Global CRM/RM-scaled nutrient gridded dataset GND13

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Abstract. A global nutrients gridded dataset that might be the basis for studies of more accurate spatial distributions of nutrients in the global ocean was created and named GND13. During 30 cruises, reference materials of nutrients in seawater or their equivalents were used at all stations, and high-precision measurements were made. The precision of the nutrient analyses was better than 0.2%. Data were collected from the hydrographic cruises in JASMTEC R/V *Mirai* cruises, JMA cruise, CARINA, PACIFICA and WGHC datasets from which nutrient data were available. Analyses were conducted at 243 crossover stations. Cruises that used certified reference materials or reference materials (CRMs/RMs) for seawater nutrient concentration measurements were used as reference of unbroken chain of comparison to determine correction factors which made nutrient concentrations obtained by other cruises to be SI traceable. Dissolved oxygen concentration data was additional parameter of GND13 using same methodology to create nutrients gridded data, but not traceable to SI. Finally, a dataset of nitrate, phosphate, silicate concentrations was created at latitude and longitude intervals of 0.5° and on 136 isobaric surfaces to depths of 6500 meters as SI traceable dataset. This dataset has already been published at doi:10.17596/0000001.

1 Introduction

Global oceanic biogeochemical cycles are being significantly altered by the direct and indirect impacts of human activities. It is therefore necessary to obtain accurate information about changes and trends of concentrations of inorganic carbon and dissolved inorganic nutrients in both shallow and deep ocean waters. For this information to be of practical use, it is critical that results from different laboratories can be compared with complete confidence. A global consensus about nutrient concentrations requires that there be access to certified reference materials (CRMs), and there must be a requirement or ethos for the use of these CRMs when oceanic nutrient concentrations are measured and subsequently when they are recorded in global databases, incorporated in climate models, and ultimately used to quantify changes to the Earth system.

The 2007 IPCC Report highlighted the problem inherent in comparing datasets by stating that “Uncertainties in deep ocean nutrient observations may be responsible for the lack of coherence in the nutrient changes. Sources of inaccuracy include the limited number of observations and the lack of compatibility between measurements from different laboratories at different times” (Bindoff et al., 2007). Analyses of nutrient concentrations from crossover stations have shown consistent disagreement of up to 10 % for deep water nutrient data during the last three decades (Aoyama et al., 2013; Tanhua et al., 2009). Results of inter-laboratory comparison studies since 2003 have shown biases of a similar magnitude between some participant laboratories (Aoyama et al., 2007; 2008; 2010; 2016; 2018). This pattern indicates that analytical problems may be the main cause of the large discrepancies in reported deep water nutrient concentrations. The reported results imply that these biases are also present throughout the water column. These comparisons were based on only a small number of specific studies, but there are many oceanic nutrient datasets reported, published, and stored on international databases with no references to CRMs at all. Although this situation has improved somewhat since 2011 after CRM of nutrients became available, it is still difficult to ascertain with total confidence any temporal changes in oceanic nutrient concentrations. We can now detect changes in deep ocean temperature (and hence heat content) (Levitus et al., 2009; 2012; Kouketsu et al., 2009; Rhein et al., 2013) because of the excellent comparability of temperature measurements over a number of years. Changes to the carbonate system parameters in the deep ocean have also been reported with comparability ensured by the use of CRMs (e.g., Wanninkhof et al., 2010). Similarly, changes in oceanic oxygen concentrations can now be determined (Stendardo and Gruber, 2012).

Reference materials (RMs) and CRMs for nutrients in seawater have been developed for oceanographic use. These currently include a Danish RM (Eurofins), NRC-Canada CRM (MOOS-3), a new RM developed by Korea (K-RMS), and one developed by KANSO-Japan. The reference material for nutrients in seawater produced by KANSO has been used in the inter-laboratory comparison exercise organized by Meteorological Research Institute, MRI, and jointly by International Ocean Carbon Coordination Project, IOCCP and Japan Agency for Marine-Earth Science and Technology, JAMSTEC, since 2003 (Aoyama et al., 2007; 2008; 2010; 2016; 2018). The results of the latest inter-laboratory comparison exercise (IC), “IOCCP-JAMSTEC 2017/18 Inter-laboratory Calibration Exercise of a Certified Reference Material for Nutrients in Seawater”, are now available (Aoyama et al., 2018). It is clear from the current results (see Figs. 6, 7, and 8 in the 2017/2018 report) that the normalized cumulative distributions of nitrate and phosphate were better in 2018 than in previous years. The curves were flatter than the normalized cumulative distributions in previous IC exercises.

The implication is that comparability of silicate analyses among the laboratories did not improve between 2008 to 2018 to the same degree that it did for nitrate/phosphate, and the correction factors for silicate were indeed more variable and uncertain than the correction factors for nitrate and phosphate. This improvement might be a reflection of the fact that the number of laboratories that use CRM/RMs was increasing during those years.

This difference of comparability between nitrate/phosphate and silicate analyses can be also seen in the results of correction factors estimation with uncertainty in this study. In particular, correction factor of silicate were more variable and were associated with greater uncertainty than the correction factors for nitrate and phosphate. Consensus standard deviations of nutrient concentrations of nitrate, phosphate and silicate were one order of magnitude larger than the homogeneity of the currently available CRM/RMs and were about double the reported precision of measurements of the individual laboratories. These IC results therefore showed that use of CRMs should greatly improve the comparability of nutrient data among laboratories throughout the world. The current high level of analytical performance at many participating laboratories indicates that the use of certified reference materials would establish traceability. The use of CRM/RMs during global cruises in the CLIVAR (Climate and Ocean: Variability, Predictability and Change), GO-SHIP (Global Ocean Ship-based Hydrographic Investigations Program), and GEOTRACES projects has been increasing, and the author has been using CRM/RMs during the cruises of the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) R/V *Mirai* since 2003. Disagreements between cruises at depth tend to be smaller when reference materials are used.

On the other hand, the method for determining the dissolved oxygen concentration in seawater is generally the Carpenter method (Carpenter, 1965), which is an improvement of the Winkler method, but is hereafter simply referred to as the Winkler method. In this Winkler method, manganese hydroxide “fixes” dissolved oxygen under alkaline conditions, and the “fixed” dissolved oxygen quantitatively oxidizes iodine ions to free iodine under acidic conditions. Titrating the free iodine with a sodium thiosulfate solution of known concentration indirectly quantifies the dissolved oxygen concentration.

The sodium thiosulfate solution concentration is determined by titration of a potassium iodate solution of known concentration (potassium iodate quantitatively oxidizes iodine ions to free iodine under acidic conditions). In Japan, SI-traceable certified reference potassium iodate standards are supplied by the National Meteorology Institute of Japan, National Institute of Advanced Industrial Science and Technology (NMIJ). Ocean Scientific International Ltd, OSIL, UK, and FUJIFILM Wako Pure Chemical Corporation, Japan, also provides Potassium Iodate solutions, which are used to standardise the thiosulfate solution in the widely used Winkler titration method. Therefore, dissolved oxygen concentration measured around the world had some extent of comparability.

This article describes a global gridded dataset produced using CRM/RM-scaled SI traceable nutrient concentrations based on key cruises that used CRM/RM and unbroken chain of comparison. Several previous publications have provided synthesis results of data collected by several projects such as the Global Ocean Data Analysis Project (GLODAP, GLODAPv2, GLODAP v2 update), Carbon in Atlantic Ocean (CARINA), and Pacific Ocean Interior Carbon (PACIFICA) projects (Key et al., 2009; Suzuki et al., 2013; Olsen et al., 2016; Olsen et al., 2019). The time frame of this work is that cruises categorized 1 were conducted between 2003 and 2013, all of the resulted data in this work are adjusted for 2003-2013 time frame. Another positive attribute of this work is that uncertainty of correction factors could be estimated.

The author also adds dissolved oxygen concentration data as additional parameter of GND13 using same technology to create nutrients gridded data, unbroken chain of comparison, which means obtained gridded data of dissolved oxygen are traceable to a set of data obtained from 30 key cruises stated in chapter 2 and did not mean SI traceable.

This article is an effort to establish a global nutrients dataset for which comparability and traceability in space and time are explicitly ensured based on the use of CRM/RMs of nutrients in seawater. Another positive attribute of this work is that uncertainty of correction factors could be estimated.

2 Methods and Data

Data from 30 cruises that used CRM/RM for quality control of nutrient concentrations in seawater were used to obtain an accurate picture of the spatial distribution of nutrient concentrations in the ocean. The correction factors for those cruises were set to 1.00 because comparability of nutrient concentrations was ensured (Sato et al., 2010).

For oxygen data, the factors for 30 cruises were assumed to be 1.00 because gridded data of dissolved oxygen are aimed to be traceable to a set of data obtained from 30 key cruises.

2.1 Data collection and quality control

Nutrient data from the global ocean were collected from various sources and separated into categories from 1 to 7 (Table 1). Thirty cruises were assigned to category 1. Twenty-five of the 30 key cruises were carried out by R/V *Mirai* during 2003–2013. The author used RM/CRM on those cruises as working standards for nutrient measurements at all stations to ensure high quality and comparability among the stations and among the cruises. In the Atlantic Ocean, five cruises were also selected as category 1 because RM were used on two of the five cruises. Since comparability of nutrients data between JAMSTEC R/V Mirai cruises during the period from 2003 to 2013 and NIOZ cruises conducted in 2005 and 2007 was explicitly confirmed through inter-laboratory comparison study for reference materials of nutrients in seawater conducted in 2006 and 2008 (Aoyama et al., 2008; 2010) , two cruises were also added to category 1 to increase coverage by category 1 cruises in the Atlantic Ocean. Most of the data in category 2 were obtained from the CARINA project dataset. Most of the data in category 3 were obtained from the PACIFICA project dataset for the period 1991–2008. Many data were obtained from the World Ocean Circulation Experiment (WOCE) Global Hydrographic Climatology (WGHC) (Gouretski and Koltermann, 2004) data product. That dataset includes data from many cruises during the period 1925–1996, and those data were assigned to category 4. Category 5 was intentionally blank for future use. Some cruises conducted by the Japan Meteorological Agency (JMA) were not included in the CARINA, PACIFICA and WGHC datasets. They were therefore included in the dataset for this study and assigned to category 6. Data from about 80 cruises by the JMA and United States institutes that were not included in the above categories were assigned to category 7.

Figures 1–4 show the locations of all the stations where data were collected. In these figures, stations in category 1 are marked in dark blue, stations in category 2 are marked in light blue, and stations in categories 3–7 are marked in red. It is apparent from these figures that the category 1 cruises did not cover the whole ocean, but if category 1 and 2 data are used to create a global dataset, the spatial coverage increases to almost all of the ocean, and the resultant dataset is a high quality global nutrient dataset. In southern hemisphere, to cover the some sea areas where categories 1 and 2 were not there, categories 3-7 were used.

It is important to do quality control before using this historical dataset because it contains questionable data. In the WOCE dataset and later, there are quality flags (WOCE Hydrographic Programme Office, 1994). Only data associated with quality flag 2 (i.e., data quality is good) were therefore used in this study. Because the historical data and some of the data did not have quality flags, a median filter of which criteria is 3 time of standard deviation was criteria for outliers was used to identify questionable data and questionable data were removed from the dataset before vertical integration, estimation of correction factors and create global gridded data.

2.2 Crossover analysis

In general, stations from each cruise within 250 km of 243 points worldwide were selected if there were data from several stations from at least a cruise in category 1 and at least, respectively a cruise from category 2. A few exceptions were crossovers in the Pacific sector of the Southern Ocean, where crossovers were selected from category 2 cruises and category 3–7 cruises or among category 3–7 cruises to expand coverage. Figure 5 shows an example of station locations at P03-P14 crossovers at 24.2°N and 179°named CR081E, where there were two category 1 cruises and two category 3–7 cruises. Supplementary Fig. S1 shows all station locations at the 243 crossovers. Figure 6 shows examples of vertical profiles of nitrate concentrations, phosphate concentrations, nitrate-to-phosphate concentration ratios, and silicate concentrations at crossover CR081. Figure 6 also shows climatological nutrient concentrations in the WGHC dataset and WOA05 dataset for comparison. There were two cruises conducted in 2005 and 2007, which were category 1 cruises, where RMs were used as working standards at all stations by the author. The results from those cruises were in good agreement with data collected within a 250-km radius, and the error bounds (i.e., uncertainties) overlapped completely. In contrast, concentrations from two cruises conducted in 1985 and 1993 were relatively scattered (Fig. 6). To estimate correction factors based on 30 key cruises, vertical integration between depths of 1000 meters and 2000 meters, 1500 meters and 2500 meters and 2000 meters and 3000 meters for nitrate, phosphate, silicate and oxygen were done at all stations within each of the 243 crossovers. This integration was done based on the Akima interpolation method (Akima, 1970). When the number of profiles of a cruise exceeded 3, the standard deviation of the integrated values was calculated as a metric of uncertainty of correction factor. Table 2 shows the valid number of profiles obtained by vertical integration from 1000 meters to 2000 meter depths, from 1500 meter to 2500 meter depths from 2000 meters to 3000 meter depths for nitrate, phosphate, silicate, and oxygen concentrations at the P03-P14 crossover stations at 24.2°N and 179°E. As expected from the vertical profiles at the crossovers, the integrated values in units of μmol m^{-2} for the two cruises in category 1 (e.g., 49MR0505_2_1 and 49MR0706_1_) agreed to within two standard deviations for all four parameters. The standard deviations of two category 2 cruises in 1985 and 1993 were relatively large in general, and there were systematic differences that have already been identified in previous synthesis work. Because there was assurance of comparability of nutrient concentrations among the 30 key cruises, the author set the correction factor for theses cruises to 1.00. Because the measurement uncertainties during these cruises were less than 0.5% in general, the uncertainty of correction factors were assumed to be 0.00.

To estimate correction factors at all crossovers the author selected to use integrated values by vertical integration from 1500 meters to 2500 meter depths because smaller Coefficient of Variation (CV), a ratio of the standard deviations of the integrated values to a mean of the integrated value and largest total number of CV among three integration ranges for nitrate, phosphate and silicate.

The standard deviation of the integrated values for a set of profiles from each cruise within crossovers can be considered as the combined uncertainty of measurement uncertainty at each profile, station-station variability of measurement within a 250-km radius and natural variability of nutrients concentration among several stations within a 250-km radius at crossovers. It is expected that when RM/CRM were used as working standards to get a calibration curve, station-station variability of measurement within a 250-km radius becomes very small while in-house standard was used, station-station variability of measurement within a 250-km radius may contribute to increase combined uncertainty. Therefore, it is interesting to look at the Coefficient of Variation (CV), a ratio of the standard deviations of the integrated values to a mean of the integrated value of the four parameters (Table 3). Figure 7 also shows histograms of CV of integrated value of the nitrate data in categories 1–7. It is very clear that the mean of CV of integrated values were 0.005 for nitrate and phosphate for category 1 cruises and that for silicate was 0.009. The means of CV of integrated values for nitrate, phosphate and silicate were smaller than those for categories 2–7. The main cause of the smaller mean of the CV of the integrated values for nutrient concentrations measured during the category 1 cruises might be the use of CRM/RM. The mean of CV of the integrated values for nutrient concentrations were similar to the precision of each measurement, roughly 0.2–1.0%. It should be also noted that the silicate measurements were compromised by some difficulties and/or instabilities—unlike the nitrate/phosphate measurements—that were observed in the global IC study discussed in the introduction of this article. On the other hand, the corresponding values for category 1 oxygen measurements were similar to those for category 2–7 cruises because there are no seawater matrix reference materials for dissolved oxygen exist and comparability was kept by potassium iodate solution worldwide as similar magnitude.

During the timeframe of this study from 2003 to 2013, temporal variation of nutrients concentrations within a 250-km radius at crossovers at 1500-2500 meter depth was very small and it could be assumed to be negligible based on comparison at crossovers between/among category 1 curies as shown in Figure S1 especially in the Pacific Ocean. Natural variabilities of nutrients within a 250-km radius at 1500-2500 meter depth were similar to or smaller than the combined uncertainty of uncertainty of measurement and station-station variability of measurement within a 250-km radius which were observed based on the data in Table 3 and other crossover points. In other words, deep sea water within a 250-km radius at 1500-2500 meters was quite homogeneous horizontally, and the variability of nutrient concentrations observed in category 2 and 4 cruises might be due to the lower comparability of the nutrient measurements made during those cruises. The larger mean of the standard deviations of the integrated values for the four parameters at crossovers for the cruises in categories 2–7 might reflect the larger combined uncertainty of measurement uncertainty and within-cruise variability (= variability of measurements among several stations within a 250-km radius).

When we do factor correction based on synthesis or the method adopted in this study, we need to consider uncertainty of measurement and within-cruise variability (= variability of measurements among several stations within a 250-km radius) that might cause the correction factors to be uncertain. The uncertainties of the correction factors were estimated in terms of the CV of the integrated values within crossovers as a first step in estimation of correction factors. Key cruises included twothirds of the 243 crossover points (Figs. 1–4). To estimate correction factors at the remaining crossover points, correction factor estimations were done progressively. Based on the wider coverage by the cruises in category 2, those cruises were used as secondary key cruises after correction factors were applied to the integrated values with uncertainty. Factors for cruises in categories 3–7 were then estimated, with the exception of several crossover stations. Supplementary Table 1 shows estimated factors and their uncertainties for all cruises.

Comparisons were made between the factors obtained in this study and in GLODAP v2 (Olsen et al., 2016;2019). Figures 8–11 show the results. For nitrate and phosphate, the correction factors obtained in this study were in good agreement with those obtained by GLODAP v2 when the correction factors relatively deviated far from 1.00. The implication is that both synthesis work and direct comparisons as done by this study can detect differences between cruises and estimated correction factors correctly when the nutrient concentrations obviously differ from values obtained on nearby cruises. For many GLODAP v2 cruises, factors were assigned a value of 1.00, but it is obvious that direct comparisons resulted in factors that were slightly larger or smaller (Figs. 7–9) because synthesis work could not identify differences among cruises if those differences were not large. Direct comparisons, however, could determine correction factors with uncertainties more precisely. In general, the differences of the correction factors obtained by two methods, synthesis like GLODAP v2 and direct comparison as this study, for nitrate and phosphate were around +0.02 and –0.04, whereas the differences for silicate were relatively large: ±0.06. For oxygen, the differences were much larger: ±0.10.

2.3 Gridded dataset

Based on the factors obtained in this study, a dataset was created at latitude and longitude intervals of 0.5° and on 136 isobaric surfaces at intervals of50 meters. The uncertainties of the nutrient concentrations were about 2% for nitrate and phosphate and 5% for silicate and oxygen. This uncertainty was equated to twice the standard deviations of the integrated values for the category 2 cruises. The following steps were used to create the global gridded dataset.

Step 1: Profiles of which factor were determined were used to create the global gridded dataset. Then nutrients concentrations were corrected by factor and vertical interpolations were then done for each profile on 136 layers.

Step 2: To have smooth gridded data at 0 deg. E (=360 deg. E), data obtained step 1 for 0 deg. E to 20 deg. E were copied to 360 deg. E to 380 deg. E region and data for 340 deg. E to 360 deg. E were copied to -20 deg. E to o deg. E. Then to create griddeddata a surface function of The Generic Mapping Tools, GMT (https://www.soest.hawaii.edu/gmt/), were carried out on each of the 136 layers . North of 65°N, the latitude and longitude of the data points were converted to an X–Y surface. Then conduct a surface function of GMT for each depth. Convert the gridded data in the X–Y plane to latitude and longitude at 0.5° intervals.

A gridded dataset with 136 layers at latitude and longitude intervals of 0.5°—the Global Nutrient Dataset 2013— was then created. Figure 12a–d shows the horizontal distributions of nitrate, phosphate, silicate, and oxygen concentrations at a depth of 1800 meters in the Pacific Ocean as an example.

To determine the total amount of nitrate, phosphate, silicate, and oxygen in the ocean, the volume and area corresponding to each grid point were calculated using the ETOPO 2 topographic, bathymetric dataset (2-minute mesh). The concentrations were multiplied by the volume of the obtained grid point to find the number of moles of nitrate, phosphate, silicate, or oxygen at each grid point, and the results were summed for each sea area. In this way the total amounts of nitrate, phosphate, silicate, and oxygen in the ocean were estimated as well as the associated uncertainties.

3 Results

This dataset was designated the Global Nutrients Dataset 2013 (GND13). The GND13 is already available at doi:10.17596/0000001 on the JAMSTEC web site. The Fortran source code and ctl script of Grads are also available at the site. All figures of the horizontal distributions of nitrate, phosphate, silicate, and oxygen are available as supplementary figures of this article.

Table 4 shows the total mass in petagrams of nitrate, phosphate, silicate, and dissolved oxygen in the ocean. Using the same methodology, the total petagrams of nitrate, phosphate, silicate, and dissolved oxygen were also calculated for the WOA09 (Garcia et al., 2010a;2010b) and WGHC datasets. The total amounts of nitrate, phosphate, silicate, and dissolved oxygen ± uncertainty were 573 ± 11 Pg N, 89.0 ± 1.8 Pg P, 3300 ± 170 Pg Si and 7180 ± 360 Pg O_2, respectively. As can be seen in Table 4, the results of GND13 were consistent within uncertainty to the total amounts calculated from the WOA 09 and WGHC climatological concentrations, which had been published previously and were the initial values of various studies based on a current ocean general circulation model. The total amount of nitrate by GND13 was large compared with the literature values: 541 Pg N by Sarmiento and Gruber(2006) and close to 570 Pg N by Wada and Hattori (1990). The medians of the N:P molar ratios at depths >2 km were 14.6 for WOA 09 and 14.3 for GND13, and in the latter case the distribution shows high kurtosis (figure not shown). The implication is that the previous lattice point dataset was generated from a dataset with less comparability, whereas the GND13 dataset was generated from a dataset with higher comparability.

4 Data availability

The GND13 is available at doi:10.17596/0000001 at the JAMSTEC web site http://www.godac.jamstec.go.jp/catalog/data_catalog/metadataDisp/GND13?lang=en.

5 Conclusions

A global nutrients gridded dataset was created and named GND13. Thirty cruises incorporating reference materials for nutrients in seawater or their equivalent were used. The precision of the nutrient analyses was better than 0.2%, and comparability between stations was ensured. Nutrient data were collected from all of the hydrographic cruises from which nutrient data were available. Crossover analyses were conducted at 243 crossovers where data from our cruises served as references to determine factors for adjusting nutrient concentrations obtained during other cruises. Dissolved oxygen concentrations were included as an additional parameter in the dataset using the same protocol. Finally, global datasets of nitrate, phosphate, silicate, and dissolved oxygen concentrations were created at 0.5° latitude and longitude grid points on 136 isobathymetric layers to a depth of 6.5 km. This dataset will facilitate studies of the behavior of carbon:nitrogen:phosphorus:oxygen stoichiometry in the ocean in the near future.

6 Appendices

Supplementary figures

Supplementary tables

7 Supplement link (will be included by Copernicus)

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Author contribution

Michio Aoyama is the only scientist who created the dataset GND13.

Competing interests

The author declares that he has no conflict of interest.

Disclaimer

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Acknowledgments

The author thanks Yukiko Suda and Tomoko Kudo for their work in processing the nutrient data, drawing figures, and making tables.

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Table 1 Summary of data collected and used in this study

Cruise Category	# of EXPOCODE	# of Profiles	Duration From	Duration To	Main sources
		Nitrate			
1	30	2392	2003	2013	R/V *Mirai*
2	104	8857	1981	2008	CARINA
3	73	3598	1991	2008	PACFICA
4	1235	12950	1925	1996	WGHC
6	7	366	1996	2004	JMA
7	79	1931	1981	2008	JMA, USA etc.
		Phosphate			
1	30	2392	2003	2013	R/V *Mirai*
2	102	8624	1981	2008	CARINA
3	72	3580	1991	2008	PACFICA
4	2873	30386	1925	1996	WGHC
6	6	345	1996	2004	JMA
7	78	1913	1981	2008	JMA, USA etc.
		Silicate			
1	30	2392	2003	2013	R/V *Mirai*
2	103	8850	1981	2008	CARINA
3	63	3207	1991	2008	PACFICA
4	1870	22414	1929	1996	WGHC
6	6	345	1996	2004	JMA
7	81	1862	1981	2008	JMA, USA etc.
		Oxygen			
1	30	2319	2003	2013	R/V *Mirai*
2	109	9217	1981	2008	CARINA
3	77	3818	1991	2008	PACFICA
4	4636	49606	1906	1998	WGHC
6	8	426	1992	2004	JMA
7	73	1858	1981	2008	JMA, USA etc.

Table 2 Summary of means and standard deviations of Coefficient of Variation (CV), a ratio of a standard deviations of the integrated values to a mean of the integrated value, within a 250-km radius at crossovers for the 4 variables in each category

Category	Number of cruises	Mean	Standard deviation
	Nitrate		
1	112	0.005	0.003
2	381	0.012	0.013
3	81	0.008	0.005
4	207	0.014	0.016
6	14	0.008	0.005
7	135	0.014	0.014
	Phosphate		
1	115	0.005	0.003
2	360	0.015	0.013
3	80	0.009	0.006
4	373	0.017	0.012
6	14	0.013	0.003
7	132	0.016	0.014
	Silicate		
1	111	0.009	0.012
2	352	0.030	0.032
3	74	0.014	0.011
4	197	0.029	0.028
6	12	0.016	0.010
7	124	0.026	0.029
	Dissolved oxygen		
1	109	0.018	0.026
2	390	0.014	0.029
3	95	0.021	0.030
4	557	0.027	0.038
6	13	0.019	0.017
7	121	0.027	0.041

Table 3 Examples of vertical integration between depths of 1000 m and 2000 m; 1500 m and 2500 m; and 2000 m and 3000 m for nitrate, phosphate, silicate, and oxygen concentrations at CR081, P3-P14 crossovers, 180°E, 24.2°N

Name	EXPO code	category	1000-	2000 m			1500-	2500 m			2000-	3000 m	
			average	standard deviation	# of profiles		average	standard deviation	# of profiles		average	standard deviation	# of profiles
			µmol m^{-2}				µmol m^{-2}				µmol m^{-2}		
				Nitrate									
CR081	49MR0505_2_1	1	40874	247	6		39762	114	6		38635	71	6
CR081	49MR0706_1_1	1	40824	404	8		39685	190	8		38548	145	8
CR081	325023_1_3	3	40605	298	9		39327	82	9		38174	138	9
CR081	31TTTPS24_2_7	7	41343	215	4		40119	186	4		38920	175	4
				Phosphate									
CR081	49MR0505_2_1	1	2939.3	13.7	6		2833.4	9.7	6		2735.6	6.2	6
CR081	49MR0706_1_1	1	2914.9	22.3	9		2809.4	8.6	9		2713.2	8	9
CR081	325023_1_3	3	2842.4	29.4	9		2730.2	20.7	9		2637.2	17.7	9
CR081	727530_4	4	3012.9		2		2944.9		1		2854.7		1
CR081	31TTTPS24_2_7	7	2842.1	23.7	4		2742.4	19.1	4		2649	17.7	4
				Silicate									
CR081	49MR0505_2_1	1	136372	2157	6		150552	1112	6		155601	667	6
CR081	49MR0706_1_1	1	134493	3817	9		147491	2004	9		151553	1080	9
CR081	325023_1_3	3	141411	4445	8		154382	3018	9		158403	2078	9
CR081	31TTTPS24_2_7	7	137563	1057	3		152510	1599	4		157121	1043	4
				Oxygen									
CR081	49MR0505_2_1	1	71030	2352	6		94479	1489	6		113649	1211	6
CR081	49MR0706_1_1	1	75838	8050	9		96380	1875	9		115548	1576	9
CR081	325023_1_3	3	73899	7080	9		96608	3035	9		115641	1450	9
CR081	727530_4	4	82542	7715	3		93094		1		109299		1
CR081	31TTTPS24_2_7	7	76793	2588	4		97014	1228	4		116081	1561	4

Table 4 Total amounts of nitrate nitrogen, phosphate phosphorous, silicate silicon, and dissolved oxygen and nitrate vs. phosphate ratios in the global ocean

	GND13	WOA09	WGHC	Sarmiento and Gruber (2006)	Wada and Hattori (1990)
	Pg	Pg	Pg	Pg	Pg
Nitrate nitrogen	573 ± 11	570	590	541	570
Phosphate phosphorus	89.0 ± 1.8	88.3	90.5		
Silicate silicon	3300 ± 170	3330	3380		
Dissolve oxygen	7180 ± 360	7250	7240		
Nitrate vs. phosphate (wt:wt) ratio	6.44 ± 0.18	6.46	6.52		
Nitrate vs. phosphate (mol:mol) ratio	14.23 ± 0.40	14.27	14.41		

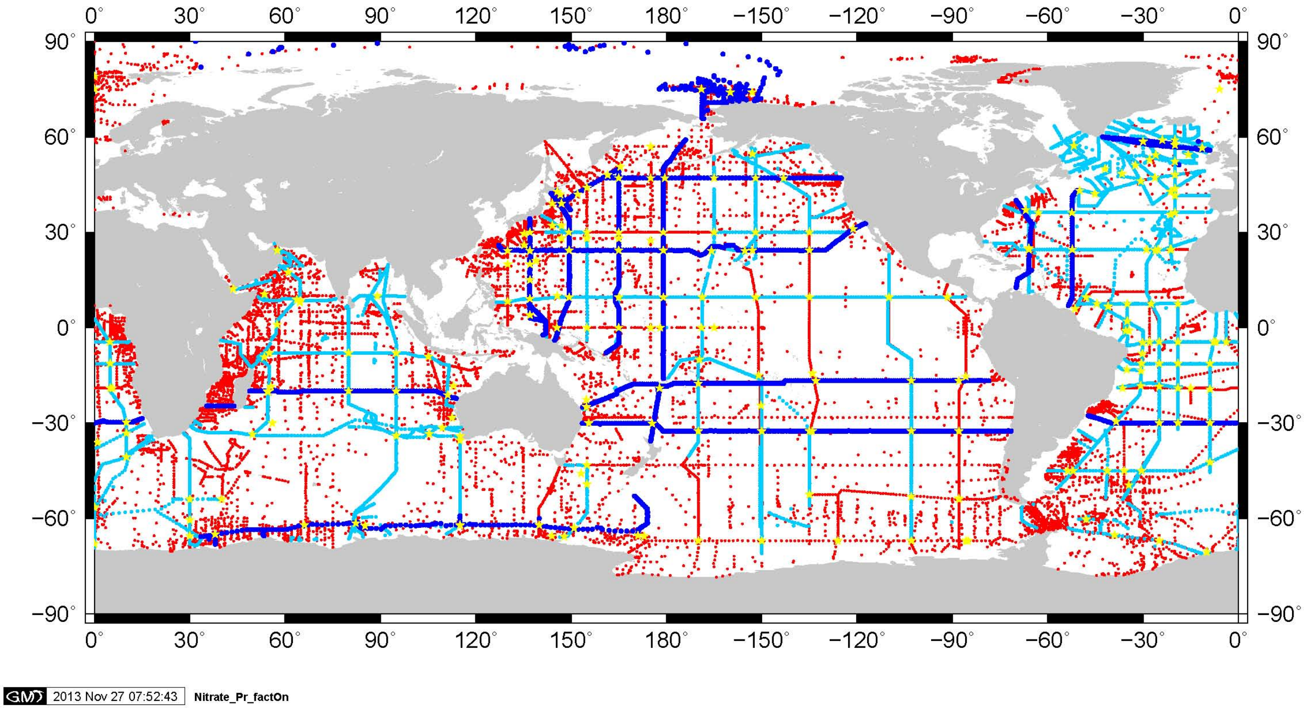


Figure 1: Sampling locations where nitrate concentrations were measured and tracks of cruises that measured nitrate concentrations. Dark blue: category 1 cruises with CRM/RM or equivalent quality control. Light blue: category 2 cruises, WOCE/GO-SHIP cruises, but no CRM/RM used. Red: cruises in categories 3-7. Yellow points are crossover points.

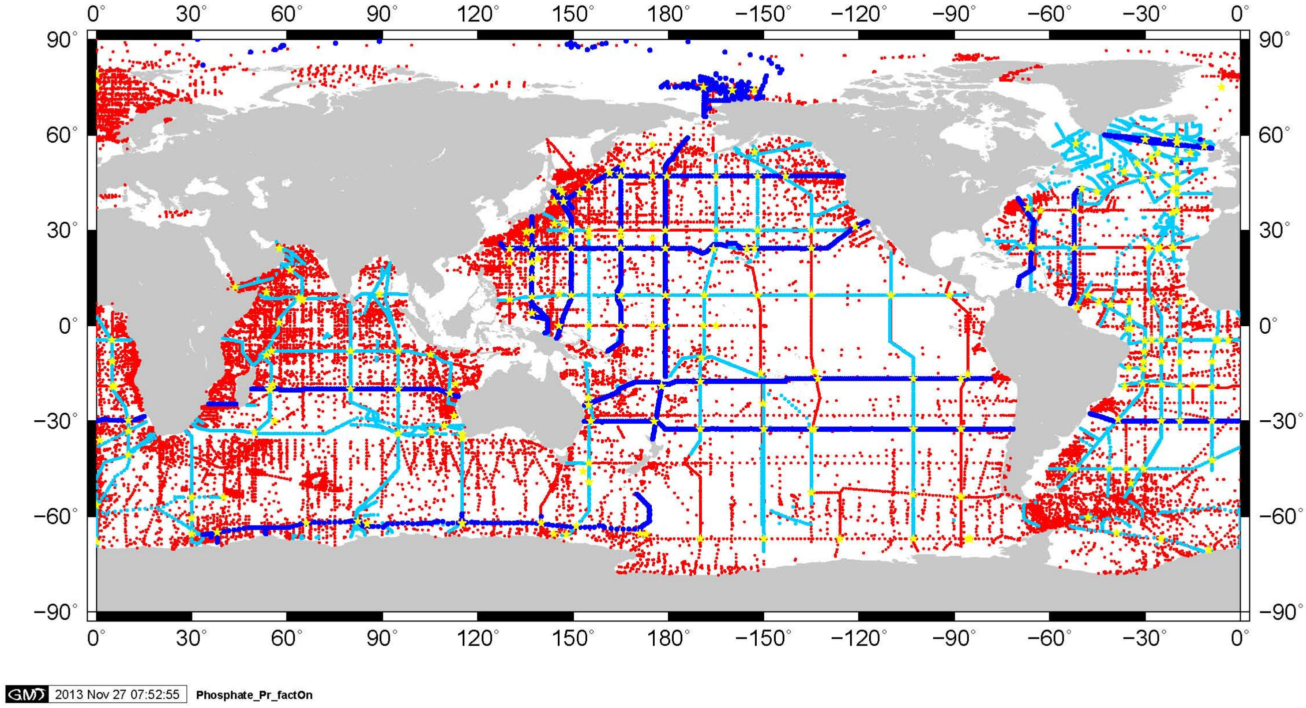


Fig. 2 same as Fig. 1 but for phosphate

Figure 2: Same as Fig. 1, but for phosphate.

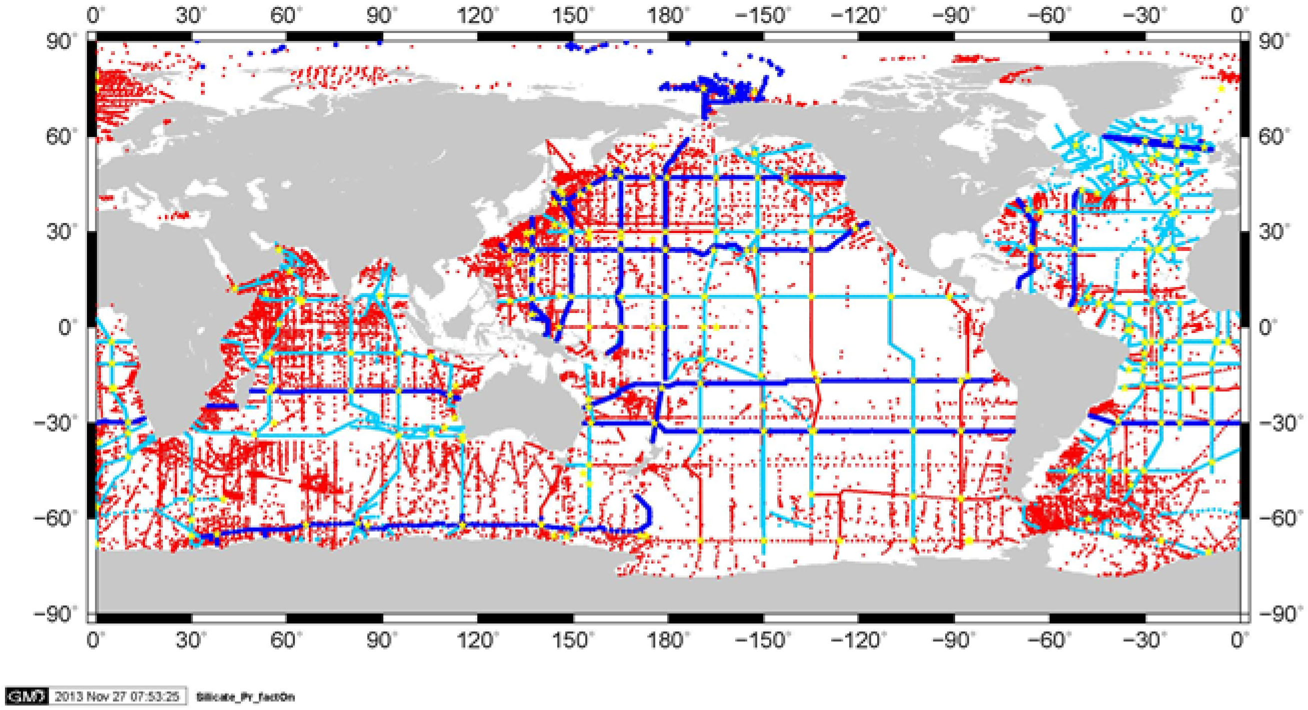


Figure 3: Same as Fig. 1, but for silicate.

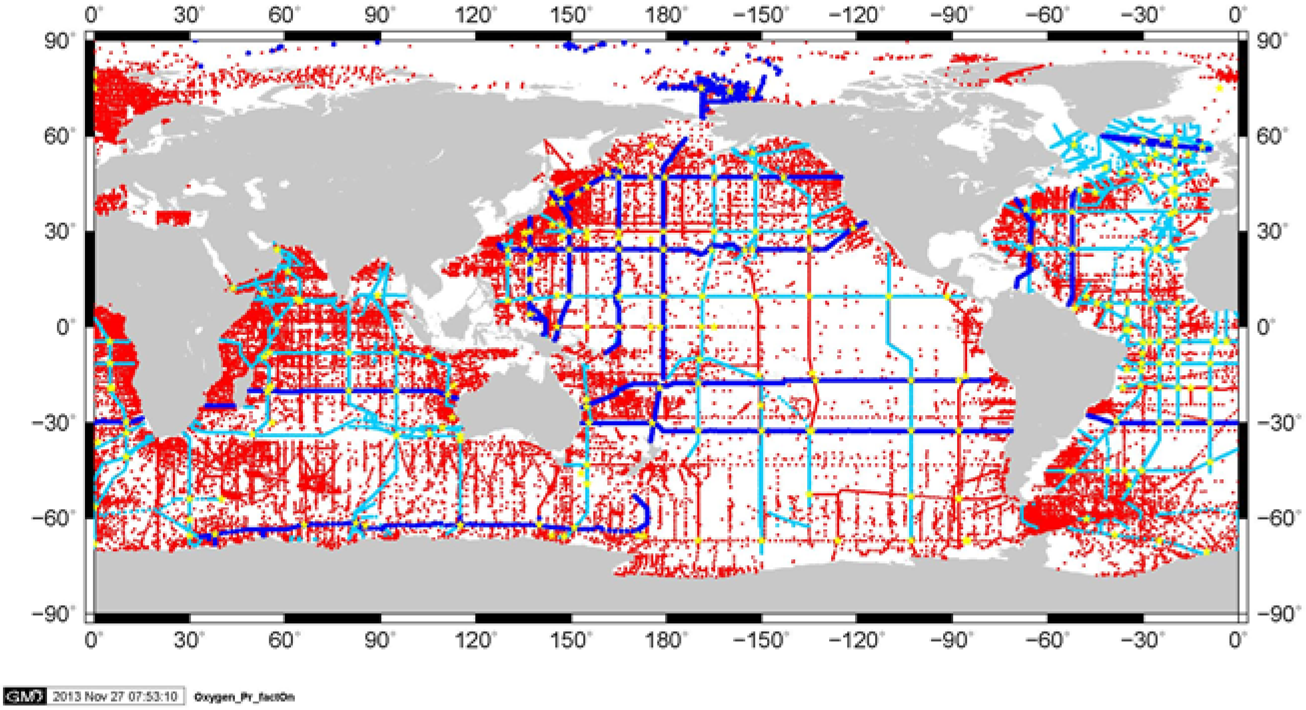


Figure 4: Same as Fig. 1, but for oxygen.

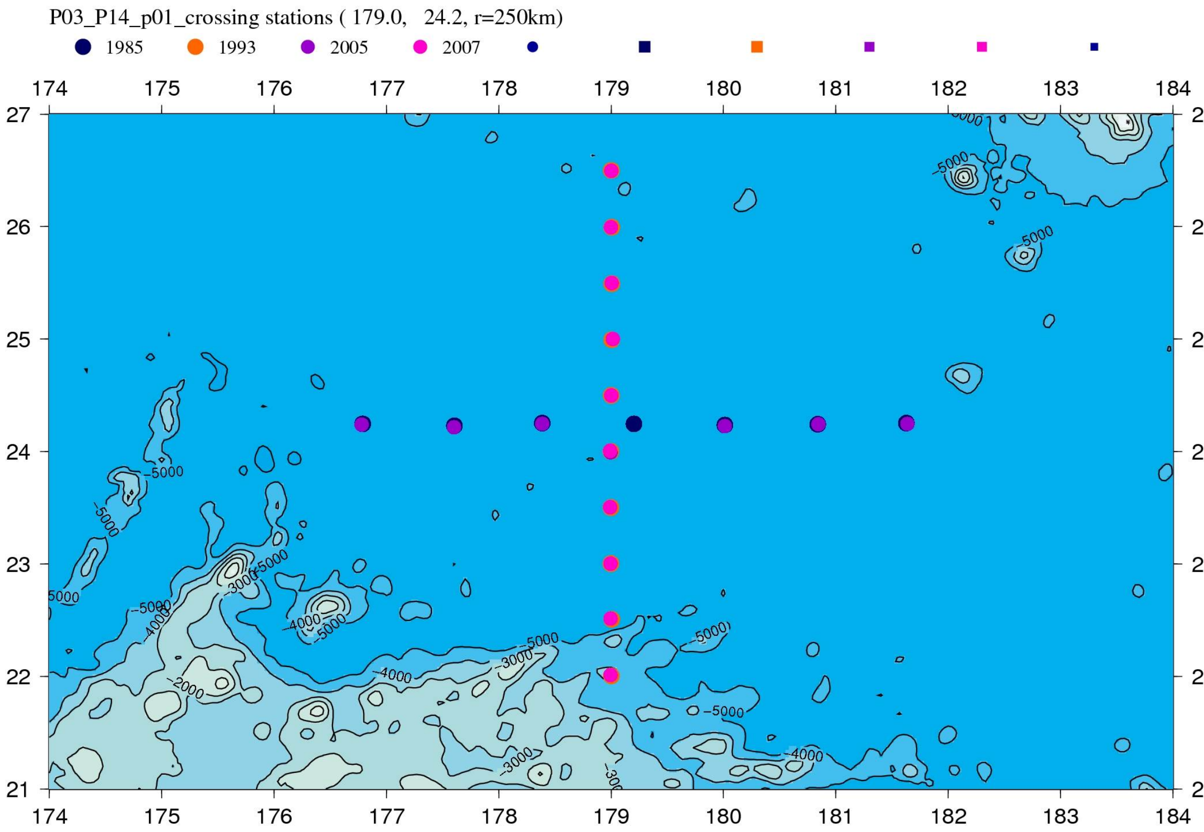


Figure 5: Example of crossover stations for comparison at P03-P14 crossover.

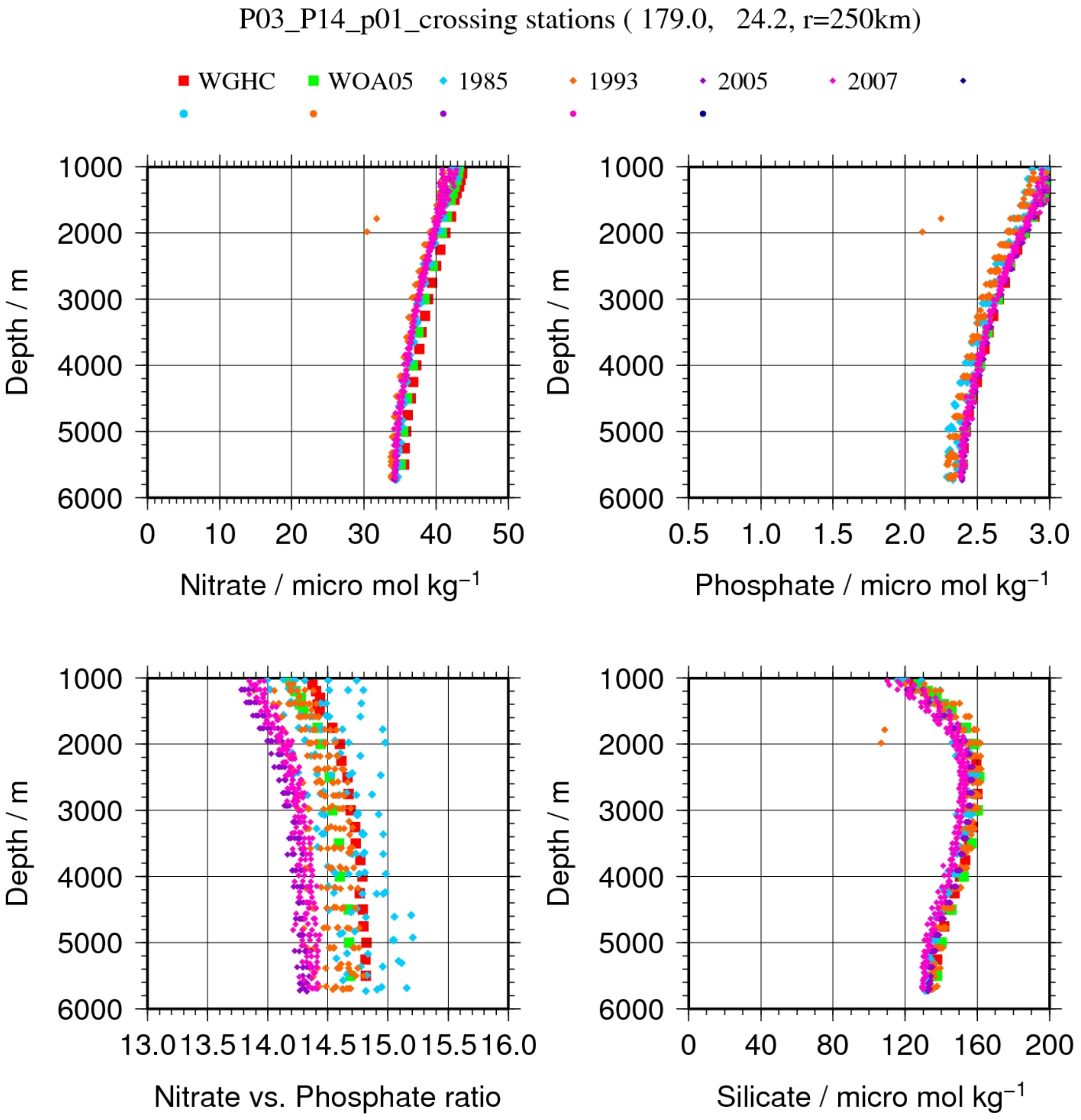
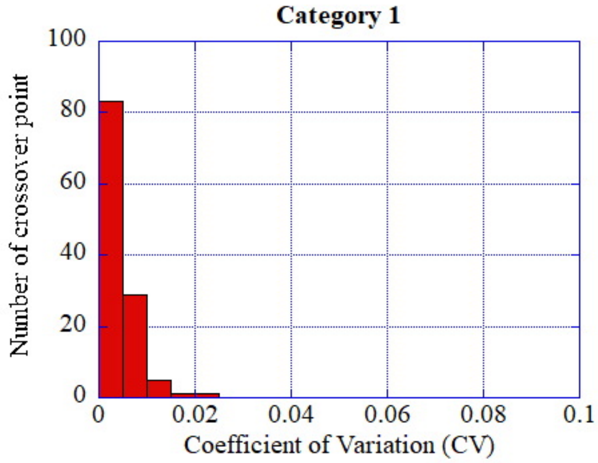
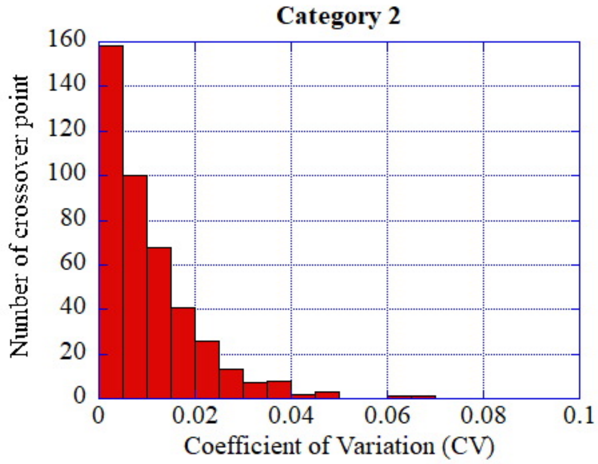


Figure 6: Example of vertical profiles of nitrate and phosphate concentrations, the nitrate:phosphate molar ratio, and silicate concentrations at the P03-P14 crossover (n.b., during the 2005 and 2007 cruises, the author used RM as an in-house standard.)

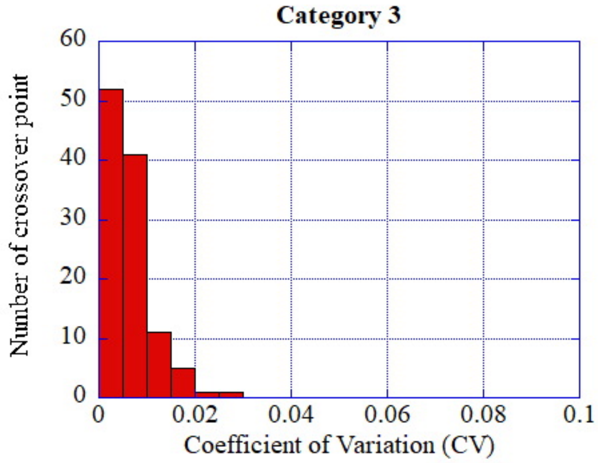
(a)


Category 1
Number of crossover point
100
80
60
40
20
0
0
0.02
0.04
0.06
0.08
0.1
Coefficient of Variation (CV)

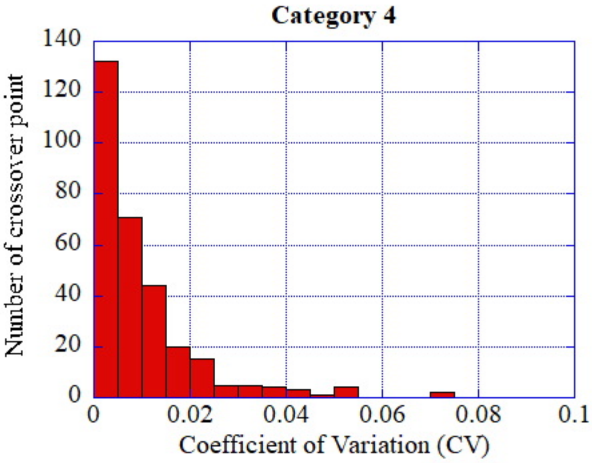
(b)


Category 2
Number of crossover point
160
140
120
100
80
60
40
20
0
0
0.02
0.04
0.06
0.08
0.1
Coefficient of Variation (CV)

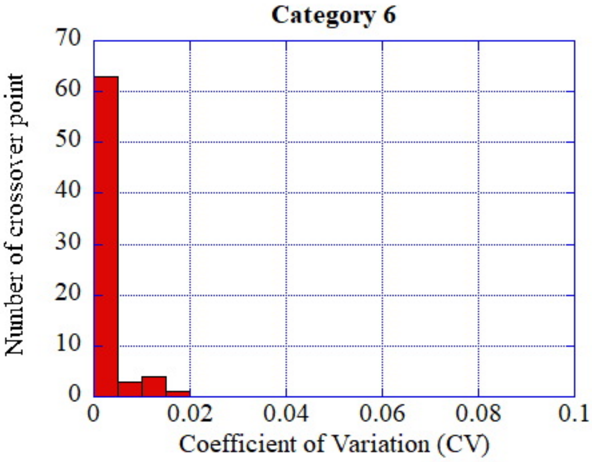
(c)


Category 3
Number of crossover point
60
50
40
30
20
10
0
0
0.02
0.04
0.06
0.08
0.1
Coefficient of Variation (CV)

(d)


Category 4
Number of crossover point
0
20
40
60
80
100
120
140
0
0.02
0.04
0.06
0.08
0.1
Coefficient of Variation (CV)

(e)


Category 6
Number of crossover point
0
10
20
30
40
50
60
70
0
0.02
0.04
0.06
0.08
0.1
Coefficient of Variation (CV)

(f)

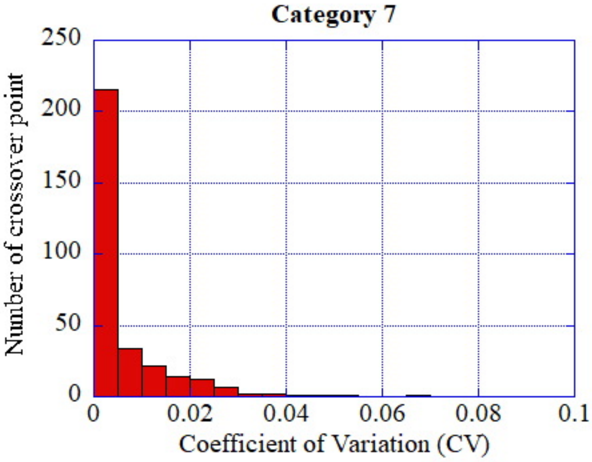

Category 7
Number of crossover point
0
50
100
150
200
250
0
0.02
0.04
0.06
0.08
0.1
Coefficient of Variation (CV)

Figure 7: Histograms of Coefficient of Variation (CV), a ratio of the standard deviations of the integrated values to a mean of the integrated value, within a 250-km radius for nitrate in (a) category 1, (b) category 2, (c) category 3, (d) category 4, (e) category 6, and (f) category 7.

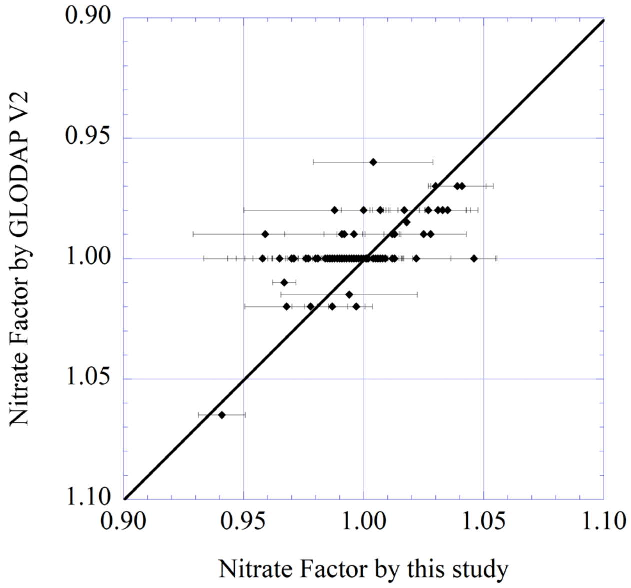


Figure 8: A comparison of correction factors for nitrate by this study with uncertainties and by GLODAP V2.

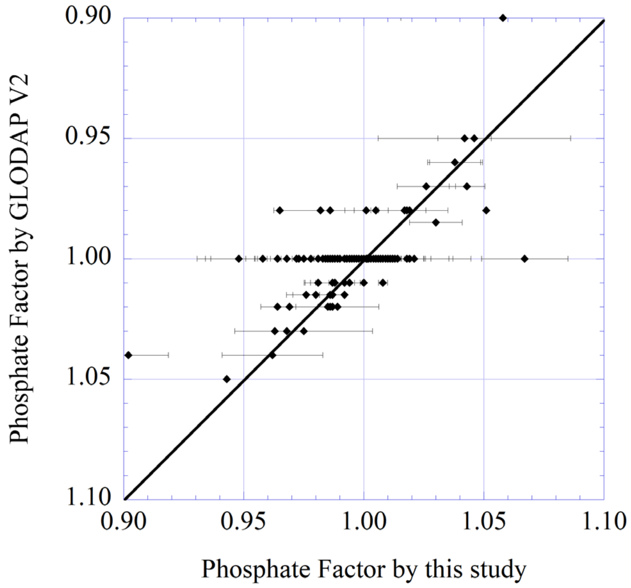


Figure 9: Same as Fig. 7, but for phosphate.

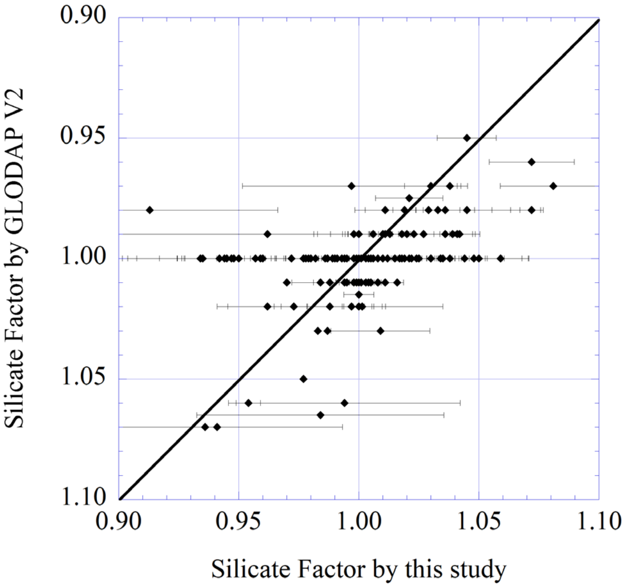


Figure 10: Same as Fig. 7, but for silicate.

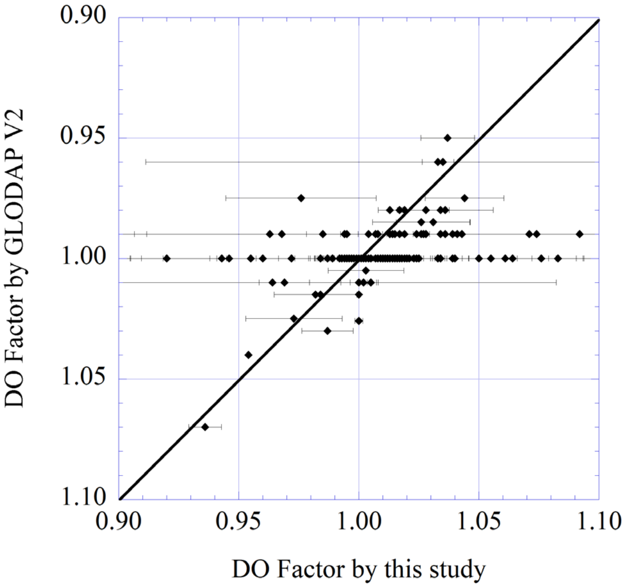
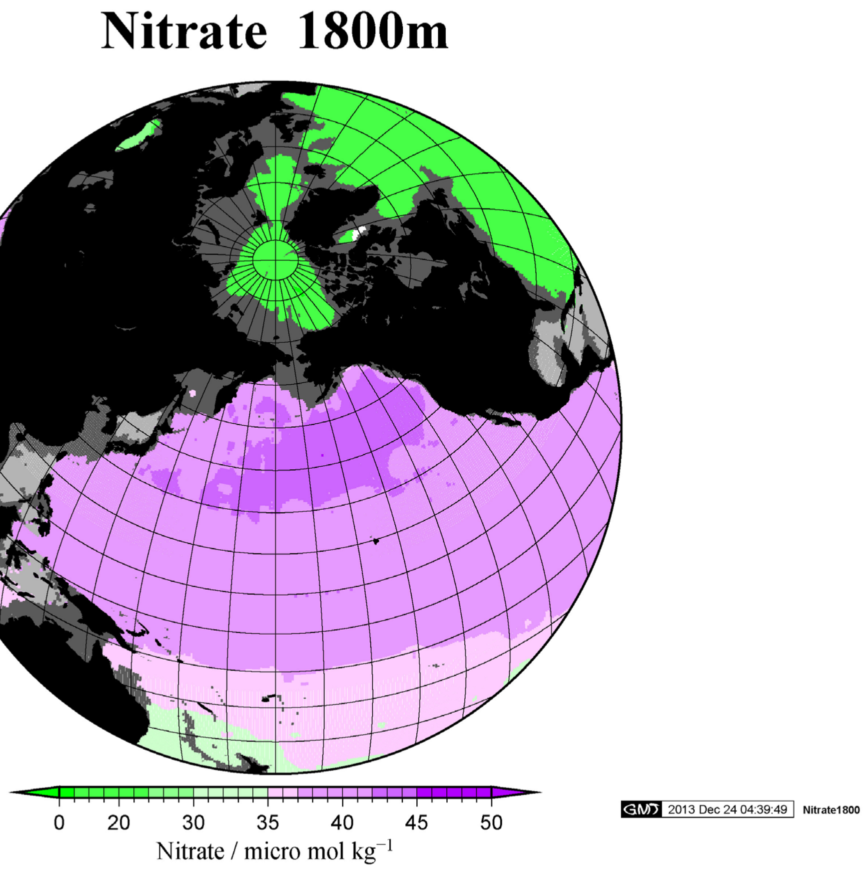
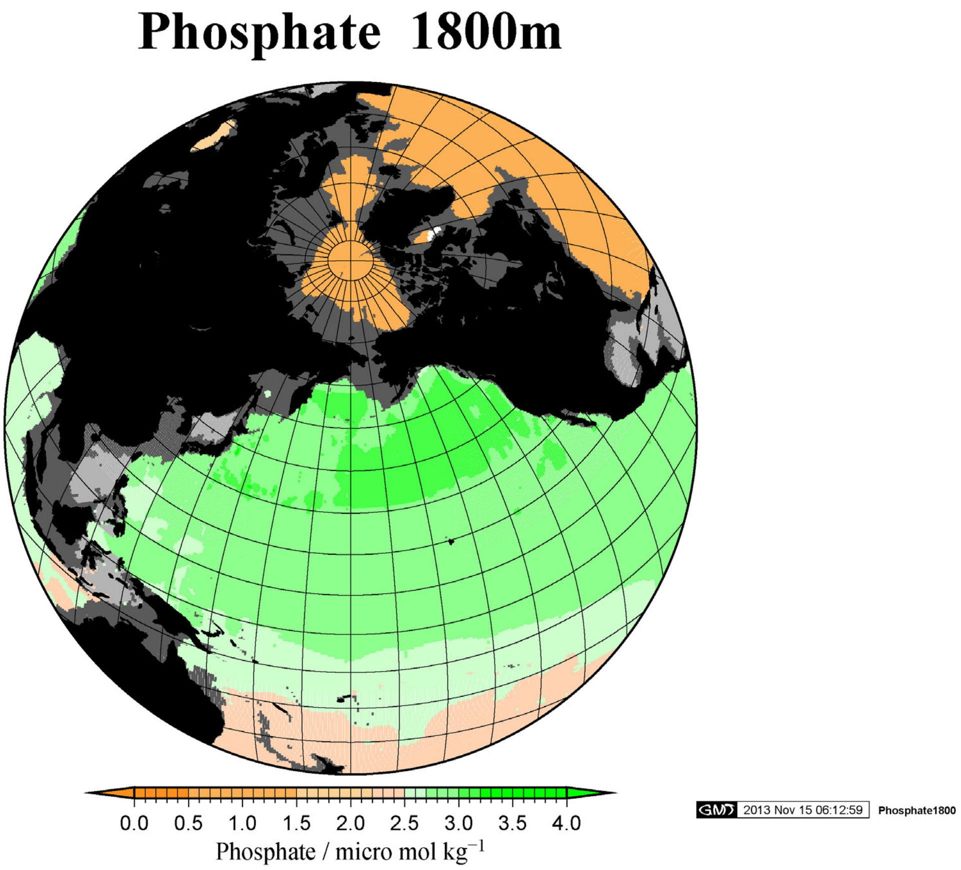


Figure 11: Same as Fig. 7, but for dissolved oxygen (DO).

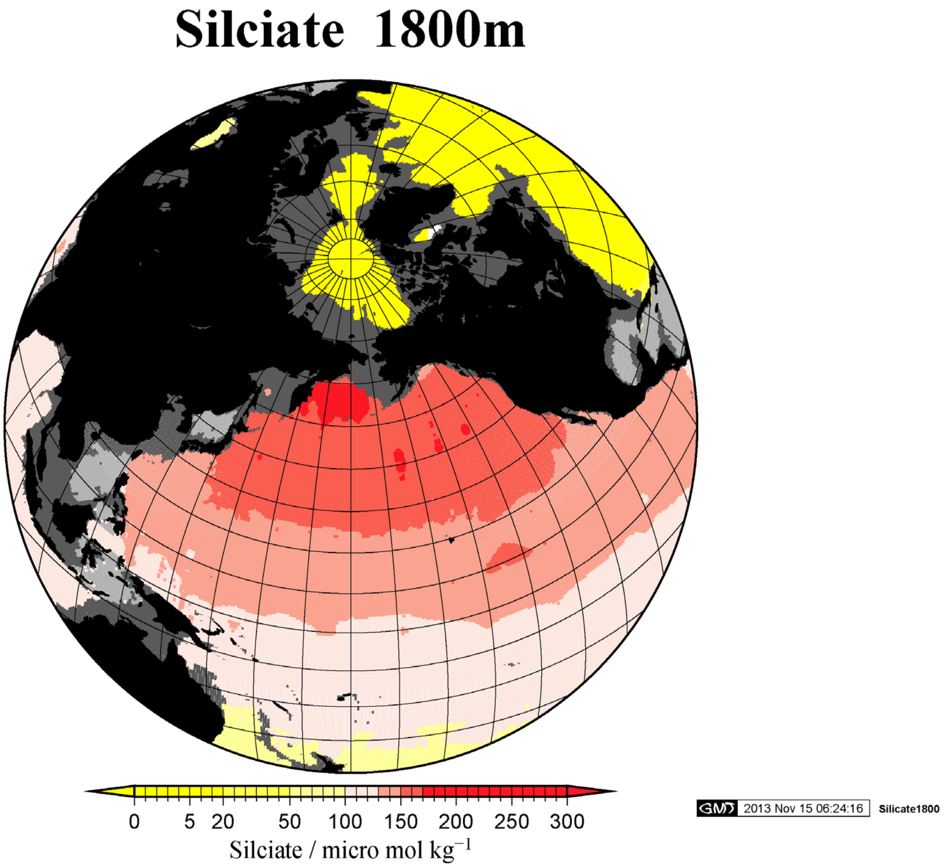
(a)


Nitrate 1800m
0
20
30
35
40
45
50
Nitrate / micro mol kg^{-1}
GMT 2013 Dec 24 04:39:49
Nitrate1800

(b)


Phosphate 1800m

(c)


Silciate 1800m

(d)

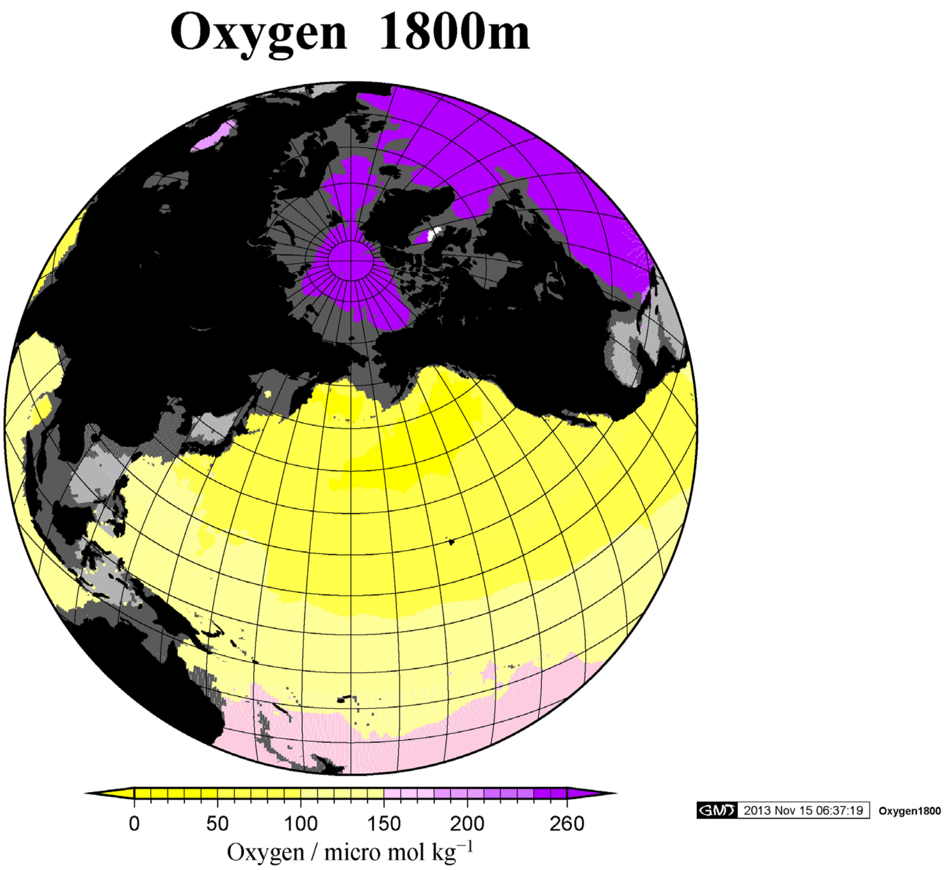


Figure 12: (a) Obtained nitrate concentration field at depth of 1800 m, (b) same as (a) but for phosphate, (c) same as (a) but for silicate, and (d) same as (a) but for dissolved oxygen.