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The Irminger Sea and the Iceland Sea time series measurements of sea water carbon and nutrient chemistry 1983–2006

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Abstract

This paper describes the ways and means of assembling and quality controlling the Irminger Sea and Iceland Sea time-series biogeochemical data which are included in the CARINA data set. The Irminger Sea and the Iceland Sea are hydrographically different regions where measurements of sea water carbon and nutrient chemistry were started in 1983. The sampling is seasonal, four times a year. The carbon chemistry is studied with measurements of the partial pressure of carbon dioxide in seawater, $p\text{CO}_2$, and total dissolved inorganic carbon, TCO_2 . The carbon chemistry data are for surface waters only until 1994 when water column sampling was initiated. Other measured parameters are salinity, dissolved oxygen and the inorganic nutrients nitrate, phosphate and silicate. Because of the CARINA criteria for secondary quality control, depth >1500 m, the IRM-TS could not be included in the routine QC and the IS-TS only in a limited way. However, with the information provided here, the quality of the data can be assessed e.g. on the basis of the results obtained with the use of reference materials.

Data coverage and parameter measured

Repository-Reference:

doi:10.3334/CDIAC/otg.CARINA.AMS.V1.2

doi:10.3334/CDIAC/otg.CARINA.ATL.V1.0

Available at: http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html

Coverage: 64° N–68° N; 28° W–12° W

Location Name: Irminger Sea and Iceland Sea

Date/Time Start: 1983-03-05

Date/Time End: 2006-02-10

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Data Product Parameter Name	Data Product Flag Name	Exchange File Parameter Name	Exchange File Flag Name	Units
station		STANBR		
day		DATE		
month		DATE		
year		DATE		
latitude		LATITUDE		decimal
longitude		LONGITUDE		decimal
depth		DEPTH		meters
temperature		CTDTMP		°C
salinity	sf	SALNTY	SALNTY_FLAG_W	
ctdsal	ctdsf	CTDSAL	CTDSAL_FLAG_W	
pressure		CTDPRS		decibars
oxygen	of	OXYGEN	OXYGEN_FLAG_W	micromole
nitrate	no3f	NITRAT	NITRAT_FLAG_W	micromole
silicate	sif	SILCAT	SILCAT_FLAG_W	micromole
phosphate	po4f	PHSPHT	PHSPHT_FLAG_W	micromole
tco2	tco2f	TCARBN	TCARBN_FLAG_W	micromole
		PCO2	PCO2_FLAG_W	microatm
		PCO2_TMP		°C

For a complete list of all parameters available in CARINA see (Key et al., 2009). Note the different names for the parameters in the Exchange files (the individual cruise files) and the merged data product.

1 Introduction

In 1983 a study of the seasonal variability of carbon-nutrient chemistry was initiated off the Iceland shelf in two hydrographically different regions of the northern North Atlantic (Takahashi et al., 1985; Peng et al., 1987). One station was in the northern Irminger Sea (IRM-TS) with relatively warm and saline ($S > 35$) Modified North Atlantic Water derived from the North Atlantic Drift. This location may also be described as representing the sub-polar gyre (Hátún et al., 2005). The other station was in the Iceland Sea (IS-TS) where cold Arctic Intermediate Water, formed from Atlantic Water and low salinity Polar Water usually predominates but the Polar Water influence in the surface layers is variable (Stefánsson, 1962; Hansen and Østerhus, 2000). Both stations are thus in regions important as sources for North Atlantic Deep Water (NADW). The seasonal variability study was expanded in time and the sampling incorporated into the quarterly cruises of the repeat hydrography network of the Marine Research Institute (MRI) in Reykjavik, Iceland. These observations have been carried out under the EC projects ESOP-2, TRACTOR and currently CARBOOCEAN and EPOCA.

2 Data Provenance and Structure

The CARINA database includes data and metadata from 188 oceanographic cruises/campaigns, of which five entries consist of multiple cruises (Key et al., 2009). The IS and IRM time series contribute to the CARINA data. However, since these stations are in relatively shallow locations compared to the CARINA secondary quality control criteria, depth > 1500 m. and considering also the high temporal variability, IRM-TS could not be included in the secondary QC. Data from the IS-TS is however included in the secondary QC for TCO₂ and nutrients as described in Olsen (2009) and Olafsson and Olsen (2009). Here we describe the methods and quality control procedures applied in gathering the two time series data sets. The IRM-TS is included in the CARINA-ATL region (Tanhua et al., 2009) and the IS-TS is included in the CARINA-

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AMS region (Olsen et al., 2009).

The repeat hydrography network of the Marine Research Institute (MRI) is carried out in quarterly 14 day cruises conducted generally in February, May, August and November each year. The time series stations are located at 64.33° N, 28.0° W (IRM-TS) where the depth is 1000 m and the IS-TS station is at 68.0° N, 12.67° W where the depth is 1850 m (Fig. 1). Occasionally, weather conditions have prevented work at these locations and data from nearby stations, if available, are used instead.

Samples from all collection depths have been taken for salinity, dissolved oxygen and inorganic nutrients. From 1983 to 1991 only surface samples for $p\text{CO}_2$ and TCO_2 were collected. Water column sampling for TCO_2 started in 1991 and for $p\text{CO}_2$ in 1994.

3 Methods and quality control procedures

3.1 Hydrography

From 1983 to the end of 1989 the station water sampling was conducted with TPN-Nansen water bottles, from HYDROBIOS GmbH, on a hydrowire. They were fitted with reversing mercury thermometers. From the beginning of 1990 the station work has been conducted using SEA-BIRD Conductivity-Temperature-Depth (CTD) profiling instruments and water bottles on a rosette. Sample salinity measurements were carried out using Guildline Autosal Model 8400 salinometers.

3.2 Dissolved oxygen

Dissolved oxygen has been determined throughout the time series by an in-bottle microburette Winkler titration and visual end point detection (Carpenter, 1965). The sample bottles are volume calibrated Quickfit brand Erlenmeyer type of 50 ml nominal volume.

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3.3 Inorganic nutrients

Samples for the determinations of the phosphate, nitrate (nitrate+nitrite) and silicate concentrations have been collected in 250 ml soft low density polyethylene acid washed bottles. They are kept refrigerated if the analysis is carried onboard, as is common in the spring, but frozen for analysis ashore as is common in the other seasons. In spring and summer, samples from the surface layer, 0–60 m, are syringe filtered through a 0.45 μm Whatman PURADISC syringe filter to avoid turbidity blank effects, particularly on phosphate. Samples from deeper water are not filtered. A Chemlab three channel autoanalyzer has been used since 1987, set up for determinations of dissolved phosphate, nitrate and silicate. The methods were those described by Grasshoff (Grasshoff, 1970) except for phosphate were a modified version of the Murphy and Riley method was automated (Murphy and Riley, 1962). A series of 5 working standards is prepared with each batch of samples and the response fitted to concentration with a polynomial regression. Prior to 1987 a one channel Technicon AutoAnalyzer II was used for nitrate and silicate and a manual method for phosphate (Murphy and Riley, 1962).

3.3.1 Nutrient analysis quality control

To assess the accuracy of the nutrient methods and procedures we have participated in and subscribed to the QUASIMEME laboratory QC programme and received materials for analysis twice a year (Wells et al., 1997) since 1993. In QUASIMEME the laboratory performance is expressed with a z-score where $|z| < 2$ is considered as acceptable results and where z is the difference between the laboratory result and the assigned value divided by the total error (Cofino and Wells, 1994). Here we prefer to express MRI long term nutrient analyses performance on the basis of the differences between reported and assigned concentrations rather than z-scores as these differences are directly comparable to the analytical uncertainty (Fig. 2). The average deviation of MRI reported values for nitrate (Fig. 2a) from 1993–2008 is $-0.12 \mu\text{mol/l}$ (standard deviation = 0.16, $n=28$), for phosphate (Fig. 2b) it is $-0.02 \mu\text{mol/l}$ (standard deviation = 0.02,

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$n=28$). From 1996 silicate has been measured (Fig. 2c) and the average deviation is $-0.11 \mu\text{mol/l}$ (standard deviation = 0.27, $n=23$). In relation to the highest nutrient concentrations found on the time series stations this gives less than 1.5% error for nitrate, 3.5% for phosphate and 2.5% for silicate.

In addition, a laboratory reference material, LRM (Aminot and K erouel, 1998), is regularly produced, assessed and compared to QUASIMEME materials. The LRM has nutrient concentrations within the range found for the regional seawater and samples of the LRM are run with each sample batch. Results from these measurements are indicative of the precision and accuracy of the daily procedures. The LRM results are generally within accepted limits, $\pm 0.2 \mu\text{mol/l}$ for nitrate and silicate, $\pm 0.03 \mu\text{mol/l}$ for phosphate. Corrections based on the LRM results need rarely to be applied but he results do occasionally give cause for re-running samples.

3.4 Partial pressure of carbon dioxide in seawater

From 1983 to spring 1993, samples for $p\text{CO}_2$ were collected onboard by recirculating 500 ml marine air in a closed system through a bubbler immersed in a surface seawater sample (4l). The equilibrated gas was isolated and sealed in a 300 ml glass flask equipped with a stopcock at each end and shipped for analysis at Lamont-Doherty Geological Observatory (LDEO) by means of a gas chromatography. Air samples were also collected in 300-ml glass flasks by suction using a hand pump and were analysed the same way. The gas chromatograph was calibrated using air- CO_2 gas mixtures which had been analysed by C. D. Keeling of the Scripps Institution of Oceanography. After mid year 1993, 500-ml seawater samples for $p\text{CO}_2$ were brought back to MRI in screw capped Pyrex bottles, inoculated with saturated HgCl_2 solutions (400 microliters) and kept in dark cold storage during the cruise. Their $p\text{CO}_2$ values were determined at a known temperature using the bubble-type equilibrator system coupled with a gas chromatograph (Chipman et al., 1993), which was calibrated with three air- CO_2 mixtures tied to the Keeling standards. The $p\text{CO}_2$ data are not included in the merged CARINA data products, but are included in the individual cruise file avail-

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able at http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html.

3.4.1 Storage experiment of $p\text{CO}_2$ samples

The effects of sample storage were evaluated by collection of two sets of 12 paired samples during spring bloom, 2 June 1998 in the Iceland Sea at 68°N , 18.8°W . One set was from the surface ($t=1.83^\circ\text{C}$) and the other from 200 m ($t=1.05^\circ\text{C}$), well below the euphotic layer. Duplicate samples were analysed ashore over the period 3 to 23 June (Fig. 3). The change with time of $p\text{CO}_2$ in the surface samples and 200 m samples were $-0.006\pm 0.05\ \mu\text{atm d}^{-1}$ and $-0.06\pm 0.08\ \mu\text{atm d}^{-1}$ respectively, and was found to be very small. The mean concentrations for 12 surface samples were $163.8\pm 1.1\ \mu\text{atm}$ and $383.4\pm 1.9\ \mu\text{atm}$ for the 200 m samples. This indicates that sample storage of up to three weeks has insignificant influence on $p\text{CO}_2$ and that the overall precision of the $p\text{CO}_2$ determinations is better than $\pm 2\ \mu\text{atm}$.

3.5 Dissolved inorganic carbon

Total dissolved inorganic carbon (TCO_2) has been determined in HgCl_2 -preserved samples by coulometry (Chipman et al., 1993) using at LDEO the Coulometrics CM-5010 instrument. HgCl_2 was found to be an effective preservation agent for TCO_2 in seawater samples in tightly sealed bottles stored up to 7 months (Takahashi et al., 1970). Prior to 1991 the samples were analysed at LDEO where the coulometer was calibrated with weighed quantities of carbonate crystals (Iceland spar (CaCO_3) and heat treated Na_2CO_3) and volumetrically determined CO_2 gas (Takahashi et al., 1985). These calibrations were consistent with Keeling's manometric values as demonstrated by (Wong, 1970) using the Keeling's manometric system. The overall precision in the period 1983 to 1990 is estimated as $\pm 4\ \mu\text{mol kg}^{-1}$ (Takahashi et al., 1985). As demonstrated extensively through the WOCE Program, the gas loop calibration method yielded TCO_2 values consistent with those in the Dickson reference waters, which were tied to the Keeling's manometric system (Rubin et al., 1998; Takahashi et al., 2006).

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From 1991 the coulometric determinations (using an improved Coulometrics Model CM-5011) were performed at MRI where the coulometer was calibrated using 99.998% CO₂ gas in fixed volume gas loops at a known temperature (Chipman et al., 1993).

The Iceland Sea time series TCO₂ data were assessed as a part of the Nordic Seas CARINA data (Olsen, 2009). They were not included in the crossover and inversion analyses but it was concluded on the basis of nitrate-TCO₂ relations that the TCO₂ data appeared reasonable (Olsen, 2009).

3.5.1 TCO₂ quality control

Accuracy of the TCO₂ determinations at MRI is maintained since 1992 by comparison of results with sea water reference material (DRM) calibrated and supplied by Dr. Andrew G. Dickson of the Scripps Institution of Oceanography. In 1999 the coulometer system gas loop volumes were reassessed on the basis of a comparison with certified reference materials (CRMs) provided by A. Dickson. The reevaluation, MRI-CRM, indicated a systematic error of $-4.7 \pm 2.0 \mu\text{mol C kg}^{-1}$ which was ascribed to errors in the gas loop volumes (Fig. 4). A correction factor of 1.0029 was hence applied to the 1991–1998 results. No analyses were conducted in 1999 and 2000. In 2001 the loop correction factor was taken account of in the TCO₂ analysis software and the coulometer was factory serviced and recalibrated. From 2001 to 2008 the observed differences (MRI-DRM) were $5.3 \pm 2.1 \mu\text{mol C kg}^{-1}$ (Fig. 4). The standard deviation for the observed differences in 212 reference material determinations in the period 1992–1999 was $2.0 \mu\text{mol kg}^{-1}$ and $2.1 \mu\text{mol kg}^{-1}$ for 169 reference material determinations after 2001 (Fig. 4). The overall precision after 2001 is estimated as $\pm 2 \mu\text{mol kg}^{-1}$ and the overall accuracy as $\pm 1 \mu\text{mol kg}^{-1}$.

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4 Summary

The ways and means of assembling and quality controlling the Irminger Sea and Iceland Sea time-series biogeochemical data are described. These stations are in relatively shallow, but oceanographically important locations. Compared to the CARINA criteria, depth >1500 m, IRM-TS could not be included in secondary QC and the IS-TS only in a limited way. However, with the information provided here, the quality of the data can be assessed e.g. on the basis of the results obtained with the use of reference materials.

5 Data access

The whole CARINA database set is published at http://cdiac.ornl.gov/oceans/CARINA/Carina_inv.html. It contains 188 individual cruise files in comma-separated, WHPO exchange format. Condensed metadata are contained in the header of each data file. In addition, the CARINA database contains three merged, comma-separated data files with the data products. These files are divided into the three geographical regions of CARINA. No special software is needed to access the data, but software for MATLAB users is offered to facilitate reading of the data.

Acknowledgements. The authors thank all colleagues at the Marine Research Institute in Iceland, who have cooperated and assisted in the time series work in its course since 1983. John Goddard and Dave Chipman of LDEO were instrumental during the early stage. This work is supported by the European Community Sixth Framework Programme CARBOOCEAN IP, Marine carbon sources and sinks assessment Contract no. 511176. T. T. is supported by a grant (NAO30AR4320179P27) from US NOAA.

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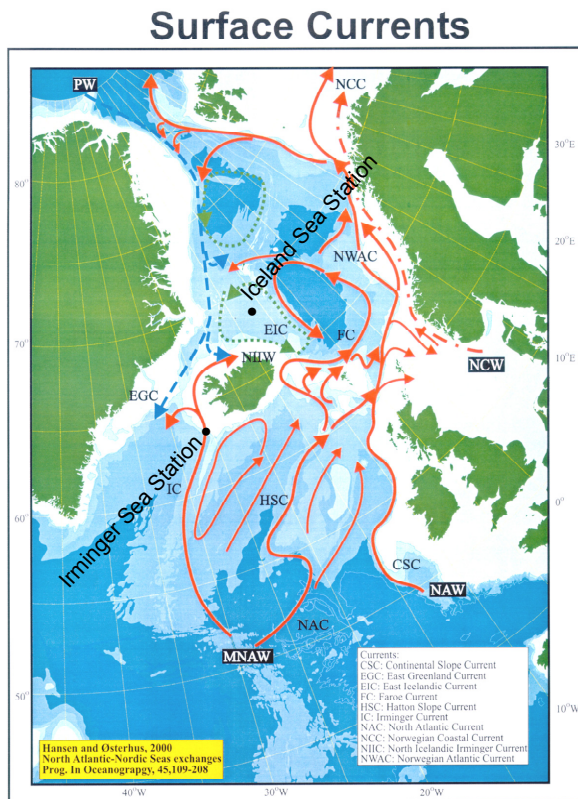


Fig. 1. Locations of the Irminger Sea and the Iceland Sea time series stations inserted on the N-Atlantic surface current chart of Hansen and Østerhus (2000).

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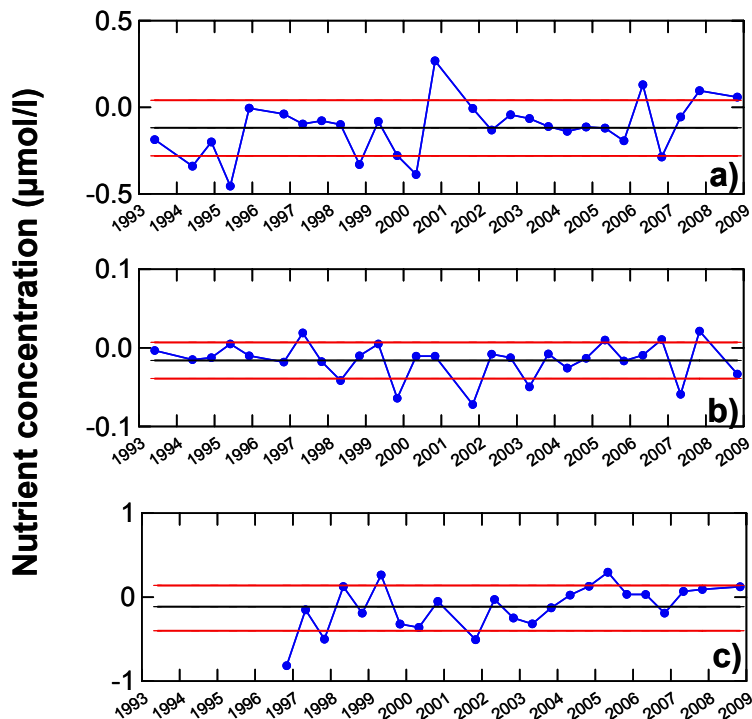


Fig. 2. Average MRI-IS deviations of **(a)** nitrate, **(b)** phosphate and **(c)** silicate concentrations (in $\mu\text{mol/l}$) from assigned values in QUASIMEME sea water test materials 1993–2008 (silicate from 1996). The overall long term mean deviations are shown with black slashed lines and their standard deviations are shown with a red dotted line. The long term mean deviation is $-0.12 \mu\text{mol/l}$ (s.d. 0.16, $n=28$), $-0.02 \mu\text{mol/l}$ (s.d. 0.02, $n=28$) for phosphate and $-0.11 \mu\text{mol/l}$ (s.d. 0.27, $n=23$) for silicate.

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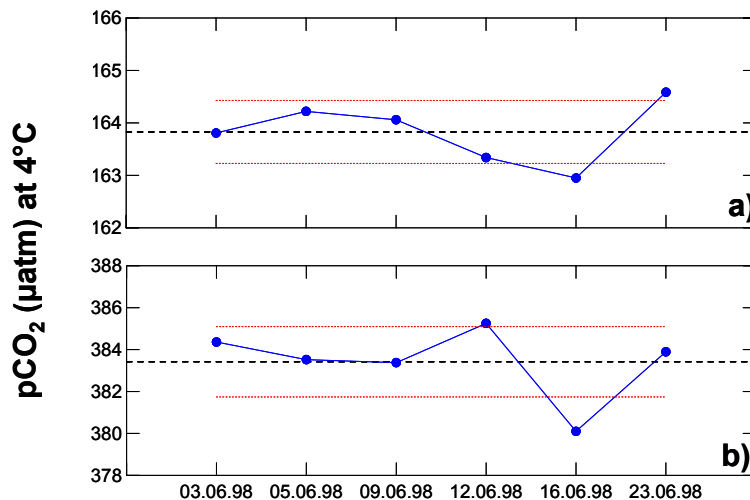


Fig. 3. Results of $p\text{CO}_2$ sample storage experiment. Average $p\text{CO}_2$ (μatm at 4°C) in **(a)** samples from 5 m depth, and **(b)** samples from 200 m depth. The average concentrations for the storage experiment are shown with a black slashed line and their standard deviations are shown with red dotted lines. The average concentration is $163.8 \mu\text{atm}$ at 5 m depth (s.d. 0.6, $n=6$) and $383.4 \mu\text{atm}$ at 200 m depth (s.d. 1.7, $n=6$).

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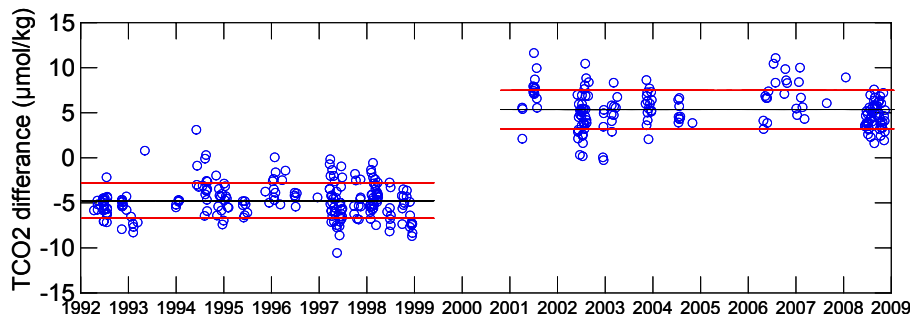


Fig. 4. Results of MRI TCO_2 determinations in Dickson's sea water reference materials (CRM) 1992–1998 and 2001–2008. The average differences (MRI-CRM) are shown as black slashed lines and their standard deviations are shown with red dotted lines. The differences of $-4.7 \mu\text{mol C kg}^{-1}$ for the period 1992–1998 are as observed and without the loop volume correction applied to data from this period. The differences observed in the period 2001–2008 and with a mean of $+5.3 \mu\text{mol C kg}^{-1}$, were found after taking account of a loop volume correction and they result from instrumental adjustments.

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