Winter measurements of oceanic biogeochemical parameters in the Rockall Trough (2009-2012)

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Abstract

This paper describes the sampling and analysis of biogeochemical parameters collected in the Rockall Trough in January/February of 2009, 2010, 2011 and 2012. Sampling was carried out across two transects, one southern and one northern transect each year. Samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were taken alongside salinity, dissolved oxygen and dissolved inorganic nutrients (total-oxidised nitrogen, nitrite, phosphate and silicate) to describe the chemical signatures of the various water masses in the region. These were taken at regular intervals through the water column. The 2009 and 2010 data are available on the CDIAC database.

Repository-Reference:
doi:10.3334/CDIAC/OTG.ROCKALL_TROUGH_2012
Available at:
http://cdiac.ornl.gov/ftp/oceans/Rockall_Trough/
Coverage: 52.8–56.2°N, 18.5–9 °W
Location Name: Rockall Trough
Date/Time Start: 2009-02-05
Date/Time End: 2012-01-12

Table 1

Data Product Parameter Name	Exchange File Parameter Name	Exchange File Flag Name	Units
Station	STNNBR		
Cast number	CASTNO		
Bottle number	BTLNBR	BTLNBR_FLAG_W	
Year/month/day	DATE		
Time	TIME		
Latitude	LATITUDE		decimal degrees
Longitude	LONGITUDE		decimal degrees
Depth	DEPTH		meters
Pressure	CTDPRS		decibars
Temperature	CTDTMP		degrees Celsius
CTD Salinity	CTDSAL	CTDSAL_FLAG_W	
Salinity	SALNTY	SALNTY_FLAG_W	
CTD Oxygen	CTDOXY	CTDOXY_FLAG_W	micromole kg^{-1}
Dissolved oxygen	OXYGEN	OXYGEN_FLAG_W	micromole kg^{-1}
Dissolved inorganic silicate	SILCAT	SILCAT_FLAG_W	micromole kg^{-1}
Dissolved inorganic nitrate	NITRAT	NITRAT_FLAG_W	micromole kg^{-1}
Dissolved inorganic nitrite	NITRIT	NITRIT_FLAG_W	micromole kg^{-1}
Dissolved inorganic phosphate	PHSPHT	PHSPHT_FLAG_W	micromole kg^{-1}
Dissolved inorganic carbon	TCARBN	TCARBN_FLAG_W	micromole kg^{-1}
Total alkalinity	ALKALI	ALKALI_FLAG_W	micromole kg^{-1}

1. Introduction

Between February 2008 and August 2010 a pilot project to initiate research in ocean carbon processes in Irish marine waters was carried out jointly by the National University of Ireland, Galway (NUIG) and the Marine Institute, Ireland (MI). The project titled "Increased Atmospheric CO_2 on Ocean Chemistry and Ecosystems" was carried out under the Sea Change strategy with the support of the Marine Institute and the Marine Research Sub-Programme of the National Development Plan 2007–2013. (O'Dowd et al., 2011). Through collaboration with annual MI winter surveys, a range of biogeochemical parameters were measured across the Rockall Trough in January or February of 2009, 2010, 2011 and 2012. The Rockall Trough plays an important role in the global thermohaline circulation as it provides a pathway for warm saline waters of the upper North Atlantic to reach the Nordic Seas. There is also a complex interaction of a range of water masses in the Trough, each with different areas of origin and histories (McGrath et al., 2012b) and therefore it is an important region in ocean-climate research. The 2009 and 2010 data have recently been compared with data measured in the Trough in the 1990s by the World Ocean Circulation Experiment (McGrath et al., 2012a; McGrath et al., 2012b).

2. Data provenance

All surveys were carried out on the RV Celtic Explorer; see exact dates in Table 2. While conductivity, temperature and depth (CTD) data are available for every station in Figure 1, inorganic carbonate parameters were generally measured every second station in 2009 and 2010. In 2011, only 5 surface carbonate samples were taken for inter-laboratory comparison with samples analysed at Scripps Institute of Oceanography, while in 2012 carbonate samples were taken at every station along the southern transect. Salinity and nutrients were measured across both transects every year. Stations were approximately 27 km apart, except for along the shelf edge where there was greater horizontal sampling resolution.

Table 2 Details of surveys with number of chemistry samples taken on each.

Survey	EXPOCODE	Date	DIC	TA	O_2	NUT	SAL
CE0903	45CE20090206	5-15 Feb 2009	64	64		144	133
CE10002	45CE20100209	5-17 Feb 2010	95	95	190	333	266
CE11001		3-10 Jan 2011	5	5	145	204	183
CE12001		5-12 Jan 2012	75	75		165	165

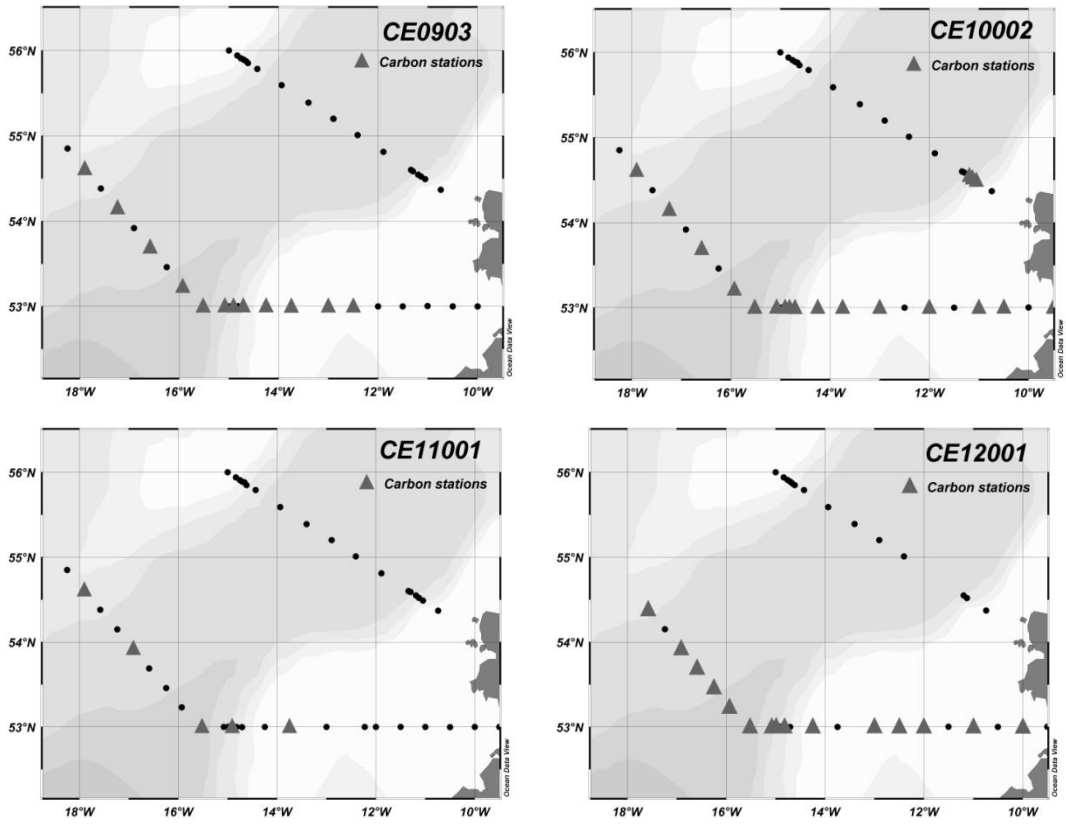

Figure 1 Station positions from the surveys CE0903 (Feb 2009), CE10002 (Feb 2010), CE11001 (Jan 2011) and CE12001 (Jan 2012). Stations with triangle symbols are where carbonate parameters were measured. Note in CE11001 only surface samples were taken, in other years samples were taken through the water column.

3. Methods and Quality Control Procedures

3.1 Hydrography

A Seabird CTD profiling instrument (SBE 911) with water bottles on a rosette was used on each survey. Temperature and conductivity sensors were sent to Seabird annually for calibration. On every survey there was a primary and secondary temperature and conductivity sensor set on the CTD, which were compared to ensure they match to a high level of precision. Also processed salinity sensor data were

compared with the discrete water samples analysed on a Guildline Portasal salinometer (Model 8410A) at the MI. On every survey the sensor-laboratory comparison resulted in an r-square greater than 0.999, therefore there were no adjustments necessary on the salinity sensor data. An SB43 oxygen sensor was deployed with the CTD, which was also calibrated annually with the manufacturer. On surveys where oxygen samples were taken, the oxygen sensor data was calibrated with the laboratory results.

3.2 Dissolved inorganic carbon and total alkalinity

The Guide to Best Practices for Ocean CO_2 measurements (Dickson et al., 2007), which describes the standard methods now in use for the determination of these parameters, was followed for the sampling and analysis of DIC and TA.

3.2.1 Sampling

DIC and TA were generally analysed from the same bottle; a 500ml Schott Duran borosilicate glass bottle with ground glass stopper. Silicone/tygon tubing was attached to the tap of the Niskin bottle, sample water was allowed to flow through the tubing to remove any air bubbles and the bottle was first rinsed before filling slowly from the bottom. The water was overflowed by approximately 1 bottle volume. Using a pipette, a headspace (~2ml) was left in the top of the bottle to allow for water expansion, then 0.1ml of saturated mercuric chloride solution was added to poison the sample. The glass stopper was greased with Apiezon L Grease before arriving at the station. After the sample was poisoned, excess water was wiped from the neck of the bottle and the stopper was twisted slowly into place, squeezing the air out of the grease. Finally the stopper was clamped in place using 3 thick elastic bands. The bottle was inverted several times to disperse the mercuric chloride and the sample was stored in a cool, dark location and analysed on land. Any seawater or materials contaminated with mercuric chloride during sample collection and analysis were collected and disposed of by a chemical waste disposal company in full compliance with hazardous waste regulations.

Where there were insufficient borosilicate glass bottles, DIC and TA were taken in separate containers using the same method described above. DIC was taken in 250ml amber glass bottles with ground glass stoppers and TA was taken in 500ml high-

density polyethylene (HDPE) bottles with screw caps. The individual TA samples were not poisoned with mercuric chloride.

3.2.2 Analysis

DIC was measured on a VINDTA-3C (Versatile Instrument for the Determination of Titration Alkalinity) system (Mintrop et al., 2000) with UIC coulometer. A known volume of sample is acidified with phosphoric acid in order to transfer all dissolved inorganic carbon to CO_2 and the resulting CO_2, forced out of the sample using nitrogen as a carrier gas, is titrated coulometrically (Johnson et al., 1987; Johnson et al., 1993).

TA was analysed by potentiometric titration with 0.1M hydrochloric acid, also on the VINDTA 3C. During the titration the bases in the TA definition (Dickson, 1981) are transferred to their acidic forms and the titration is monitored by a pH electrode that measures the electromotive force (emf). The process is controlled by the LabVIEW^{TM} software and the endpoint is determined by the change in pH against the volume of acid added to the solution. The result of the titration is evaluated with curve fitting (Mintrop et al., 2000).

3.2.3 Quality Control

The accuracy of both DIC and TA analysis was ensured by analysing duplicate Certified Reference Materials (CRMs) before every batch of samples. CRMs were provided by A. Dickson, Scripps Institution of Oceanography, USA (Dickson et al., 2003). If many samples (>10) were run in a single batch, another duplicate CRM was run at the end of the day. The mean of the measured CRM results was used to calculate a CRM correction factor to adjust DIC and TA sample results for any offset in the VINDTA.

CRM correction factor = assigned value / measured value

Sample results were then multiplied by the daily correction factors. The CRM results are shown in Figure 2. It is unclear why the TA CRMs for Batch 102 used for CE10002 had a slightly larger offset than other batches. Vertical profiles of final TA concentrations from this survey were cross-checked with TA profiles from CE12001 and two WOCE surveys in the same region (McGrath et al., 2012). All suggest that there is no problem/offset in the TA results generated from this batch. By using the

CRM correction factor, results were corrected for the larger offset in the instrument during this time. Duplicate samples from the same bottle were run every second sample, while duplicate bottles were taken for 5-10% of the total sample number from each survey. The accuracy and precision of the measurements was calculated as the average and standard deviation, respectively of the differences between duplicate samples, Table 3.

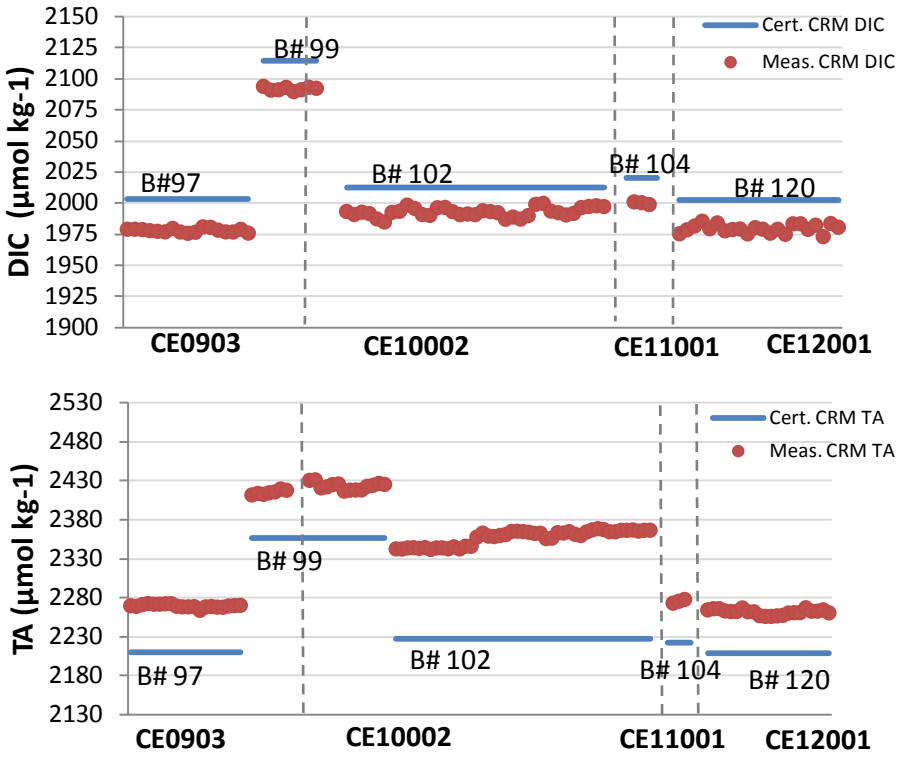

Figure 2 DIC and TA CRM measured values plotted against certified values for each of the surveys. Dashed lines indicate a new survey.

Table 3 Accuracy and precision of DIC and TA in µmol kg^{-1} for each of the surveys, calculated as the average and standard deviation, respectively of the differences between duplicate samples, where n is the number of duplicate samples.

	Accuracy DIC	Precision DIC	Accuracy TA	Precision TA	n
CE0903	2	2	1	1	64
CE10002	3	2	1	1	60
CE11001	1	1	2	2	4
CE12001	2	1	2	2	43

DIC and TA Storage Experiment

A storage experiment was carried out to investigate if storing samples for a prolonged length of time had an effect on the DIC and TA concentration. On May 21st 2010, twenty-six 500ml Schott Duran bottles were filled with water taken from 448m deep along the shelf edge (10.0322ºW, 55.2565ºN). All bottles were filled by the author (TMG), while a colleague poisoned, greased and sealed the bottles. Six 250ml glass (not-borosilicate) bottles, used for DIC only, were also tested to ensure these bottles did not affect the stored samples differently than the Schott Duran bottles. All samples were poisoned with mercuric chloride, stored at 4ºC in a dark fridge until they were analysed. The first set of samples (T=0) was run on the 29th May 2010 and a new set of samples was run monthly for the first 7 months (with one exception), with subsequent analysis every 2-3 months. A duplicate of every bottle was run, and the final result for each bottle below (Figure 3) is an average of the duplicate values.

The average DIC at T=0 was 2143µmol kg^{-1} (analysed from 4 duplicate sample bottles). The average DIC over the first full year of storage was 2142µmol kg^{-1}, and variation around the mean is less than ±3µmol kg^{-1}. Both Schott Duran and soft glass bottles had similar concentrations after a year. There was greater variability in DIC concentrations in the second year of storage, results from one month (July 2011) were discarded as concentrations were over 10µmol kg^{-1} below the mean.

The average TA at T=0 was 2331µmol kg^{-1}, and remained constant for the 26 months of storage, with variation less than ±2µmol kg^{-1} around the mean. Results from one month (June 2010) were discarded as concentrations were 8µmol kg^{-1} above all other months and appear to be a one-off error.

Results indicate while TA samples can be stored for at least two years, DIC samples should be analysed within one year of sampling. All samples collected in the Rockall Trough were analysed well within one year of sampling.

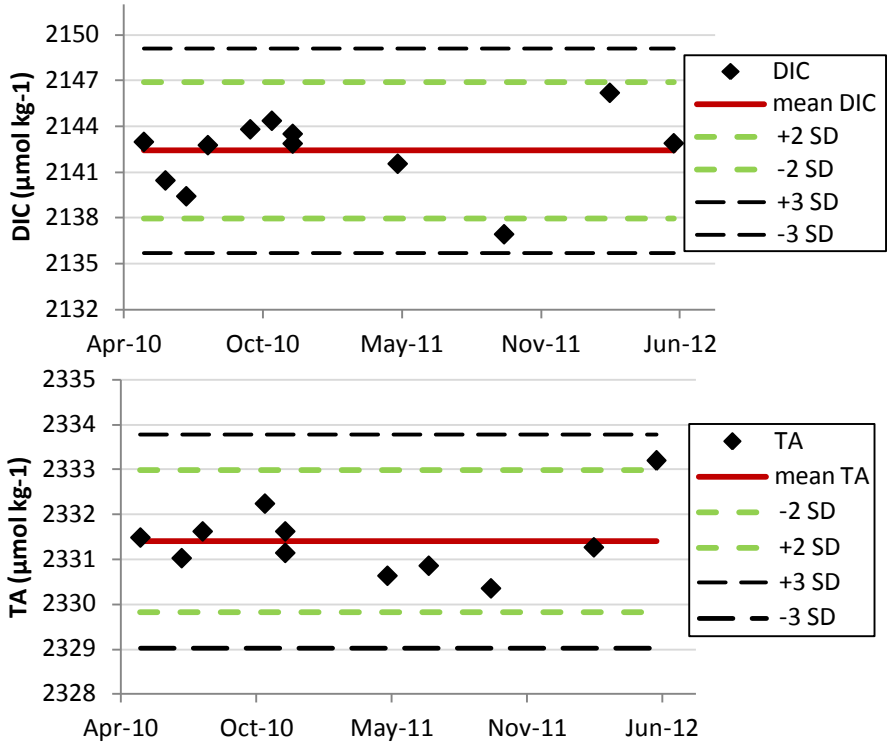

Figure 3 Average monthly (from at least 2 sample bottles) DIC and TA concentrations over 2 years of storage. The mean and standard deviations for DIC were based on the first year of storage when concentrations were within ±3µmol kg^{-1} around the mean, while both years of storage results were used for TA as they were all within ±2µmol kg^{-} of the mean.

Cross validation of DIC and TA analysed at Scripps Institution of Oceanography

In the survey CE11001 across the Rockall Trough in January 2011, a batch of surface DIC and TA samples was sent to Scripps Institution of Oceanography (SIO), USA, for analysis. Five duplicates of these samples were analysed by the author (TMG) at NUIG. DIC and TA concentrations from NUIG were within ±3.1µmol kg^{-1} and ±1.3µmol kg^{-1}, respectively, of those analysed at SIO.

3.3 Dissolved inorganic nutrients

3.3.1 Sampling

All equipment involved in the sampling and filtration of nutrient samples were acid-cleaned in 10% hydrochloric acid prior to sampling (Grasshoff, 1999). Water for nutrient samples was collected from the Niskin bottle in 1L HDPE bottles. The 1L

bottles were first rinsed 3 times with sample water before filling. The sample was filtered through a 0.40μm polycarbonate filter and the filtrate was poured into two 50ml polypropylene tubes. The tubes were immediately frozen upright at -20ºC and analysed on land.

3.3.2 Analysis

Seawater samples were analysed for total oxidised nitrogen (TOxN), nitrite, silicate and phosphate on a Skalar San^{++} Continuous Flow Analyser at the Marine Institute (Grasshoff, 1999). The Skalar San^{++} System uses automatic segmented flow analysis where a stream of reagents and samples, segmented with air bubbles, is pumped through a manifold to undergo treatment such as mixing and heating before entering a flow cell to be detected. The sample is pumped into the system and split into 4 channels where it is mixed with reagents. The reagents act to develop a colour, which is measured as an absorbance through a flow cell at a given wavelength.

TOxN

The Skalar method for the determination of TOxN is based on Greenberg et al. (1980), ISO 13395 (1996), Navone (1964) and Walinga et al. (1989). The sample is first buffered at a pH of 8.2, with a buffer reagent made of ammonium chloride and ammonium hydroxide solution, and is then passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite, originally present plus reduced nitrate, is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form a strong reddish-purple dye which is measured at 540nm.

Nitrite

The Skalar method for the determination of nitrite is based on EPA (1974), Greenberg et al. (198) and ISO 13395 (1996), where the diazonium compounds formed by diazotizing of sulfanilamide by nitrite in water under acidic conditions (due to phosphoric acid in the reagent) is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple colour which is measured at 540nm.

Silicate

The Skalar method for the determination of silicate is based on Babulak and Gildenberg (1973), ISO-16264 (2002) and Smith and Milne (1981). The sample is

acidified with sulphuric acid and mixed with an ammonium heptamolybdate solution forming molybdosilicic acid. This acid is reduced with L(+)ascorbic acid to a blue dye, which is measured at 810nm. Oxalic acid is added to avoid phosphate interference.

Phosphate

The Skalar method for the determination of phosphate is based on Boltz and Mellon (1948), Greenberg et al. (1980), Walinga et al. (1989) and ISO 15681-2 (2003), where ammonium heptamolybdate and potassium antimony(III) oxide tartrate react in an acidic medium (with sulphuric acid) with diluted solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex by L(+)ascorbic acid and is measured at 880nm.

Based on the daily calibration standards, concentrations of nutrients can be quantified up to the maximum calibration standard concentration. If sample concentrations fall above this range (Table 4), they must be diluted with artificial seawater.

Table 4 Limit of detection (LOD), limit of quantification (LOQ), both in µmol l^{-1}, and uncertainty of measurement (UCM) for the nutrient analysis. The ranges given are the linear calibration ranges, concentrations that fall above these are diluted into the linear range.

	LOD	LOQ	UCM	Ranges
TOxN	0.02	0.26	2.3%	LOQ – 15
Nitrite	0.01	0.04	6.7%	LOQ – 1.5
Silicate	0.03	0.38	0.5%	LOQ – 15
Phosphate	0.01	0.16	1.3%	LOQ – 1.5

3.3.3 Nutrients Quality Control

The accuracy of the nutrient analysis was ensured by running Eurofins CRMs (http://www.eurofins.dk/dk/milj0/reference-materialer.aspx) with every batch of samples, which must fall within specified limits within a standard deviation of 2. The system is also calibrated in every run using seven calibration standards made up daily in the laboratory. A replicate of every sample is analysed and the relative percent

difference (RPD: difference between the two values / mean * 100) of the results greater than the limit of quantification should be ≤ 10.

To assess the accuracy of the nutrient methods and procedures the MI participates in the QUASIMEME laboratory quality control programme (www.quasimeme.org). Test materials, analysed twice a year, have a large range of concentrations from below the detection limit to high concentrations that have to be diluted. The laboratory performance is expressed with a z-score where $|z| < 2$ is considered acceptable, where z is the difference between the laboratory result and the assigned value divided by the total error (Cofino and Wells, 1994). Between Oct 2008 and May 2012 the MI participated in 8 rounds of QUASIMEME proficiency testing scheme exercises (51 samples) for nutrients in the marine environment. The average z-score for all nutrients was <0.5, see Figure 4. The MI is accredited to ISO 17025 for nutrient analysis in seawater and is audited annually by the Irish National Accreditation Board, INAB.

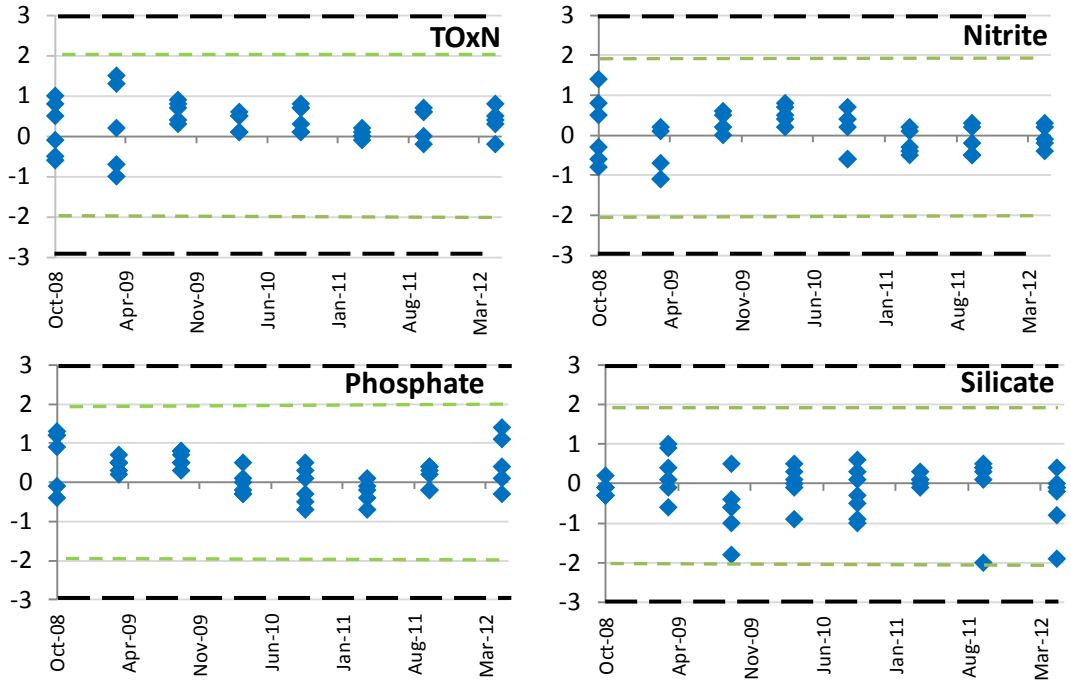

Figure 4 z-scores of 8 QUASIMEME rounds of nutrients in the marine environment between October 2008 and May 2012, where the green dashed lines indicate a z-score of 2. The dashed black line at a z score of ±3 designates unsatisfactory performance. Most of the Quasimeme samples were in the range of oceanic values measured in the Rockall Trough.

3.4 Salinity

3.4.1 Sampling

Salinity samples were collected in clear glass salinity bottles with plastic screw caps. The bottle was first rinsed three times with the sample water before filling up to the shoulder of the bottle. The neck of the bottles was dried well with clean kim wipes to prevent salt crystals forming on the top. A plastic insert was then placed into the bottle to produce a tight seal to prevent evaporation, followed by closing the bottle with the screw cap. Samples were stored upright at room temperature.

3.4.2 Analysis

Salinity was analysed on a Guildline Portasal Salinometer at the MI, where 4 electrode conductivity cells suspended in a temperature-controlled bath, measure the conductivity of the sample. The conductivity is related to salinity by calibration from a known standard. Two consecutive conductivity readings within 0.00002 units of each other must be taken before the salinity can be recorded. The temperature of the salinometer water bath must be set and stabilized to ~1-2ºC above ambient room temperature and samples must reach room temperature before analysis.

3.4.3 Salinity Quality Control

IAPSO seawater standards from OSIL (Ocean Scientific International Ltd) are used to calibrate the instrument daily and run as CRMs with every batch of samples. A P-series IAPSO standard (salinity ~35) is used to calibrate the system and is run every 4 hours during analysis and at the end of the days' analysis. DI water (salinity= 0), a 10L IAPSO standard (salinity ~10) and a 38H IAPSO standard (salinity ~38) are tested at the beginning of every batch of samples. P Series standards (salinity ~35) should fall within an allowable error of $\pm$0.003. The average z-score over 8 rounds of QUASIMEME proficiency testing scheme exercises for salinity between Oct 2008 and May 2012 was 0.36, see Figure 5. The MI is also accredited to ISO 17025 for salinity analysis in seawater and is audited by the Irish National Accreditation Board, INAB.

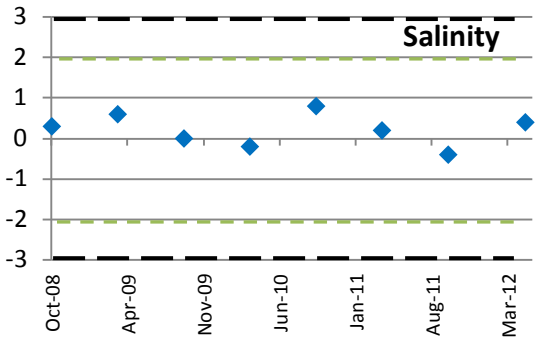

Figure 5 z-scores of 8 QUASIMEME rounds of salinity in the marine environment between October 2008 and May 2012, where the green dashed lines indicate a z-score of 2. The dashed black line at a z score of ±3 designates unsatisfactory performance.

3.5 Dissolved oxygen

Dissolved oxygen (D.O.) samples were collected and analysed as per the standard operating procedure of Dickson (1995).

3.5.1 Sampling

D.O. was the first parameter to be sampled from the CTD, with deepest samples drawn first, and collected in 250ml iodine bottles with plastic stoppers. All bottle-stopper pairs are individually calibrated and exact bottle volumes are used in final oxygen calculations. The bottle was filled from the bottom using silicone/tygon tubing, care was taken to minimize bubbles when filling and the water was overflowed by 3 flask volumes. Two millimetres of the pickling reagents, $MnCl_2$ (no. 1) and NaOH/NaI (no. 2), were added immediately to the sample, before carefully inserting the stopper and inverting the bottle several times. After the precipitate had settled at least half way, the bottle was shaken again. Samples were then stored in a cool dark location until titration, which was mostly carried out within 12 hours of sampling.

3.5.2 Analysis

Oxygen samples were analysed using a modified Winkler method (Dickson, 1995), where the titration is carried out in the sample bottle. The sample is first acidified with sulphuric acid (H_2SO_4) to a pH between 1 and 2.5, which dissolves the hydroxide precipitates, and iodide ions added by reagent no.2 are oxidised to iodine by the manganese (III) ions, which are reduced to Mn(II) ions in the process. In the final

step, the iodine is reduced to iodide by titration with sodium thiosulfate, the amount of iodine generated, which is equivalent to the amount of oxygen in the sample, is determined by the amount of thiosulfate required to reach the endpoint. A Metrohm 848 Titrino Plus, with a Metrohm combined Pt electrode was used to determine the endpoint, i.e. potentiometric endpoint determination, measuring the change in redox potential of the sample, which reaches a minimum at the endpoint (Furuya and Harada, 1995). This method of determination was also used effectively by numerous WOCE cruises in the Atlantic and Pacific Oceans, and also on some Hawaii Ocean Time Series (HOT) cruises
(http://www.soest.hawaii.edu/HOT_WOCE/).

3.5.3 Oxygen Quality Control

Before titration of the samples, duplicate reagent blanks were determined and duplicate standardization of the sodium thiosulfate titrant was carried out. The reagent blank should ideally be less than 0.01ml, while the duplicate thiosulfate standardization should typically fall within 0.002ml of each other (Dickson, 1995). Standardization of the thiosulfate is carried out in precisely the same conditions that the samples are analysed under so that any iodine lost through the volatilization or gained by the oxidation of iodide while analysing the seawater samples is compensated for with similar errors occurring during the standardization procedure (Knapp et al., 1989). Precision of the samples is estimated by running duplicate samples every 10-15 samples.

4. Data access

The 2009 and 2010 datasets are currently available on CDIAC database (http://cdiac.ornl.gov/ftp/oceans/Rockall_Trough/), and discussed in McGrath et al. (2012a) and McGrath et al. (2012b). The 2011 and 2012 datasets are currently being quality checked and will be submitted to CDIAC once this is completed.

Acknowledgements

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