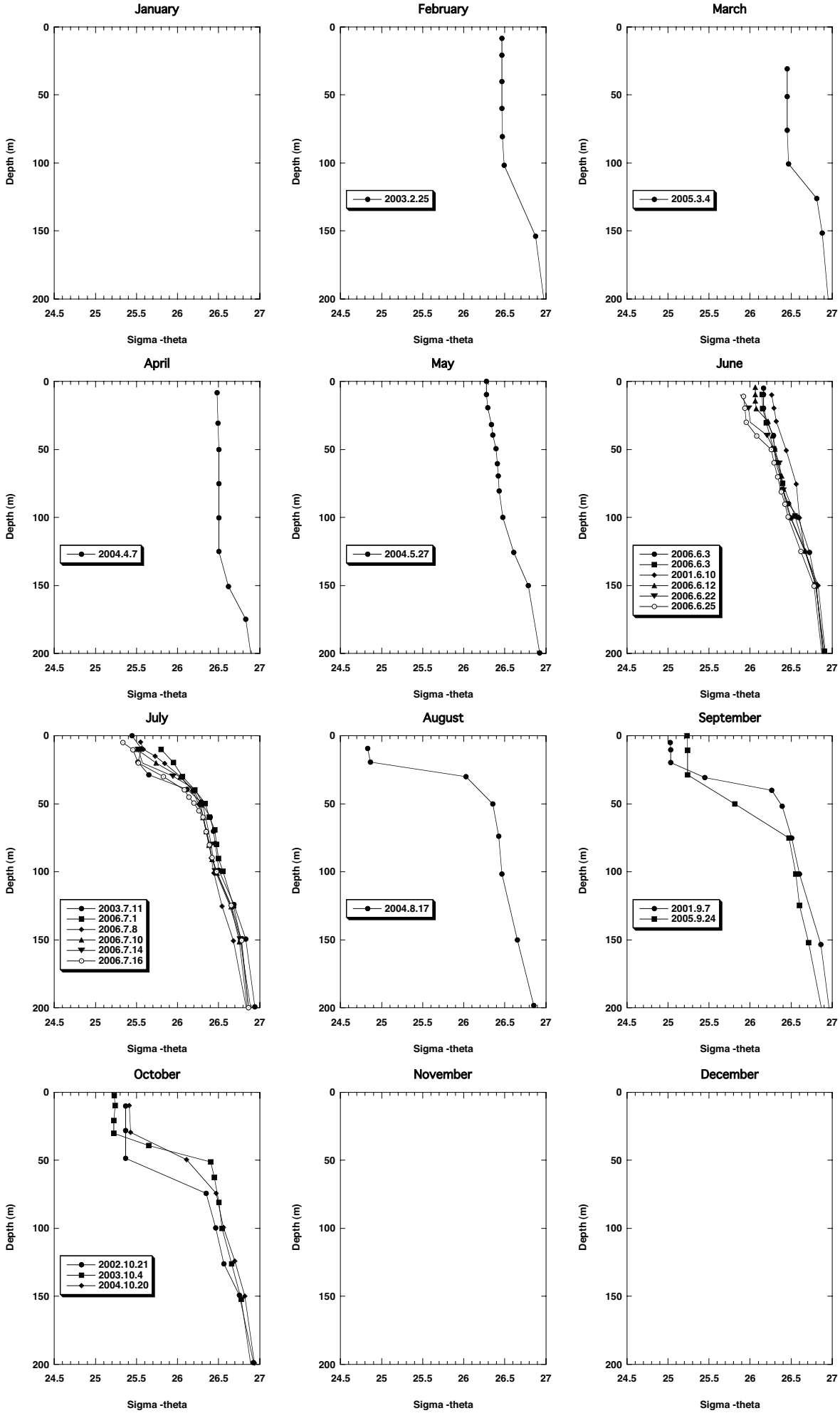
Appendix 1 Temperature



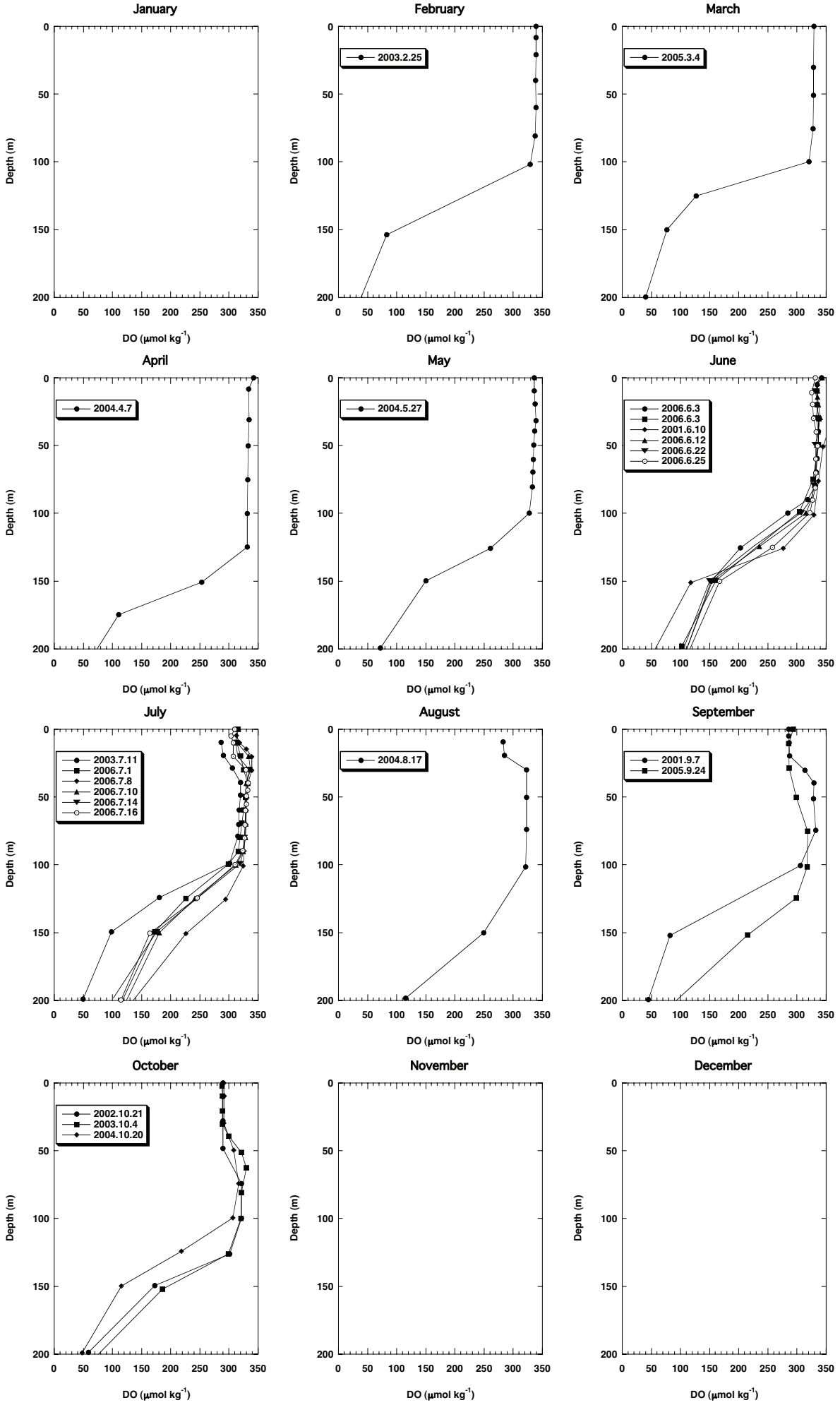
Appendix 1 Salinity



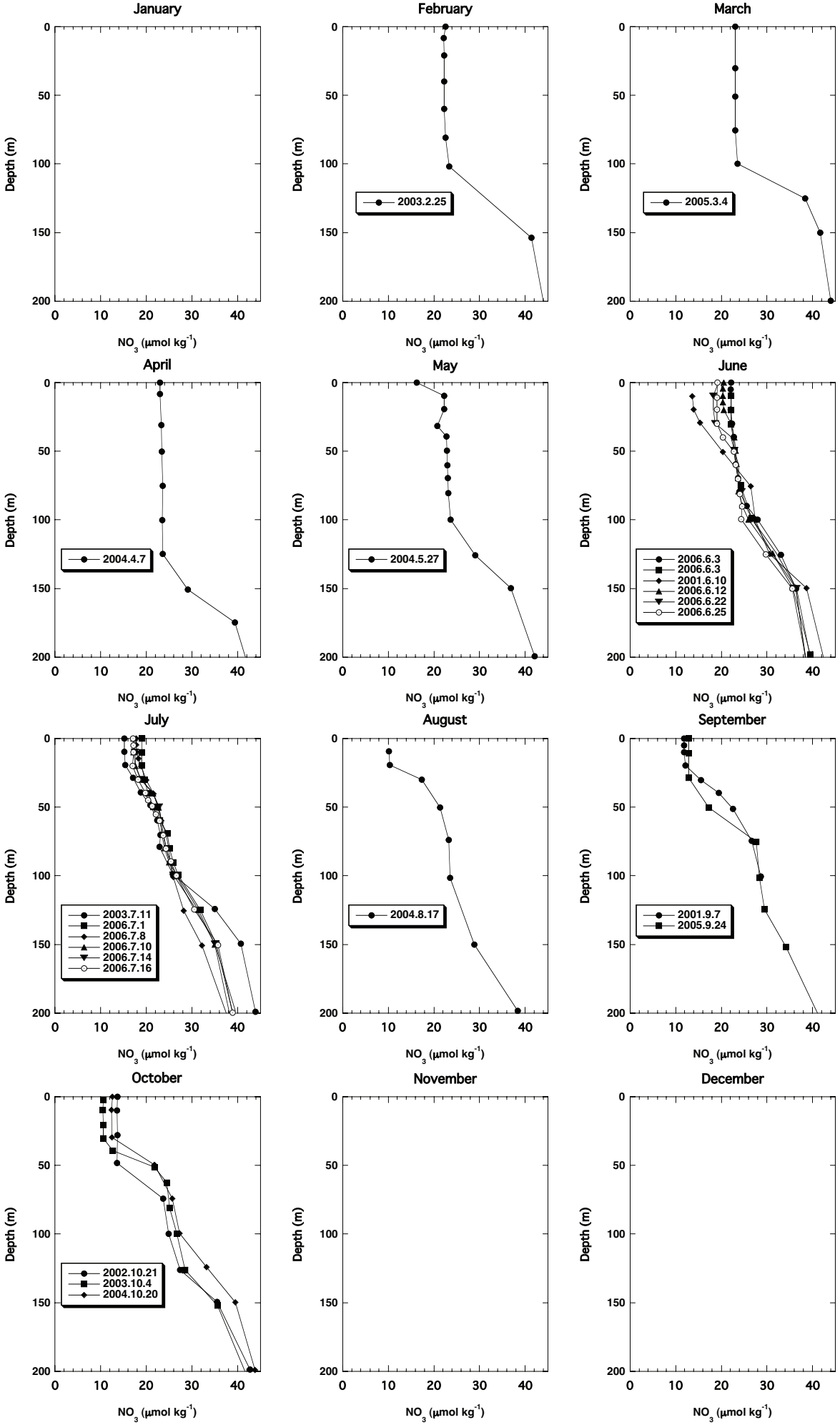
Appendix 1 Density



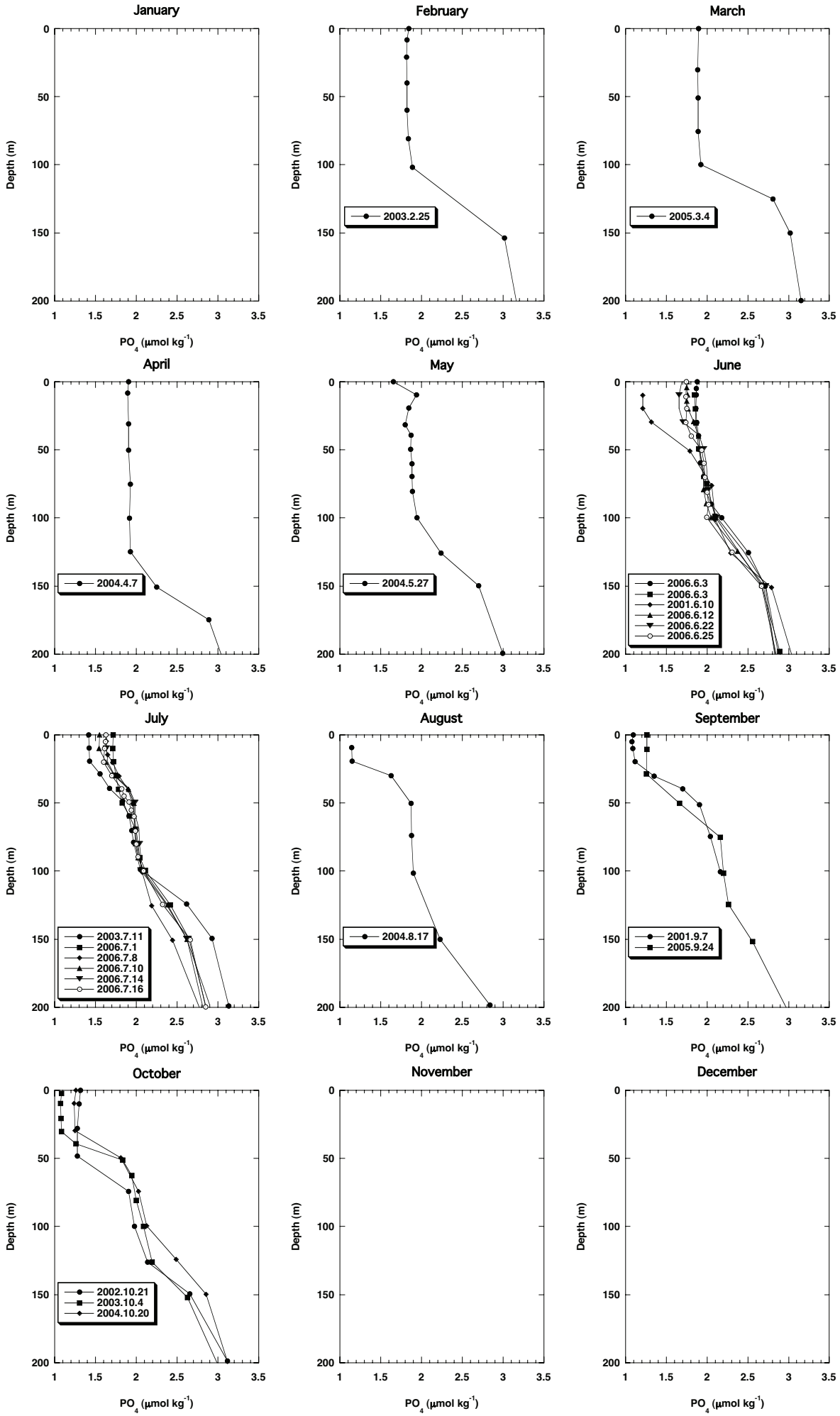
Appendix 1 Dissolved Oxygen



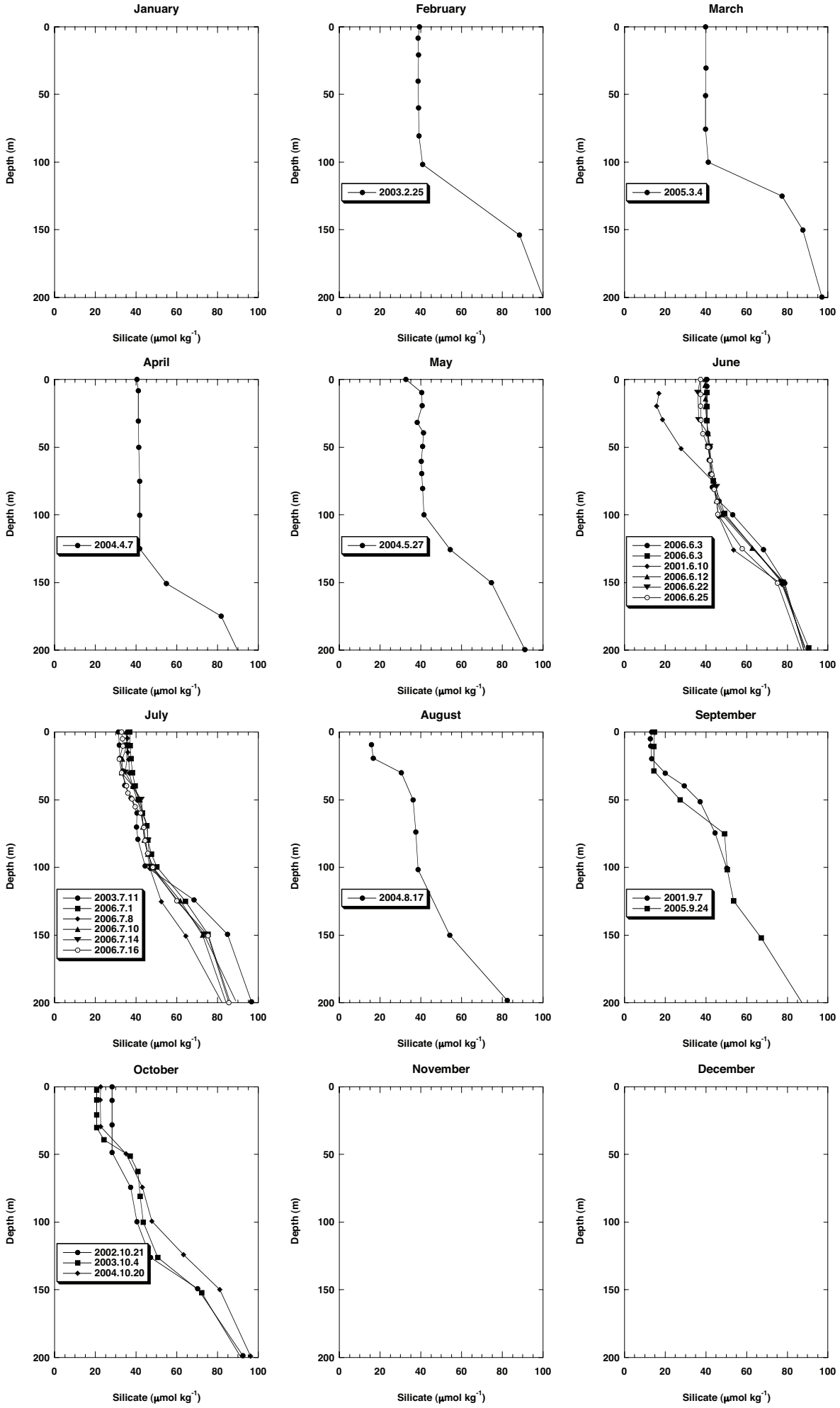
Appendix 1 Nitrate



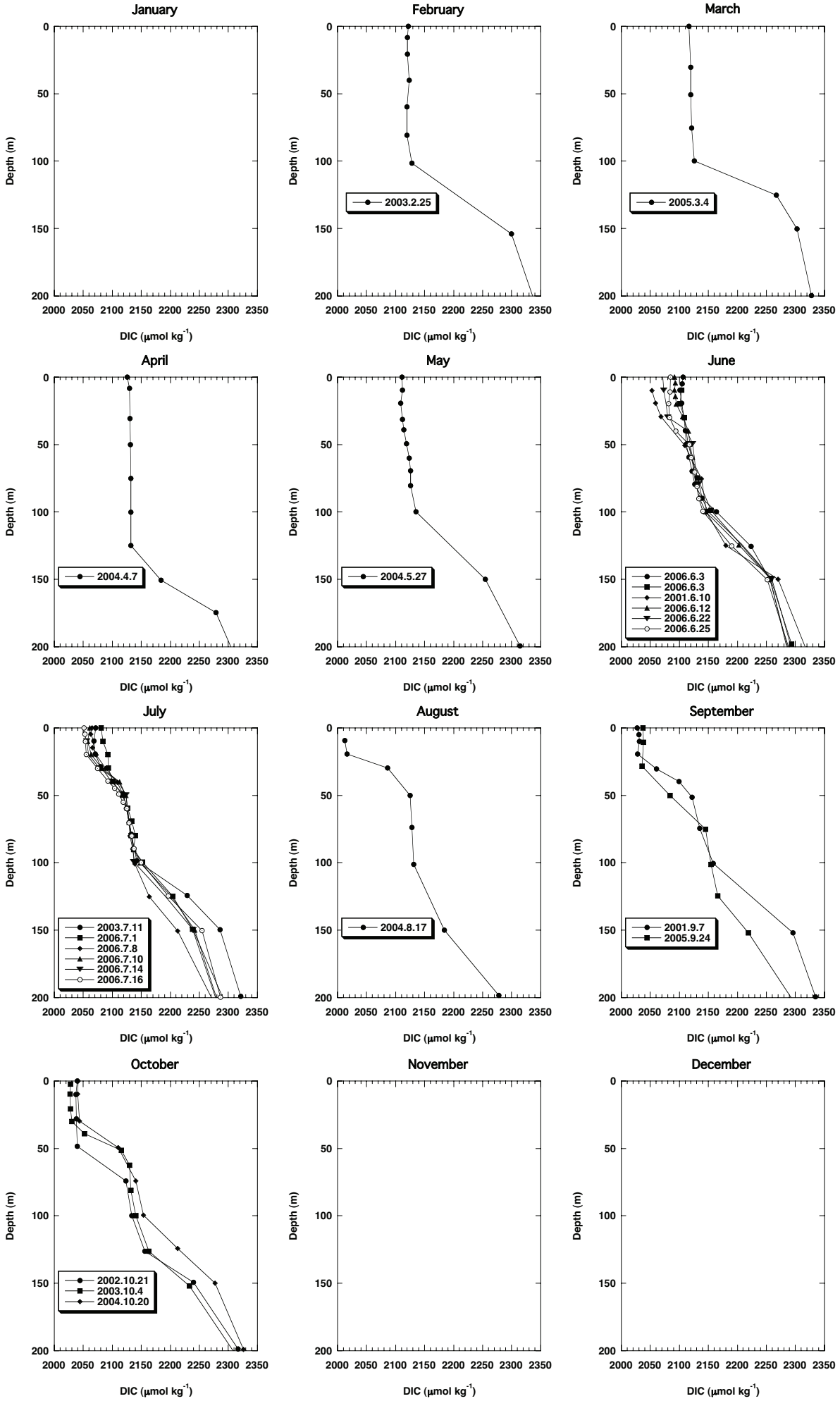
Appendix 1 Phosphate



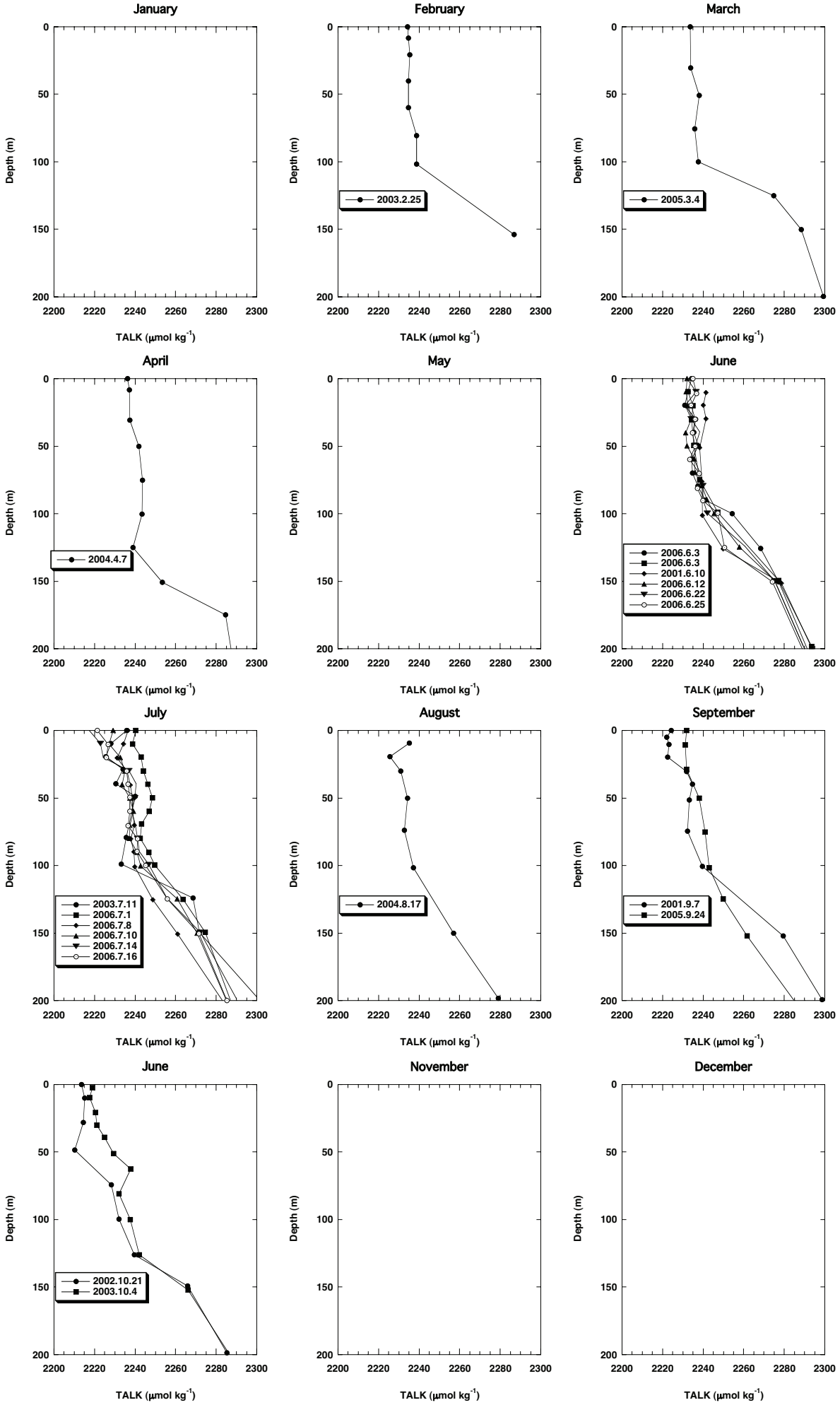
Appendix 1 Silicate



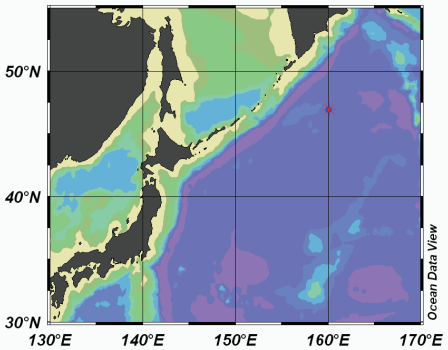
Appendix 1 Dissolved Inorganic Carbon

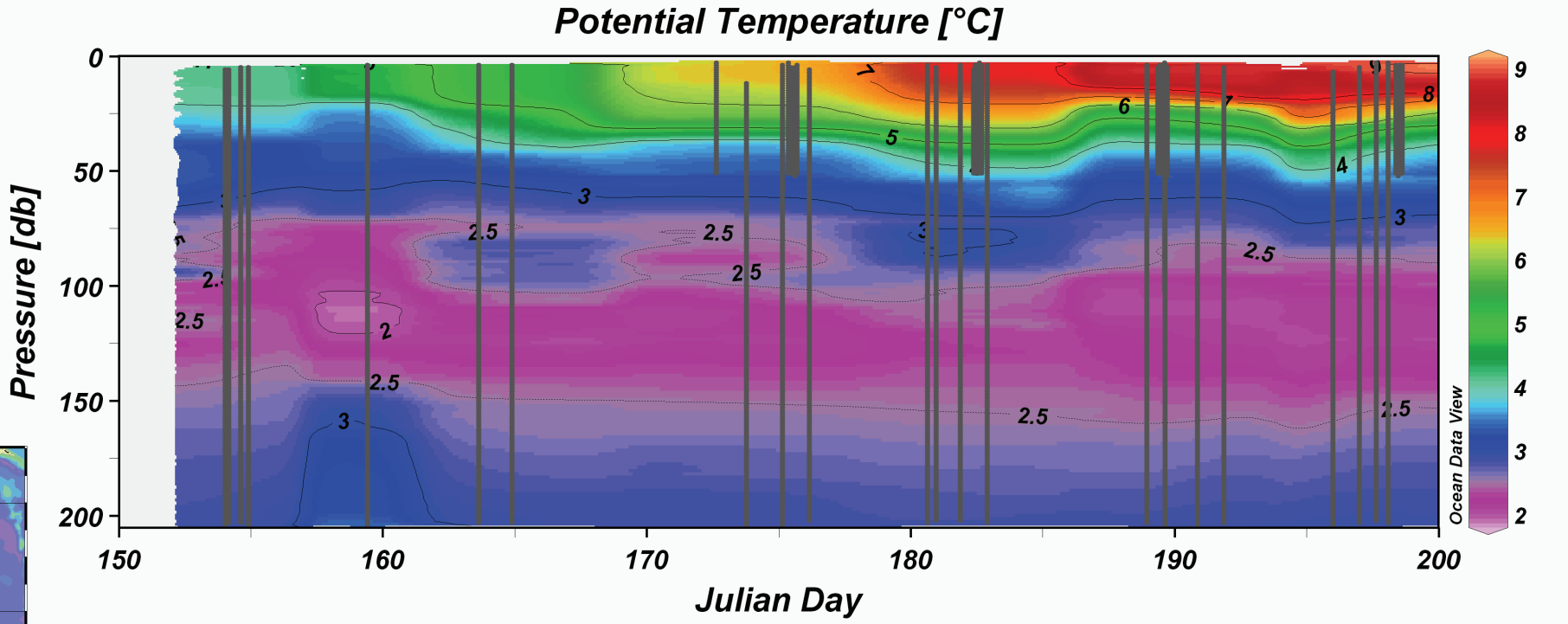


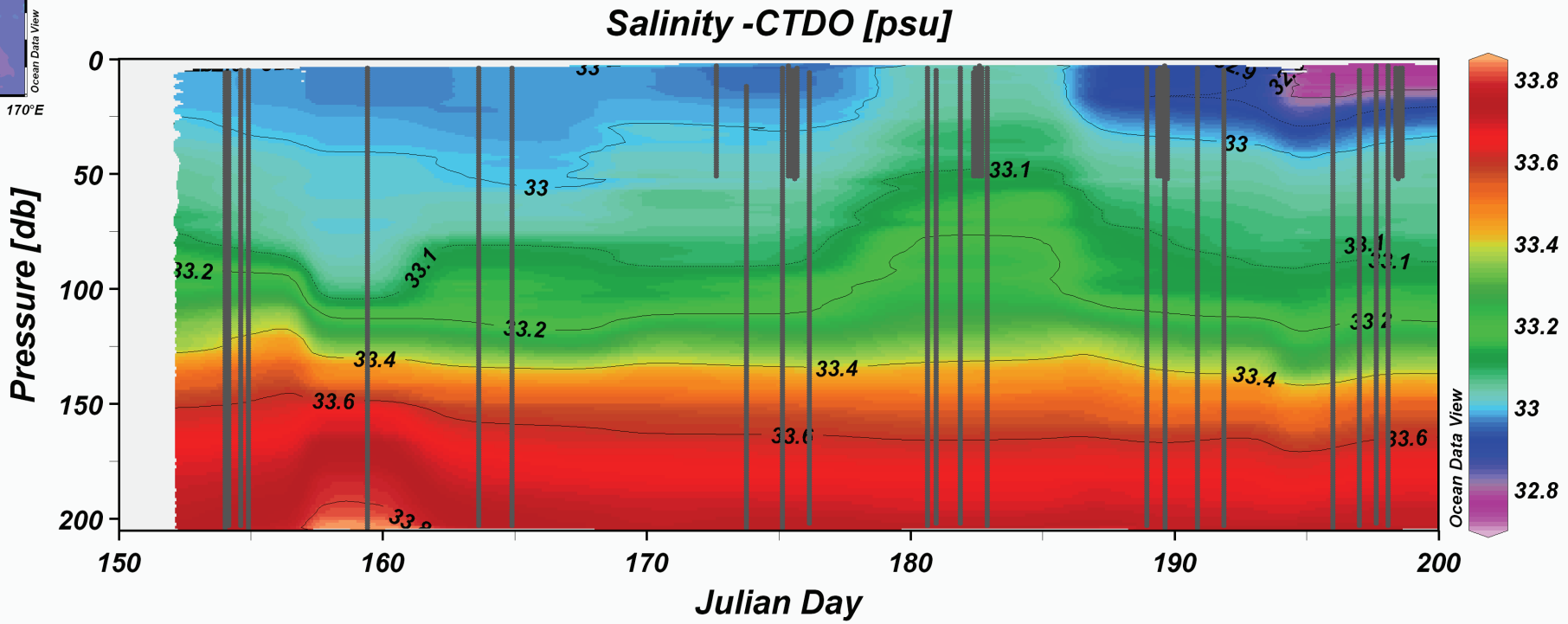
Appendix 1 Total Alkalinity



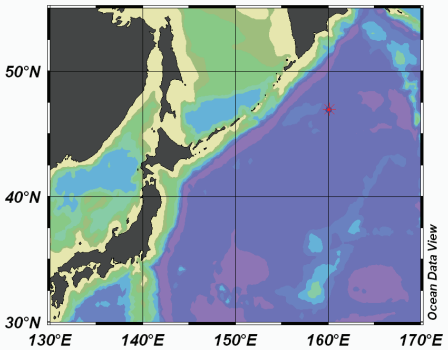
Appendix 2

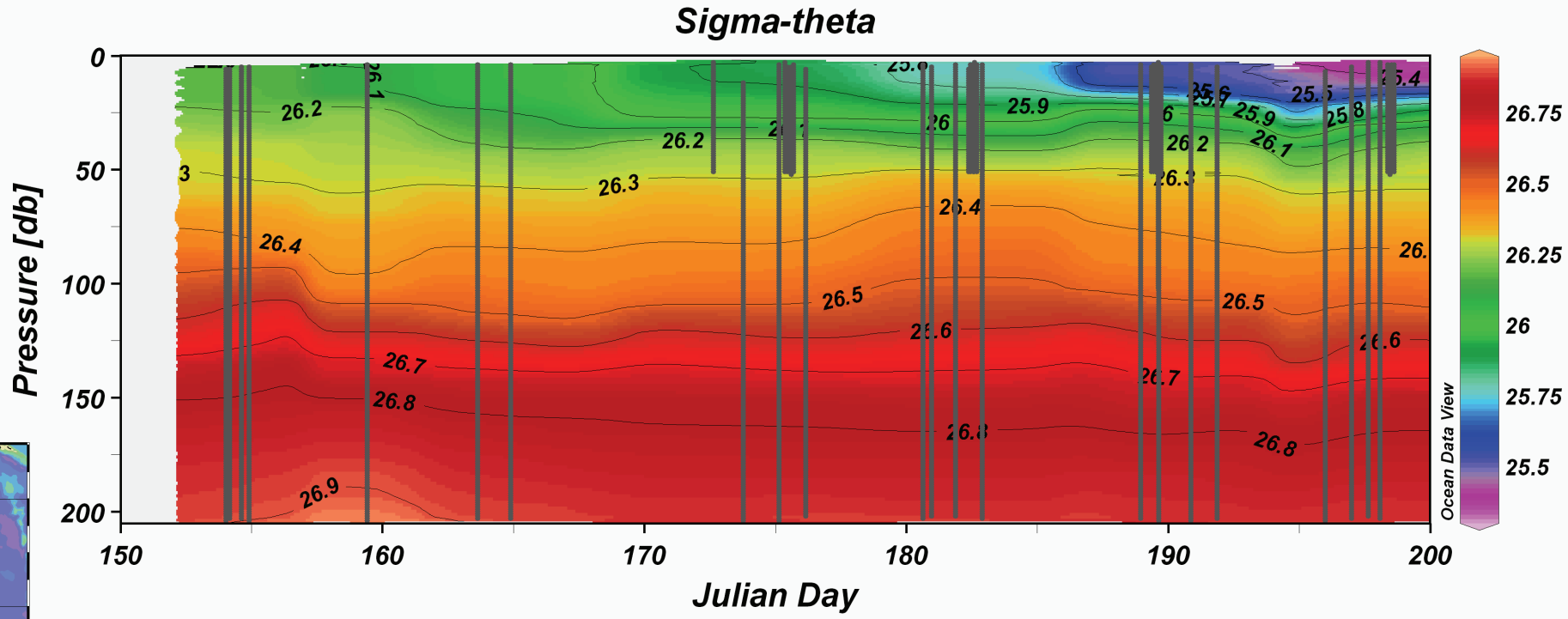

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

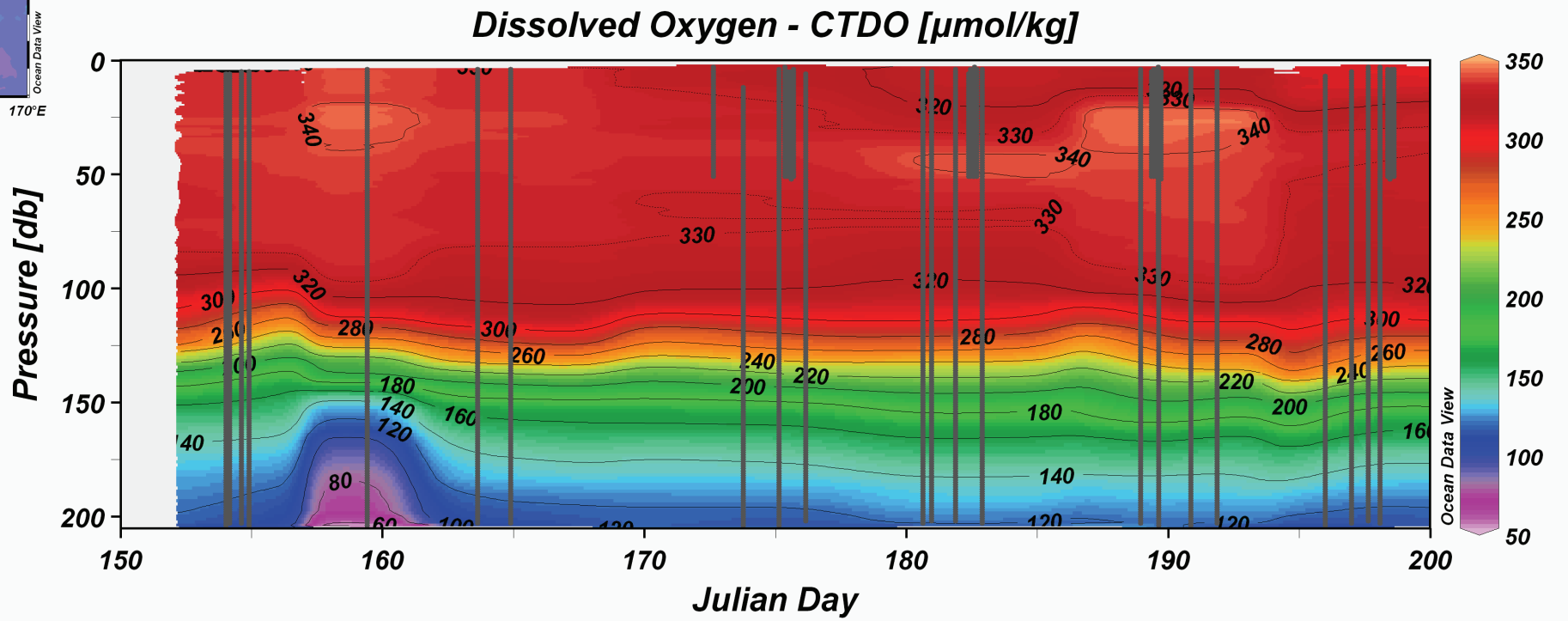

Potential Temperature [°C]
Pressure [db]
Julian Day
Ocean Data View


Salinity -CTDO [psu]
Pressure [db]
Julian Day
Ocean Data View

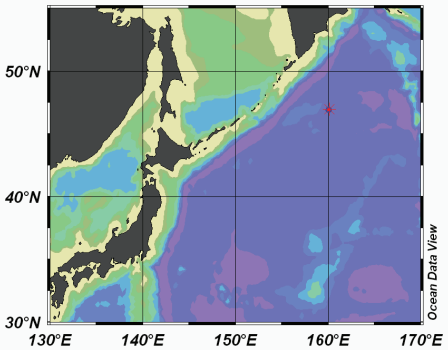
Appendix 2

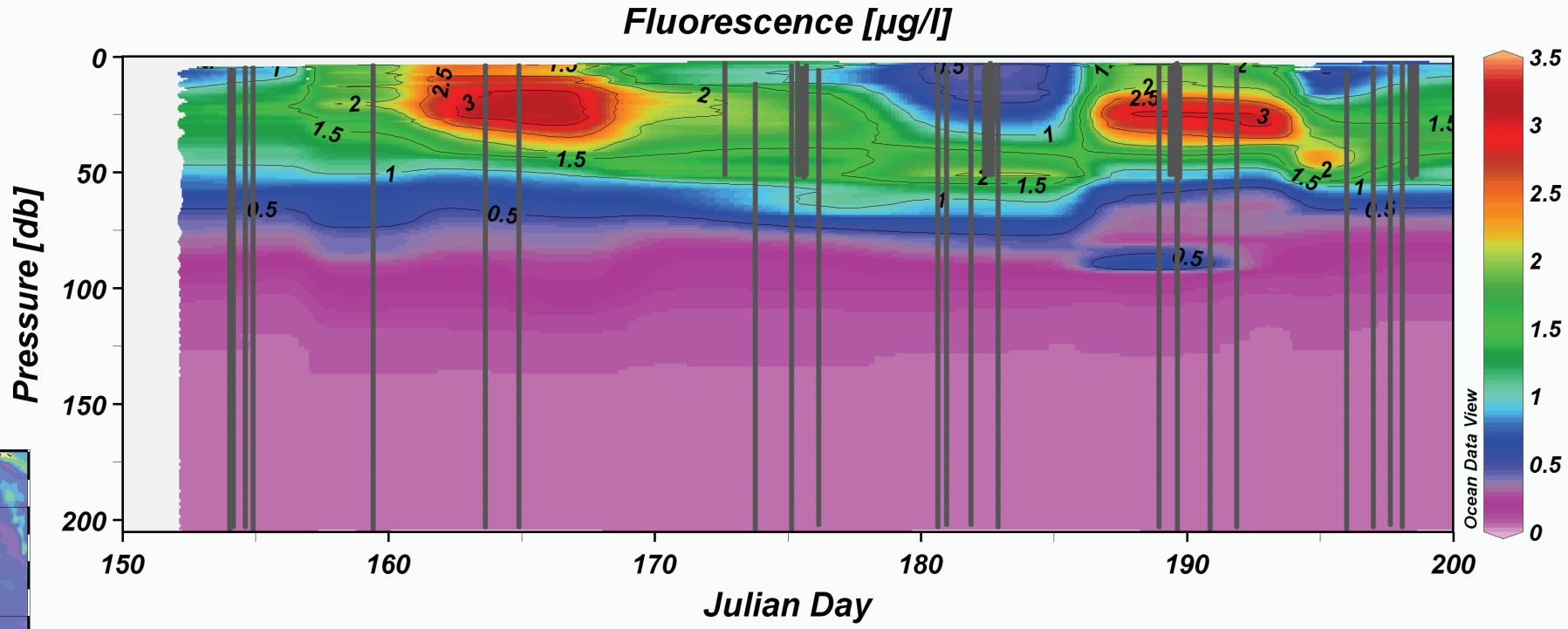

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

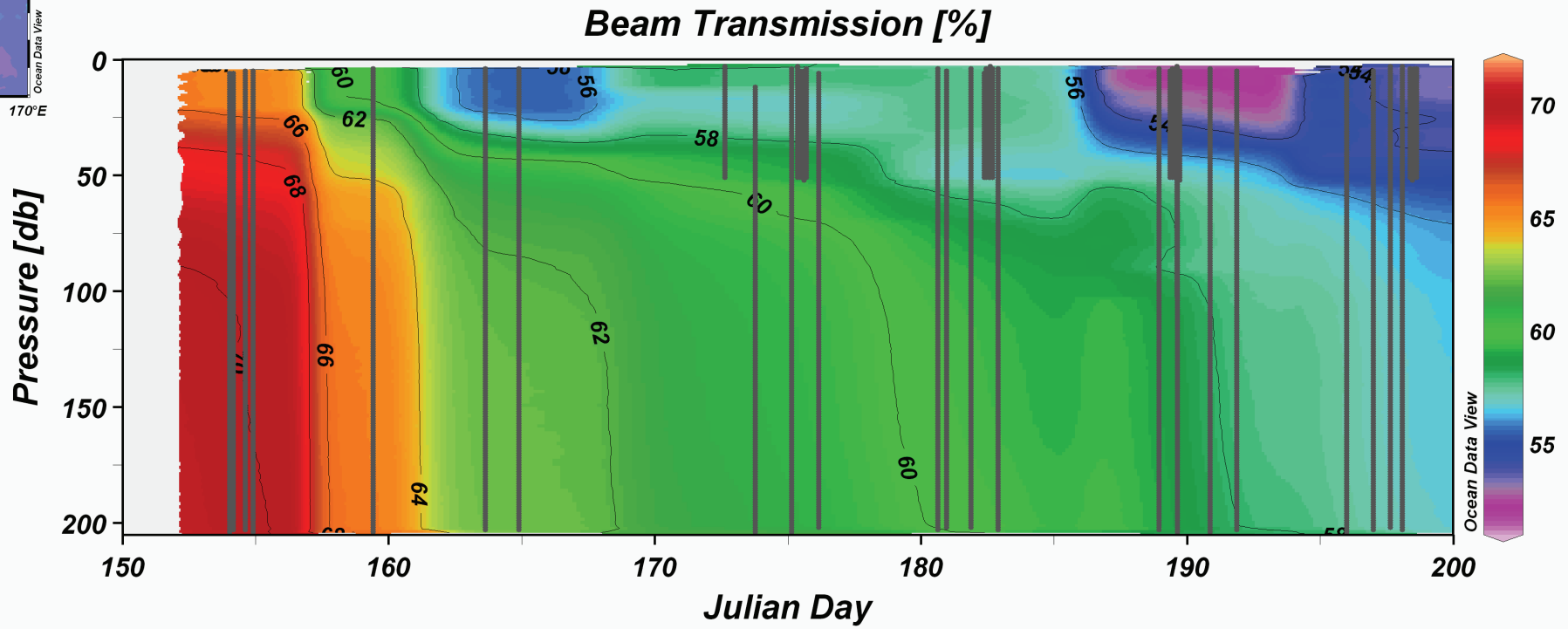

Sigma-theta
Pressure [db]
Julian Day
Ocean Data View


Dissolved Oxygen - CTDO [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View

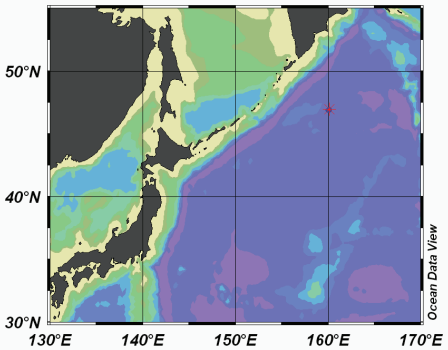
Appendix 2

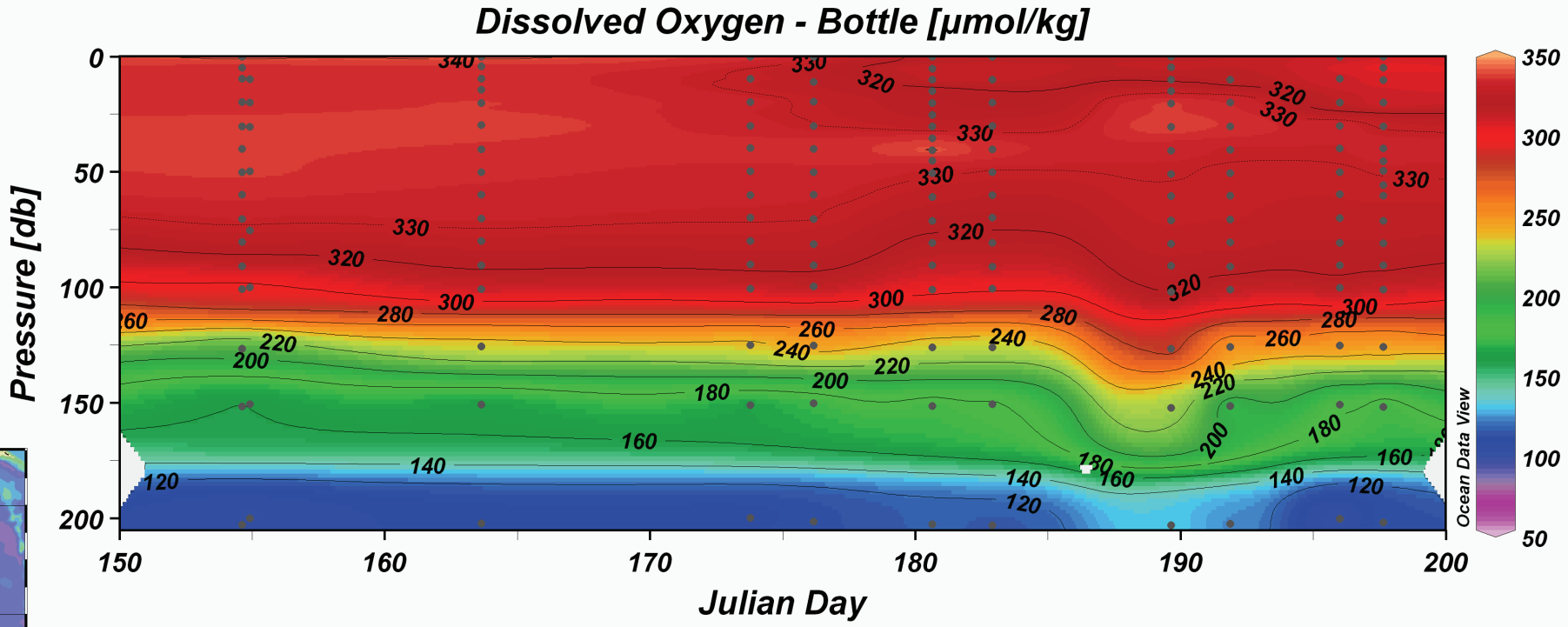

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

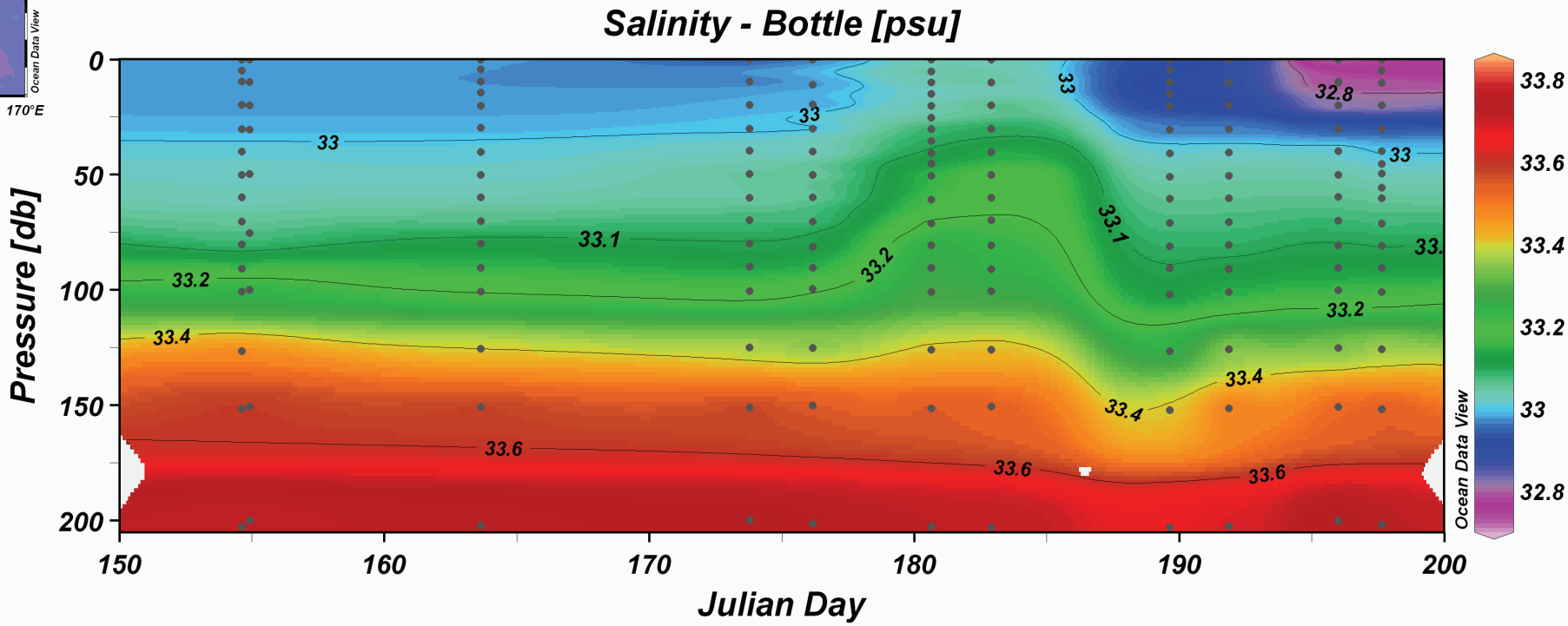

Fluorescence [µg/l]
Pressure [db]
Julian Day
Ocean Data View


Beam Transmission [%]
Pressure [db]
Julian Day
Ocean Data View

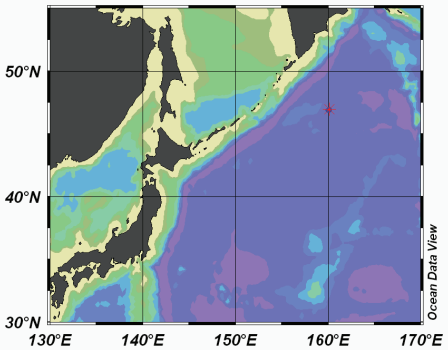
Appendix 2

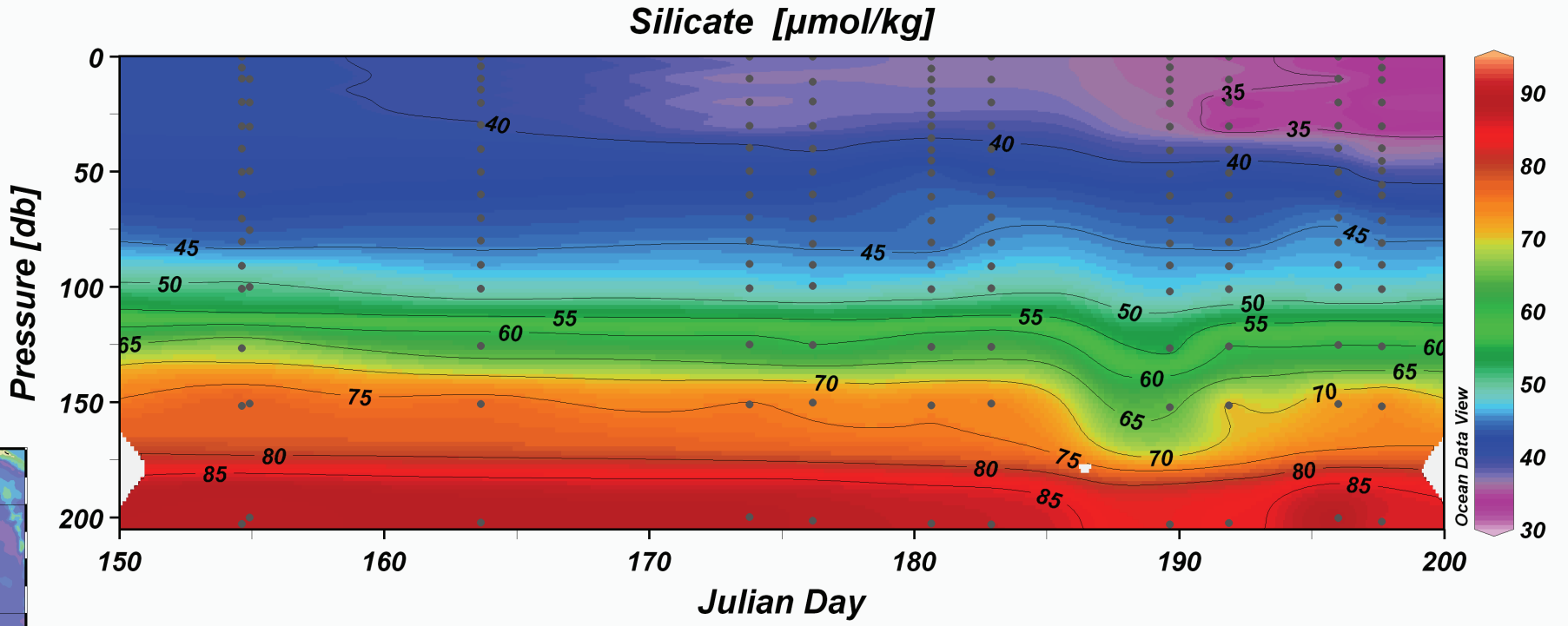

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

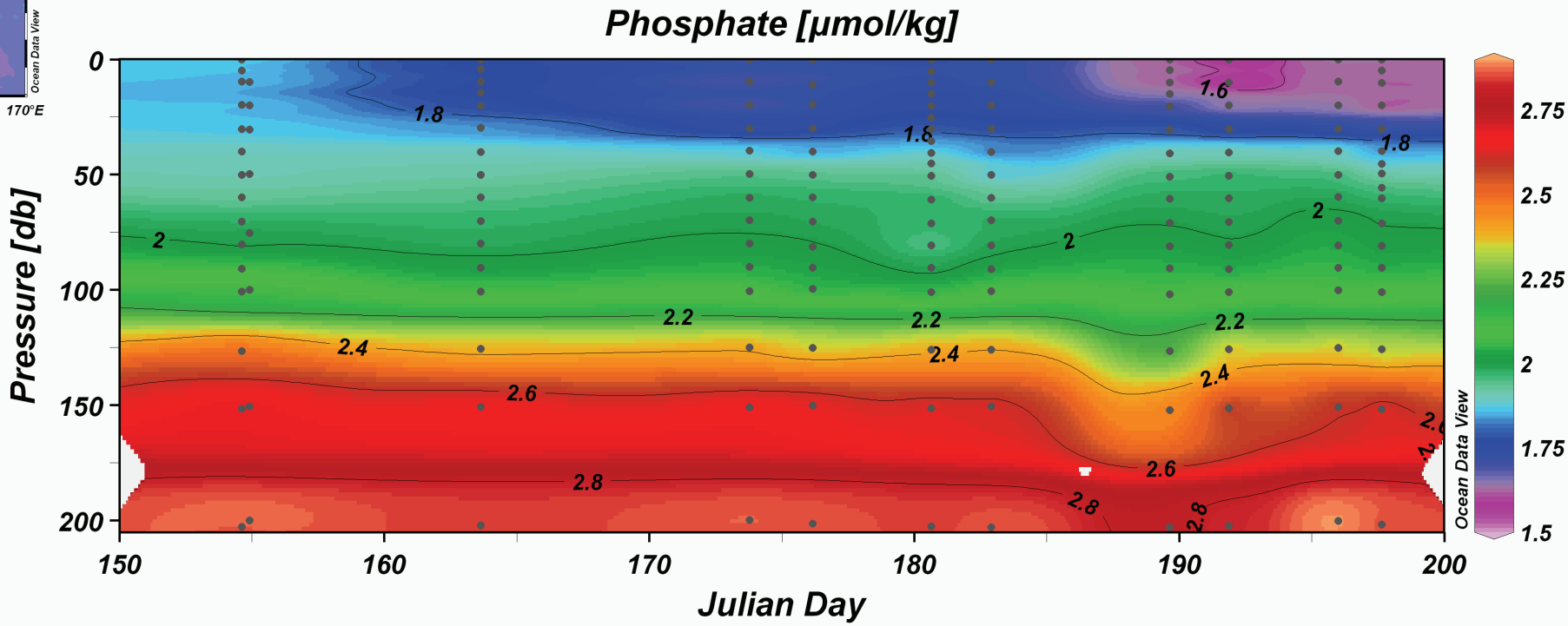

Dissolved Oxygen - Bottle [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View


Salinity - Bottle [psu]
Pressure [db]
Julian Day
Ocean Data View

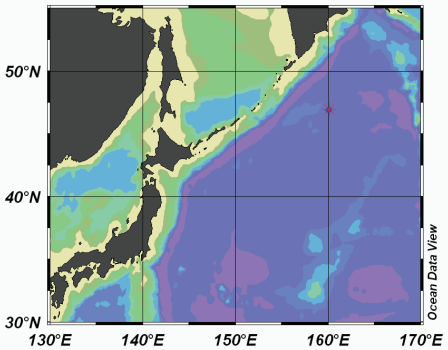
Appendix 2

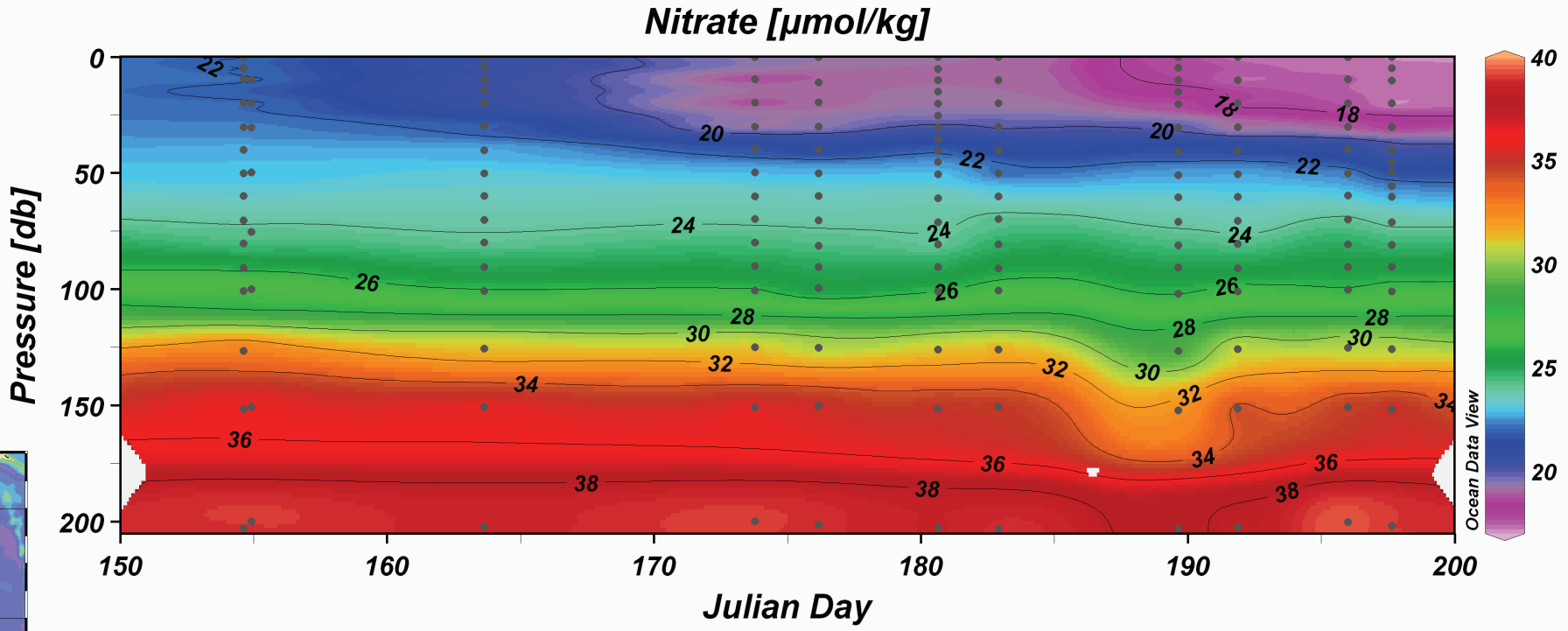

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

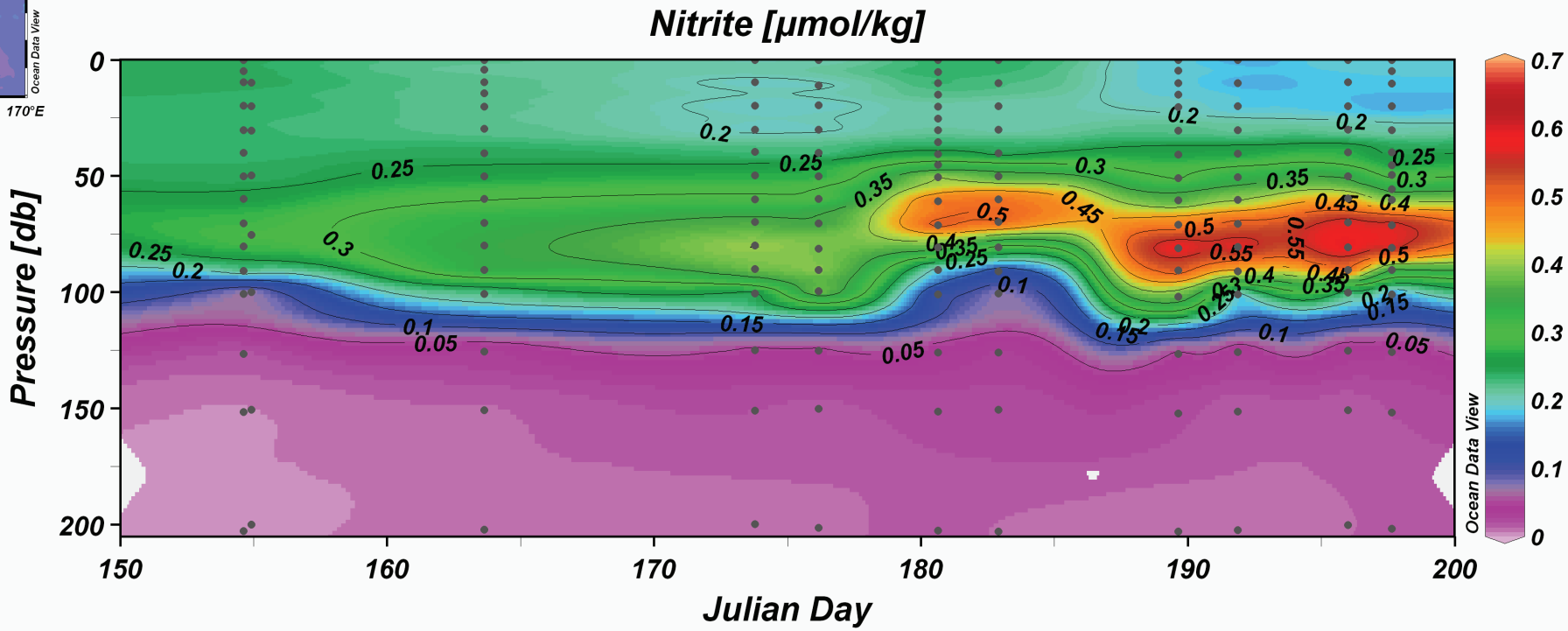

Silicate [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View


Phosphate [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View

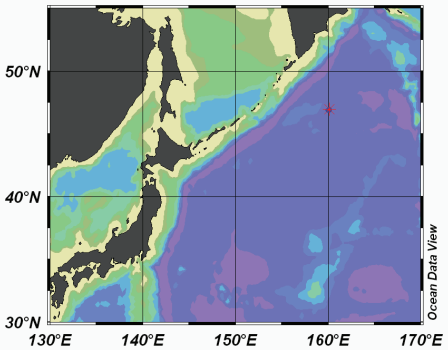
Appendix 2

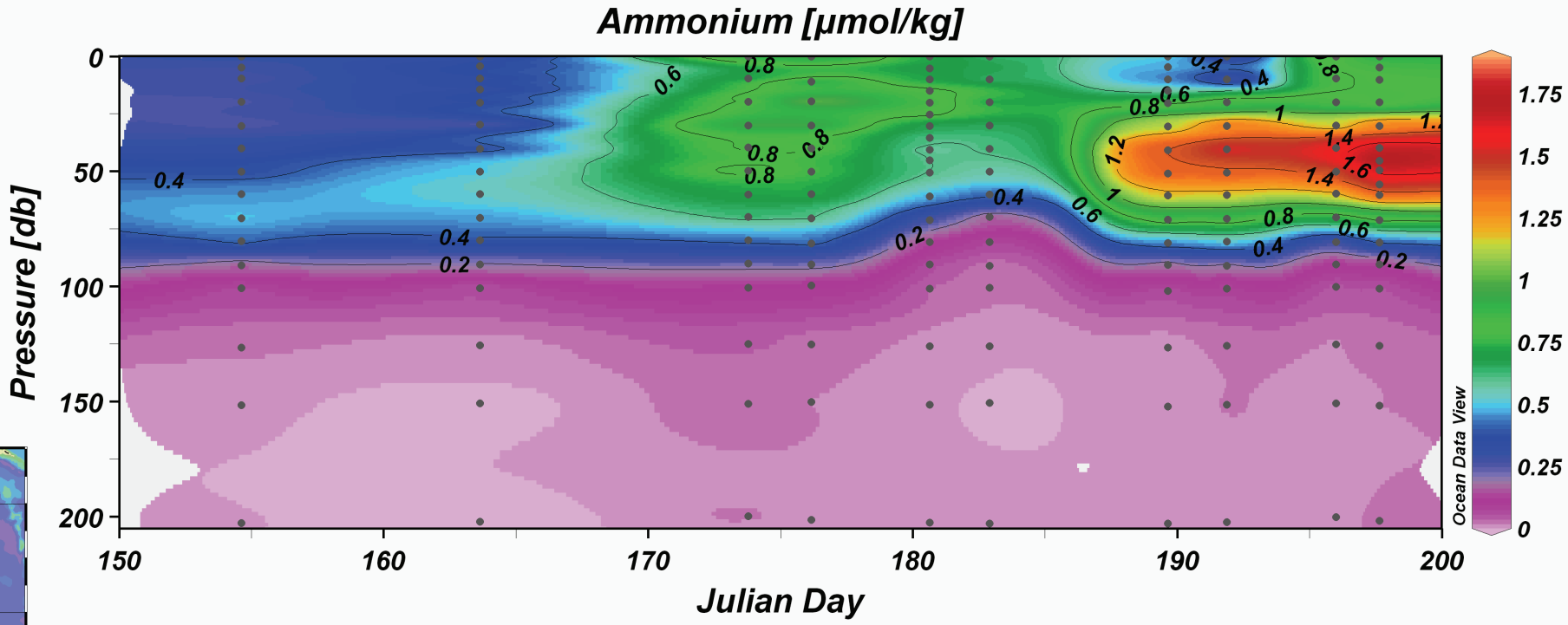

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

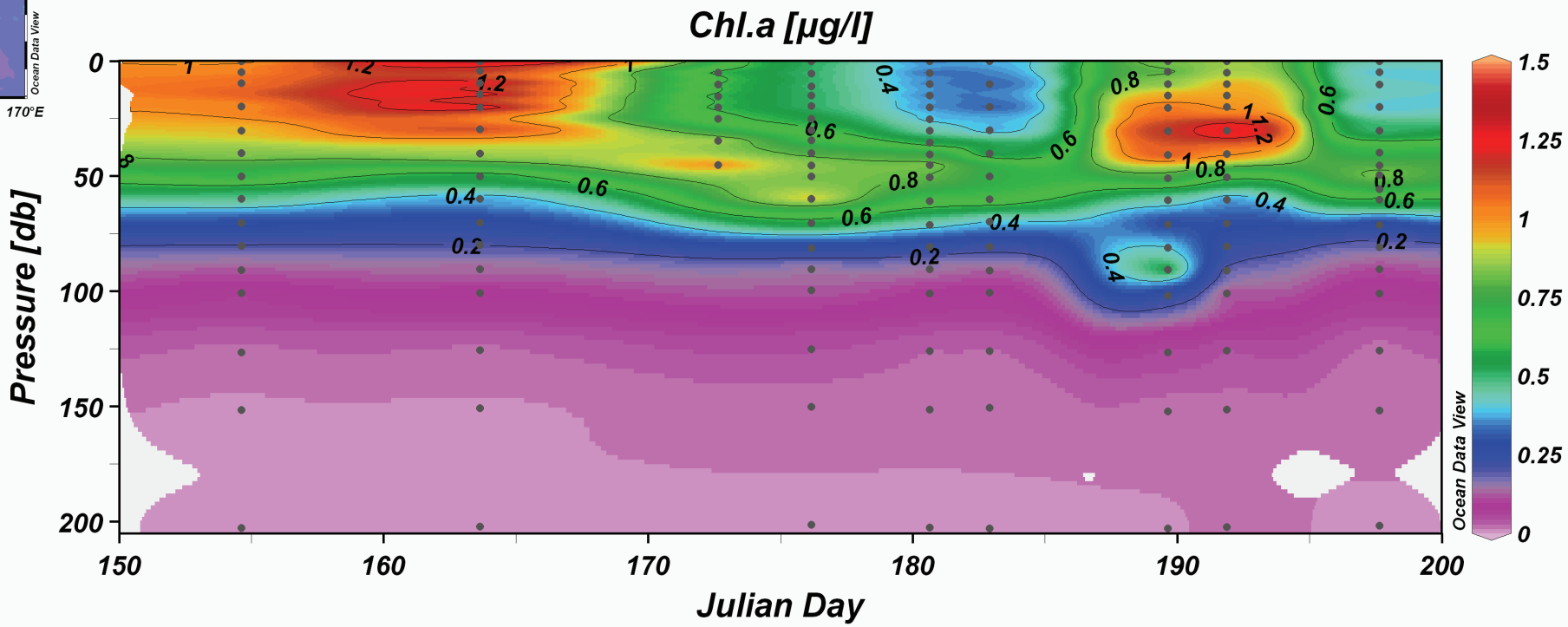

Nitrate [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View


Nitrite [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View

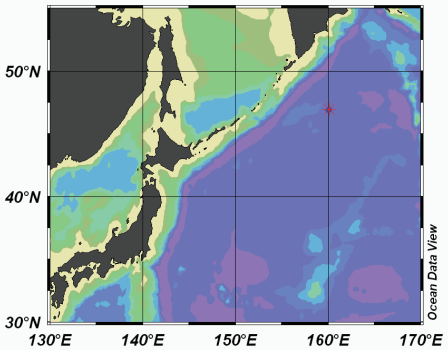
Appendix 2

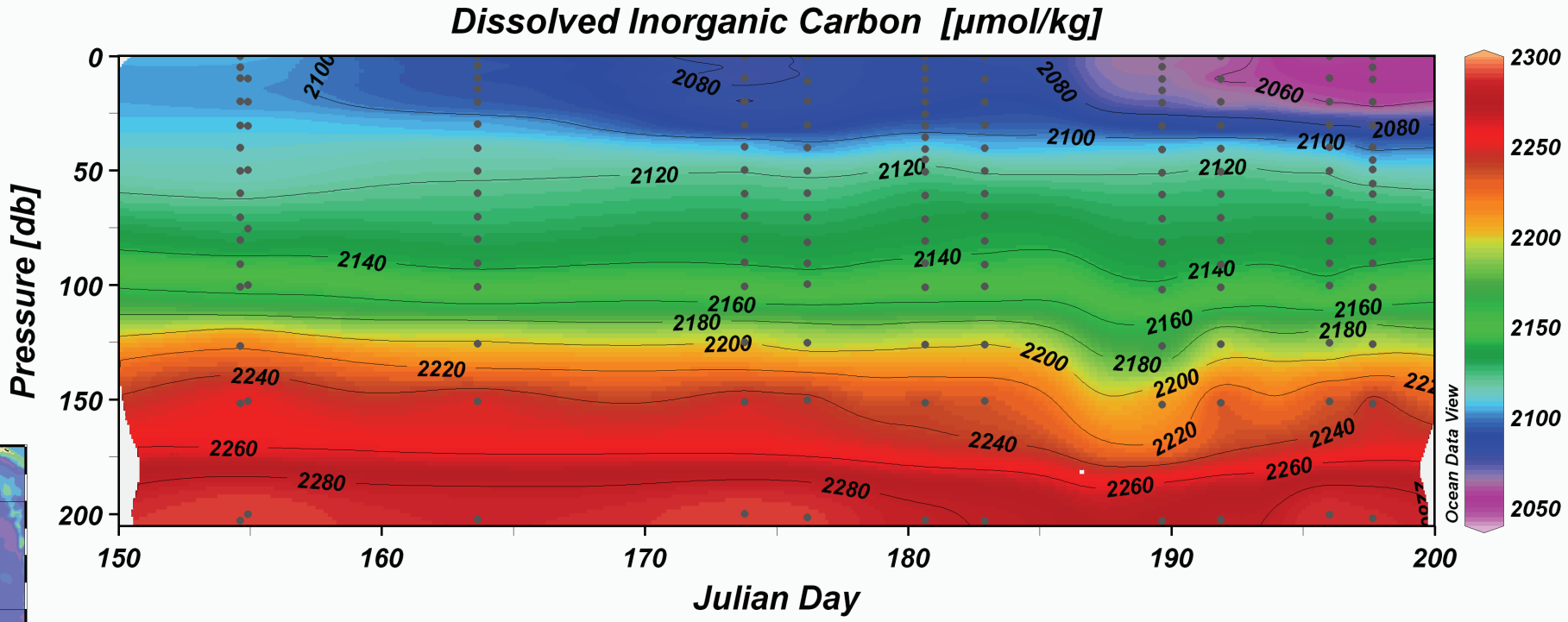

50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View

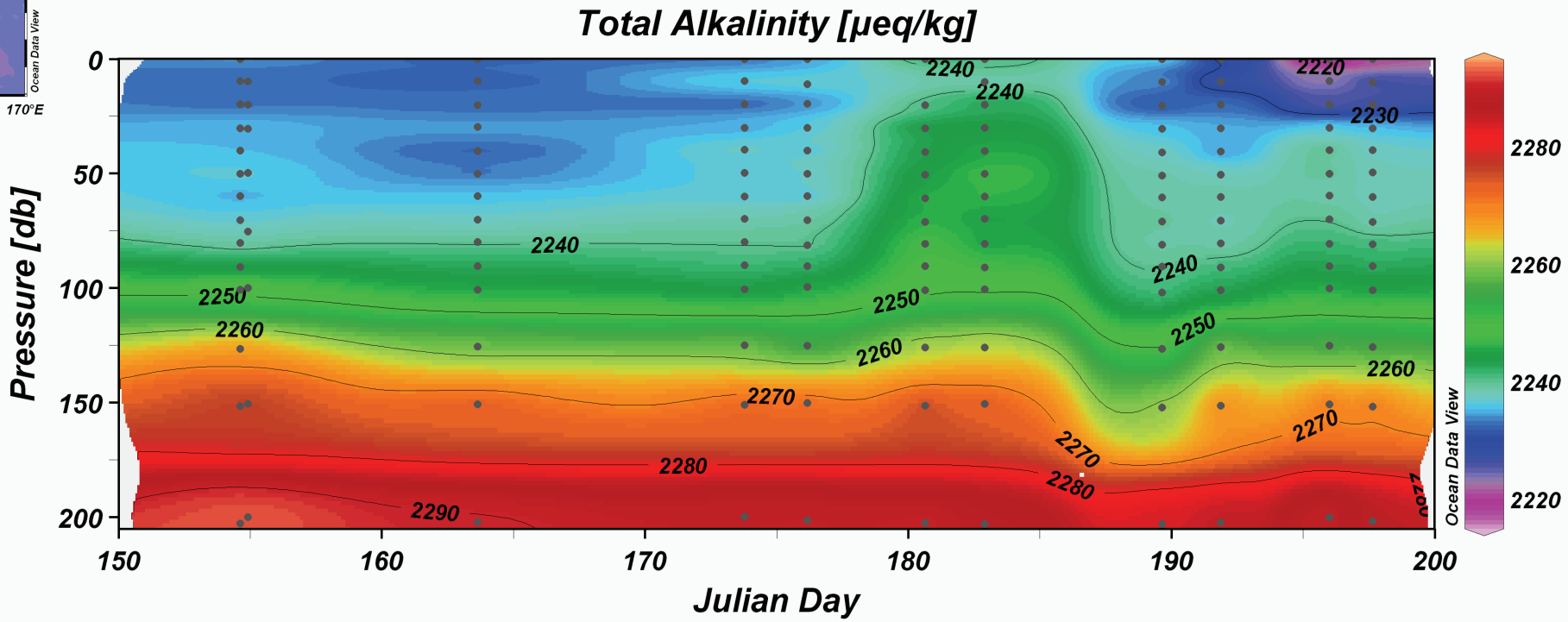

Ammonium [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View


Chl.a [µg/l]
Pressure [db]
Julian Day
Ocean Data View

Appendix 2


50°N
40°N
30°N
130°E
140°E
150°E
160°E
170°E
Ocean Data View


Dissolved Inorganic Carbon [µmol/kg]
Pressure [db]
Julian Day
Ocean Data View
0
50
100
150
200
150
160
170
180
190
200
2300
2250
2200
2150
2100
2050
2100
2080
2060
2120
2140
2160
2180
2200
2220
2240
2260
2280


Total Alkalinity [µeq/kg]
Pressure [db]
Julian Day
Ocean Data View
0
50
100
150
200
150
160
170
180
190
200
2280
2260
2240
2220
2230
2250
2270
2290