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UK Ocean Acidification Coastal Monitoring Network
Expanding the UK Network
Defra Contract C5801/ME5309

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Marine Scotland is the directorate of the Scottish Government responsible for the integrated management of Scotland's seas. Marine Scotland Science (formerly Fisheries Research Services) provides expert scientific and technical advice on marine and fisheries issues. Scottish Marine and Freshwater Science is a series of reports that publishes results of research and monitoring carried out by Marine Scotland Science. It also publishes the results of marine and freshwater scientific work that has been carried out for Marine Scotland under external commission. These reports are not subject to formal external peer-review.

This report presents the results of marine and freshwater scientific work carried out by Marine Scotland Science.

Executive Summary

1. The OSPAR ICES Study Group on Ocean Acidification (SGOA) and the Global Ocean Acidification Observing Network (GOA-ON) have both identified the need for a commitment to long-term monitoring at sites in coastal and inshore waters to distinguish long-term anthropogenic signals from short-term spatial and temporal variability.

2. Limited monitoring of the changes in ocean acidification is undertaken in coastal waters around the UK. A short UK Integrated Marine Observing Network (UK-IMON) demonstration study was commissioned to monitor coastal waters for the first half of 2013 for the carbonate chemistry parameters, Total Alkalinity (TA) and Dissolved inorganic carbon (DIC).

3. The project was divided into two distinct parts, namely a preliminary feasibility study, to examine the use of moored water samplers to collect water samples for the analysis of dissolved inorganic carbon (DIC), and discrete sampling at various locations around the UK for Total Alkalinty (TA) and DIC analysis.

4. Automated water samplers deployed on existing instrumented moorings may provide a cost effective means of collecting water samples for monitoring ocean acidification in coastal waters and a preliminary assessment of the utility of an automated water sampler for monitoring DIC was undertaken. A small but statistically significant difference was found between the concentrations of DIC measured in water samples collected simultaneously using an automated water sampler and rosette samples. At the present time it is not possible to determine whether this difference is due to the way samples are collected by the automated sampler or small differences in the way the two sets of samples were processed.

5. The authors recommend that a further, more detailed comparison should be undertaken to include a moored sampler with sample preservation. The introduction of a procedure to minimise aeration of samples during processing and filtration, together with any effect of long-term (weeks) storage of samples (during automated sampler deployment) on sample integrity should also be investigated.

6. Discrete water samples were collected for TA and DIC analysis between January 2013 and August 2013 (site dependant) at five locations around the UK; the Minch North (Scottish West Coast), Stonehaven (Scottish East Coast)

and the Cefas Smart Buoys in Liverpool Bay and the Celtic Deep and at the AFBI Mooring in offshore waters of the western Irish Sea.

7. Discrete surface water samples were collected in the Minch North between January and July 2013, TA and DIC mean concentrations were 2289 µM/kg, (n = 27) and 2106 µM/kg (n = 28), respectively. TA and DIC concentrations dropped towards the end of May, this drop coincided with the algal bloom in the region at the time. A decrease in DIC concentrations during the spring bloom is to be expected. However, TA concentrations would be expected to increase around an algal bloom and it is unclear why the concentration decreased at this time. The initial six month sampling period financed by UK-IMON does not allow for observation of seasonal trends, but informs the design of future long-term monitoring at this location and has therefore been very useful.

8. Discrete surface water samples were collected at the Cefas SmartBuoys, located in the Celtic Deep and Liverpool Bay, and at the AFBI mooring in offshore waters of the western Irish Sea in March, May and August 2013 for TA and DIC analysis. Mean concentrations of TA and DIC in water samples collected at the offshore sites (Celtic Deep Buoy and AFBI mooring) were 2313 µM/kg (n=15) and 2080 µM/kg (n = 15), respectively, while at the coastal Liverpool Bay SmartBuoy mean concentrations were 2283 µM/kg (n=9) and 2076 µM/kg (n=9), respectively. Due to only sampling at the sites on three occasions, there was insufficient data to make any assessment of seasonal trends, but begins to build the baseline for future long term monitoring.

9. Monitoring for TA and DIC at MSS's long term monitoring site at Stonehaven was initiated in 2009 as part of the NOC Defra pH project and UK Ocean Acidification programme. This programme ended in 2010, however, a further year's funding was provided through the UK Ocean Acidification programme and now continues as part of the MSS Ocean Acidification ROAME (Rationale, Objectives, Appraisal, Monitoring, Evaluation, ST012). Since 2009 water samples have been collected on a weekly basis (weather permitting) at two depths (1 m and ~ 45 m) and analysed for TA and DIC.

10. An initial assessment of the TA and DIC data collected at Stonehaven (2009-2013) was made. DIC concentrations, at this site, ranged from 2002-2134 µM/kg (mean = 2092 µM/kg, n = 375), while TA concentrations ranged from 2170 – 2309 µM/kg (mean = 2275 µM/kg, n = 375).

11. TA concentrations increase as a result of nitrate uptake by phytoplankton cells during an algal bloom such as in spring and autumn, before decreasing over winter. A strong TA seasonal cycle was observed at Stonehaven between 2009 and 2011 inclusive, however, no seasonal trend has been observed since 2012. DIC concentrations mirror that of nitrate with concentrations decreasing during the algal bloom. A strong DIC seasonal cycle was observed at Stonehaven with DIC concentrations increasing over the winter months maximising around March. Similar to the TA no seasonal DIC trend was observed in 2012. However, 2013 the seasonal cycle returns and appears to be following a similar pattern to previous years.

12. The long-term monitoring at Stonehaven highlights the requirement for a robust data set to distinguish changes as a consequence of anthropogenic inputs from that of natural seasonal and inter-annual variability. To understand the changes that occurred during 2012 it is clear there is a need for integrated monitoring, which includes measurement of the biological parameters such as phytoplankton.

Introduction

Ocean acidification is the decrease in the pH of the earth's oceans as a result of uptake of anthropogenic carbon dioxide (CO_2) from the atmosphere[1]. It has been reported that a third of the anthropogenic CO_2 (from activities such as fossil fuel burning) produced over the past 200 years has been absorbed by the oceans, resulting in a decrease in pH of 0.1 units[2]. By 2100 the pH is predicted to decrease by 0.4 units. Although the input of CO_2 from the atmosphere has only small spatial variation, some marine regions will be more rapidly affected; the susceptibility of water chemistry to change is dependent on the chemical composition and temperature of the water. The limited data available worldwide shows that acidification does not occur uniformly. Spatial, seasonal and annual variations have been reported[3-5], with variability naturally highest in coastal regions. It is, therefore, important to establish these natural variations by routine monitoring before changes due to anthropogenic inputs can be assessed. Ocean acidification and climate change share a common cause, increasing carbon dioxide (CO_2) in the atmosphere. However, ocean acidification must be distinguished from climate change as it is not a climate process but rather an alteration to the chemistry of seawater.

There has been a great deal of interest in ocean acidification in recent years because of its potential effects on marine biogeochemistry and ecosystems. Atmospheric CO_2 is in equilibrium with CO_2 in the aqueous phase. As

concentrations of CO_2 increase in the atmosphere, DIC will increase resulting in an alteration to the carbonate system such that HCO^{-3} and CO_2 will increase while CO_3^{-2} and pH will decrease (Figure 1). $CaCO_3$ saturation decreases with water depth, therefore, any reduction of CO_3^{-2} will potentially result in lowered saturation levels with increased dissolution and reduced saturation depths of marine carbonates such as aragonite, calcite and magnesian calcites[6,7].

The effects of the decrease in seawater pH and changes to the saturation states of carbonates may be corrosive to the shells and skeletons of marine organisms, while the decrease in carbonate ions may affect organisms' abilities to build skeletons and shells, particularly among calcifying organisms[7]. In planktonic and benthic communities many may require more energy to obtain and produce the calcium carbonate required for skeletal or shell production. This may impact on other energy using functions such as fertilisation, development and growth. Studies have shown a decreased calcification when pH is decreased, with early life stages being particularly sensitive to acidification. CO_2 effects will impact the metabolism and physiology of organisms in many ways, since factors such as acid - base balances and oxygen transport in cells and body fluids are affected by their pH.

Cold-water corals found in coastal areas, such as Mingulay reef complex in the Hebrides, may also be particularly sensitive to decreases in pH and CO_2^{-3}. These coral colonies serve as shelter, feeding and breeding habitats for fish. Changes to coral habitats may, therefore, also impact the fish and other organisms living within them. Organisms which produce calcium carbonate from aragonite and magnesian calcite may be more susceptible to increases in CO_2 concentrations because of the increasing solubility of these in acidifying seawater [7-10].

Ocean acidification may also have socio-economic implications for the UK economy. Estimating the impact of ocean acidification to the economy, however, is difficult because the ability of marine species to adapt is unknown. Any impact on fertilisation, development and growth of marine species, as a result of ocean acidification, may impact fisheries as a food resource. It is estimated that 20% of the world's protein intake is from marine sources[11]. In 2010, 606,295 tonnes fish and 245,856 tonnes shellfish, were landed in the UK and Ireland. It is estimated that 30,000 people in the UK, alone, are dependent on fishing for their livelihoods[12]. The Marine Climate Change Impacts Partnership (MCCIP) 2013 science review[13] predicted that ocean acidification (assuming a doubling of atmospheric CO_2 and a 10-25% reduction in growth calcification) would result in a 10-25% loss in shellfish landings, equating to a loss of £100–500 million per year by 2080 from the UK economy. Coastal areas are also an important part of the UK leisure and recreation

industry supporting employment and small businesses for activities such as diving, kayaking, sea angling, and marine mammal observations. Any change in coastal marine biodiversity as a result of ocean acidification may impact potential revenue. The effects of ocean acidification may, therefore, impact those involved in the fisheries and aquaculture industry, retailers, consumers and coastal communities.

In September 2010 the UK signed up to the OSPAR Bergen Statement, to which effect ministers have agreed to respond to new challenges and priorities including ocean acidification. Following on from the Bergen statement the OSPAR Coordination Group (CoG) met and agreed that ocean acidification will be a requirement of the Joint Assessment and Monitoring Programme (JAMP) 2010-2014[14]. The UK also has a commitment to fulfill Marine Strategy Framework Directive (MSFD) requirements. Annex 3 of the Directive includes 'pH, pCO_2 profiles or equivalent information used to measure marine acidification' as a characteristic under physical and chemical features.

The OSPAR Quality Status Report, published in September 2010[5], identified ocean acidification as an emerging concern for ecosystems and indicated that ecosystem-wide effects would be observed in the next 50 years. ICES highlighted the lack of data on seasonal and inter-annual variability, and advised that measurements should cover a range of waters[15]. Charting Progress 2 also highlighted 'the lack of baseline measurements of pH against which changes can be judged' and indicated that there was an upward trend in ocean acidification which could pose a threat to marine species and ecosystems. Both the OSPAR/ICES Study Group on Ocean Acidification (SGOA)[16] and the Global Ocean Acidification Observing Network (GOA-ON)[17] have identified particular gaps in data for coastal and inshore waters.

Limited monitoring of the changes in ocean acidification is undertaken in coastal waters around the UK. The UK Ocean Acidification Programme (UKOA) funded a baseline study of carbonate chemistry parameters in UK waters, which included monitoring at the Cefas SmartBuoy sites over a 3 year period. It was agreed that additional monitoring would be undertaken for a short period in 2013 as a UK-IMON demonstration study.

The project was divided into two distinct parts, firstly a preliminary feasibility study to examine the use of moored water samplers to collect water samples for the analysis of dissolved inorganic carbon (DIC) and secondly discrete sampling for TA and DIC analysis at five locations around the UK. Reported here are the results of both parts of the project.

Materials and Methods

Feasibility Study

A mooring consisting of a McLane RAS (Remote Access Sampler) suspended below a subsurface buoy at depth two metres was deployed in the North Channel (54° 57.4' North 005° 51.7' West) and firmly anchored to the sea bed. The RAS sampler is a self-contained instrument designed to collect up to 48 individual water samples. Each of the 30 ml polypropylene sample holders was connected to a filter unit fitted with a GF/F paper. Addition of a preservative solution was not possible with this model of sampler. The RAS sampler was programmed to collect duplicate samples at 30 minute intervals and to coincide with the moored RAS sampler's programme a Sea-Bird discrete water sampler was deployed to take duplicate samples at depth two metres. As far as practically possible both sets of samples were treated in a similar manner. Samples collected using the Sea-Bird sampler were also filtered through a GF/F paper and stored refrigerated in 40 ml glass EPA vials fitted with septa. At the conclusion of the study the mooring was recovered and 19 samples taken in duplicate) were removed from the RAS sampler and transferred to glass EPA vials and stored refrigerated. Both sets of samples were returned to the laboratory and remained refrigerated for a period of four days prior to analysis for DIC.

Samples were analysed at AFBI for DIC using an automated Apollo 9000 TOC analyser (Teledyne Instruments, Ohio, USA). Following acidification inorganic carbon in the sample was converted to carbon dioxide and the response from a nondispersive infrared detector was compared to stored calibration data to calculate sample concentration in mmol C/l. Calibrants (solutions of sodium carbonate in the range of 0-3 mmol C/l) were run both before and after samples were analysed. Samples were analysed in triplicate.

Measurement of Discrete Samples

Sample Collection

Water samples were collected in the Minch North (Scottish West Coast) by the crew of the *MV Isle of Lewis* and transported via the SEPA Stornoway office to the laboratory in East Kilbride where salinity and nutrients were analysed. Samples were taken weekly from January to July 2013, however, on several occasions the crew were not able to take samples due to technical issues on the ferry. TA and DIC samples were stored at room temperature prior to being sent to NOC for analysis.

Water samples were collected weekly, weather permitting, from the MSS long term monitoring site at Stonehaven from the *MRV Temora* between January and July 2013, inclusive. Water samples were collected for nutrients, salinity, TA and DIC analysis. Samples for nutrient analysis were stored frozen, while salinity, TA and DIC samples were stored at room temperature. Samples were analysed for nutrients and salinity by MSS, samples for TA and DIC analysis were sent to NOC.

AFBI collected water samples while undertaking routine maintenance at the Cefas SmartBuoys at the Celtic Deep and Liverpool Bay in March, May and August 2013. TA and DIC samples were stored at room temperature prior to being sent to NOC for analysis.

Total Alkalinity (TA) and Dissolved inorganic Carbon (DIC)

Discrete water samples (250 ml) were collected, by individual laboratories, for the determination of DIC and TA into 250 ml glass bottles (Schott Duran) and poisoned with 50 µl saturated $HgCl_2$ solution to prevent biological alteration during storage. A head-space of 2.5 mL was left to allow for water expansion and the bottles were sealed using a greased ground glass stoppers to ensure they remained gas-tight. Samples were shipped to National Oceanography Centre Southampton (NOC) for analysis at the Natural Environment Research Council (NERC) laboratory. Analysis was performed using colorimetric and potentiometric open titration cell techniques. Samples were analysed using the Versatile Instrument for Analysis of Titration Alkalinity (VINDTA 3C, Marianda, Germany) on the two NERC Ocean Biogeochemistry and Ecosystems group carbonate facility (VINDTA units 11 and 24).

All the samples were heated to 25ºC using a water bath (F12, Julabo, Germany) immediately before analysis. The guidelines followed for analysis are outlined in Mintrop[18] and Hartman *et al.*[19]. DIC and TA were analysed in batches of between 9 and 24 samples. Duplicate samples were, where possible, analysed on different NOC Vindta instruments.

Dissolved Inorganic Carbon

DIC was measured by a coulometric titration (coulometer 5011, UIC, USA) following the extraction of CO_2 from a ~20 ml sub-sample. The DIC section of the VINDTA 3C consists of two main parts where reactions take place. In the first, the sample is acidified with phosphoric acid (H_3PO_4, 10%) and bubbled through with the inert

carrier gas (nitrogen), thereby reducing the pH and converting the carbon species into CO_2 gas. The CO_2 gas is then transferred into the second part by the inert carrier gas being cooled to remove water vapour enroute into the coulometer cell, where it is titrated colorimetrically.

The coulometer cell consists of two chambers separated by a sintered glass frit, the cathode and the anode chamber, with a platinum and silver electrode, respectively, and connected to the coulometer to produce a current. The cathode cell is filled with a dimethylsulfoxide solution containing monoethanolamine ($HOCH_2CH_2 NH_{2,}$) and the pH indicator thymol blue. The produced CO_2 reacts with the monoethanolamine to form hydroxyethyl carbamic acid ($HOCH_2CH_2NHCOOH$) causing the indicator to turn colourless, increasing the transmittance. The current is activated and the electrons titrate the hydroxethyl carbamic acid returning the pH to the value before the CO_2 addition, returning the indicator to blue and the transmittance to 29.6%. At the beginning of each session, a blank measurement was undertaken adding only H_3PO_4, generating an amount of counts (ideally below 100), which then are subtracted from the end count as well as used to determine the titration endpoint. Analysis concluded after four end-points had been achieved.

Total Alkalinity

Total alkalinity (TA) was determined by a potentiometric open-cell titration on a ~100 ml sub-sample using a pH half-cell electrode (Orion, Ross, USA) and Ag/AgCl reference electrode (Metrohm, Switzerland). The sample was titrated against hydrochloric acid (HCl, 0.1M) prepared in sodium chloride solution (NaCl, 0.7 M). HCl was added via a Metrohm titrator (0.15 ml additions) until the carbonic acid equivalence point was reached. The pH of the titration was monitored by the pair of electrodes which measured the difference in electromotive force (emf) caused by the change in pH. The emf and the amount of acid added allows the calculation of total alkalinity by a curve fitting method based on a Gran plot approach (Dickson [20]) by the VINDTA software.

Quality Control

Precision

Repeat measurements on a previously analysed samples were undertaken before sample analysis each day (n>3). Instrument precision was better than ± 1.5 µM/kg for DIC and TA. The standard deviation for DIC and TA was calculated for each day of analysis (Figure 2).

The overall precision was calculated as the mean of the standard deviation of all the daily analysis. The precision of Vindta instrument 11 was 1.26 µM/kg and 1.29 µM/kg for DIC and TA, respectively and for Vindta instrument 24 the precision was 1.31 µM/kg and 1.11 µM/kg for DIC and TA, respectively. There is little difference in the standard deviations on the two instruments, showing overall good performance and coherence between both systems. The differences between duplicate samples was higher at 7.49 µM/kg and 7.48 µM/kg for DIC and TA respectively, which may be a consequence of poor sampling.

Instrument Calibration and Monitoring Analytical Performance

Reference Materials (RM) from Dr Andrew Dickson (Scripps Institution of Oceanography) were used for calibration to assure the accuracy of the measurements. RMs were analysed at the beginning, middle and end of the sessions. The result of the first RM analysis was used in the final calculation to avoid bias in DIC due to gas exchange providing a correction factor (k) for each analysis session.

$K = RM_{measured} / RM_{certificate}$

RMs were monitored on control charts for each individual instrument. RM lot number 123 was used for the duration of the project.

The mean concentration for RM on Vindta 11 was 2005 (SD 3.42) µM/kg and 2125 (SD 8.29) µM/kg for DIC and TA respectively, while for Vindta 24 it was 2013 (SD 2.13) µM/kg and 2129 (SD 3.15) µM/kg for DIC and TA, respectively (Figure 3).

Supporting Determinand Measurements

The supporting determinands, nutrients (phosphate and total oxidised nitrogen) and salinity, were analysed by individual laboratories collecting the discrete water samples. The data was provided to NOC to permit accurate calculation of the TA and DIC concentrations.

SEPA, additionally, collected and analysed water samples for chlorophyll-a to aid data interpretation.

Correction for Salinity

The VINDTA software assigns a default salinity of 35 psu. However, if the sample salinity was known at the time of analysis the TA was corrected for this within the instrument software. The DIC was corrected for salinity post analysis as per the procedure of Friis *et al.* [21].

CO_2SYS Routine

The marine carbonate system can be characterised from any two of the four parameters: DIC, TA, pCO_2 and pH. The Excel program "CO_2SYS" can be used to calculate the partial pressure of CO_2, pH, calcite and aragonite saturation states, Revelle factor, carbonate and bicarbonate ion concentrations [22]. The combination of input parameters DIC, TA, phosphate and silicate concentrations and laboratory pressure and temperature (0 dbar, 25 Cº) and output conditions (Real temperature and pressure when the sample was taken) were used to calculate the two other carbonate chemistry parameters pCO_2 and pH.

The dissociation constants of carbonic acid (pK_1 and pK_2) determined in real seawater by Millero[23] were used as constants in the CO_2SYS calculation. The pCO_2 calculation comes from the inaccuracies of the thermodynamic dissociation

constants (mainly pK_1 and pK_2) and the experimental measurements of the variables used for calculation and can be in the order of ± 7 µatm[23].

Results and Discussion

Feasibility Study

Nineteen samples collected in duplicate were collected in the North Channel using a McLane RAS (Remote Access Sampler) suspended below a subsurface buoy at depth two metres was deployed in the North Channel. Samples were analysed for DIC using an automated Apollo 9000 TOC analyser.

During analytical runs, which were typically 10 hours, problems were encountered with drift in instrument response. It was uncertain if the drift was caused by a faulty sensor or temperature fluctuations in the laboratory. The problem was highlighted when differences were observed when comparing pre and post calibration data. The analysis was repeated several times until a batch of data demonstrated no drift with good agreement between pre and post calibrations. Data from pre and post calibration data were combined (Figure 4) and used to determine the DIC concentration in each sample.

DIC mean concentrations from duplicate samples taken by moored and discrete water samplers are reported in Table 1. The difference between the two data sets (Table 1) was generally small with a maximum difference of 5.2%. However, the concentration of DIC in samples collected using the rosette Seabird sampler was higher in 16 (84%) of the 19 pairs of samples. The bias can be seen in Figure 5.

The Lins's concordance coefficient statistic (Lin[24]) was used to determine the level of agreement between corresponding pairs of DIC concentrations from the two sets of samples. The concordance correlation coefficient (ρ_c) 0.71 (ρ_c <0.9) indicates that there were significant differences between the concentration of DIC measured in the water samples collected by the RAS sampler and those collected using the Sea-Bird sampler.

Despite repeated attempts, some questions remain over the quality of the analytical data because of the drift encountered with the instrument response. In addition, other method errors such as the possibility of air being introduced during removal and filtration of water samples from the Seabird rosette sampler and discrepancy in depth and sample timing, in relation to the moored sampler, when deploying the Seabird water sampler are likely to have contributed to the lack of agreement

between DIC concentrations in samples collected by the two sampling techniques. The purpose of this study was to undertake a preliminary assessment of whether automated water samplers deployed on instrumented moorings could be used to collect samples for DIC. At the present time it is not possible to answer this question and a further, more detailed comparison should be undertaken to include a moored sampler with sample preservation, the introduction of a procedure to minimise aeration of samples during processing and filtration, a more robust analytical procedure with regular quality control and precise judgement of depth and sample timing.

Discrete Samples

Discrete Samples Collected at Stonehaven

Water samples have been collected at the MSS long term coastal monitoring site at Stonehaven (Figure 6) for TA and DIC analysis since November 2008. Samples were collected at the surface (1 m) and just above the seabed (45 m). Water samples collected between January 2009 and August 2011 were collected and analysed, by the NOC, as part of the Defra PH project and UK Ocean Acidification project. Samples collected since Sept 2011 have been analysed, by NOC, as part of a Marine Scotland Science ROAME.

An initial assessment of the entire TA/DIC data collected at Stonehaven (2008-2013) was made. DIC concentrations ranged from 2002 - 2134 µM/kg (mean 2092 µM/kg, n = 375). TA concentrations ranged from 2170 – 2309 µM/kg (mean of 2275 µM/kg, n = 134). As a consequence of nitrate uptake by phytoplankton cells during an algal bloom TA concentrations will increase. Therefore, it would be expected that TA concentrations will follow an annual cycle around the algal bloom (Figure 7). A strong TA seasonal cycle was observed at Stonehaven between 2009 and 2011, inclusive, however no seasonal cycle has been observed since 2012 (Figure 7). DIC concentrations would also be expected to follow an annual seasonal cycle, mirroring that of nitrate where concentrations decrease during the algal bloom. Stonehaven DIC concentrations increase over the winter months to a maximum in March before decreasing to minimise around July (Figure 8). The Defra pH study reported that this maximum could potentially be attributed to calcite dissolution in the area. MSS are investigating calcifying organisms (cocolithopohres) at Stonehaven as part of a schedule of service programme, the results of which will be reported as part of the MSS ROAME. Similar to TA, where the seasonal cycle was lost at Stonehaven in 2012, the DIC seasonal decrease at the time of the algal bloom was not observed. In 2013 the DIC seasonal cycle appears to have returned, minimising in May (Figure 8),

however, analysis of samples collected since July have yet to be undertaken any assumption should be treated with caution at this stage.

The pH, calcite and aragonite saturation states were calculated using CO_2SYS (version 2.1). At Stonehaven the $CaCO_3$ saturation state (Ω) was >1 for both calcite and aragonite at both depths (1 and 45 m) and all years, indicating that the waters are supersaturated and organisms should be able to calicify. The pH has remained consistent at both sampling depths since 2009 (Figure 9) following a seasonal cycle maximising during the summer months. The calculated pH at the site ranged from 7.8 to 8.4 mol/kg (seawater scale, mean = 8.1 mol/kg, n = 331).

SGOA and GOA-ON have both identified the need for a commitment to long-term monitoring at sites in coastal and inshore waters to distinguish long-term anthropogenic signals from short-term spatial and temporal variability. The long-term monitoring at Stonehaven highlights this, with the seasonal cycle in TA and DIC breaking down at the site during 2012. To understand the changes that occurred during 2012 it is clear there is a need for integrated monitoring, which includes measurement physical, chemical and biological parameters such as phytoplankton and temperature.

Discrete Samples Collected in the Minch North (West of Scotland)

Fifty-eight discrete water samples were collected on the *MV Isle of Lewis* between January and July from the Minch North and analysed for TA and DIC by NOC. Salinity, chlorophyll and nutrient analysis was undertaken by SEPA. A number of sample bottles broke during transit from the SEPA office to the NOC. In total 28 samples were analysed for DIC and 27 for TA. Salinity and nutrient corrected TA and DIC concentrations are shown in Figure 10. Where duplicate results are available, the maximum and the minimum values are displayed additionally to the mean (Figure 10). DIC concentrations ranged from 2057 µM/kg to 2194 µM/kg (Mean = 2106 µM/kg, SD = 29.3, n = 28) while TA concentrations ranged from 2169 µM/kg to 2345 µM/kg (Mean = 2289 µM/kg, SD = 31.7, n = 27). As a consequence of the limited project duration there is insufficient observations to determine the seasonal cycle. However, both DIC and TA concentrations drop at the end of May. SEPA measured the chlorophyll-a concentrations for the same period (January-July) in the Minch North and are shown in Figure 10 along with the TA and DIC concentrations. The reduction in the TA and DIC concentrations tie in with an algal bloom at the end of May to early June. A decrease in DIC concentrations during the spring bloom is to be expected. However, TA concentrations would be expected to increase around an algal bloom and it is unclear why the concentration decreased at this time.

The initial six month sampling period financed by UK-IMON does not allow for observation of seasonal trends, but informs the design of future long-term monitoring at this location and has therefore been very useful.

Discrete Samples Collected at Buoys

Discrete water samples were collected at the three sites (Celtic Deep SmartBuoy, Liverpool Bay SmartBuoy and AFBI's mooring in offshore waters of the western Irish Sea.) in March (except Celtic Deep SmartBuoy), May and August 2013 by AFBI. Samples were collected just below the surface to a depth of approximately 4 m (AFBI mooring only). Water samples were stored at room temperature prior to analysis for TA and DIC by NOC. Mean concentrations of TA and DIC in water samples collected at the offshore sites (Celtic Deep Buoy and AFBI mooring) were 2313 µM/kg (n=15) and 2080 µM/kg (n = 15), respectively (Figure 11).

Mean TA and DIC concentrations at the coastal site of Liverpool Bay were 2283 µM/kg (n=9) and 2076 µM/kg (n=9), respectively (Figure 11). This is similar to the surface TA and DIC mean concentrations at the Stonehaven coastal site during the same period (March-August 2013) of 2260 µM/kg (n=18) and 2104 µM/kg (n=18), respectively.

As a consequence of the limited sampling (March, May and August) at the sites it was not possible to observe a seasonal cycle for TA or DIC. A seasonal cycle for TA and DIC in Liverpool Bay has previously been observed with TA concentrations reaching a maximum around the spring algal bloom in May and June[25].

Conclusions

1. There is a requirement for a commitment to long-term monitoring of carbonate chemistry at sites in coastal, inshore and offshore waters to distinguish long-term anthropogenic signals from short-term spatial and temporal variability.

2. The use of automated water samplers deployed on instrumented moorings for the collection of water samples for DIC analysis was trialled by AFBI at their mooring in 2013. DIC concentrations were lower for samples collected by the automated water sampler, which may be as a consequence of the effect of longer storage. Results demonstrated that this methodology is not an advanced enough stage to permit routine use. A further, more detailed comparison should be undertaken to include a moored sampler with sample preservation, the introduction of a procedure to minimise aeration of samples

during processing and filtration, a more robust analytical procedure with regular quality control and precise judgement of depth and sample timing.

3. TA and DIC have been measured at MSS's long term monitoring site at Stonehaven since 2009. A seasonal trend was observed for both TA and DIC in nearly all years. TA concentrations reach a maximum around the spring bloom while DIC concentrations were lowest during this period. However, in 2012 no seasonal cycle was observed and there is no indication it has returned for TA in 2013. The long-term monitoring at Stonehaven highlights the need for robust data set to distinguish temporal variability.

4. Discrete water samples were collected in the Minch North between January and August 2013**.** Both TA and DIC concentrations dropped during May. Analysis for chlorophyll-a indicated there was an algal bloom at the end of May beginning of June. Although you would expect a decrease in DIC, TA concentrations would be expected to increase around an algal bloom and it is unclear why the concentration decreased.

5. Discrete water samples were collected at the three buoys (Celtic Deep, Liverpool Bay and AFBI mooring) in March (except Celtic Deep), May and August 2013 by AFBI. TA and DIC concentrations were higher at the offshore buoys (Celtic Deep and AFBI mooring) than at the coastal sites (Liverpool Bay and Stonehaven).

6. The initial six month sampling period financed by UK-IMON does not allow for observation of seasonal trends, but informs the design of future long-term monitoring programmes.

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Table 1

DIC concentrations (µM/kg) of moored and discrete samples collected as part of the feasibility study. Δ is difference between the samplers.

Sampling time	**Rosette sampler**	**Moored sampler**	Δ	Δ
13-May-13	DIC uM/Kg	DIC uM/kg	uM/kg	%
12:00	2129	2021	108	5.0
13:00	2285	2168	117	5.1
13:30	2266	2148	118	5.2
14:00	2275	2207	68	3.0
14:30	2314	2324	-10	-0.4
15:00	2344	2354	-10	-0.4
15:30	2363	2373	-10	-0.4
16:00	2334	2314	20	0.8
16:30	2275	2266	9	0.4
17:00	2305	2217	88	3.8
17:30	2285	2275	10	0.4
18:00	2324	2266	58	2.5
18:30	2275	2256	19	0.9
19:00	2275	2227	48	2.1
19:30	2285	2275	10	0.4
20:00	2246	2168	78	3.5
20:30	2217	2139	78	3.5
21:00	2119	2158	-39	-1.8
21:30	2148	2080	68	3.2

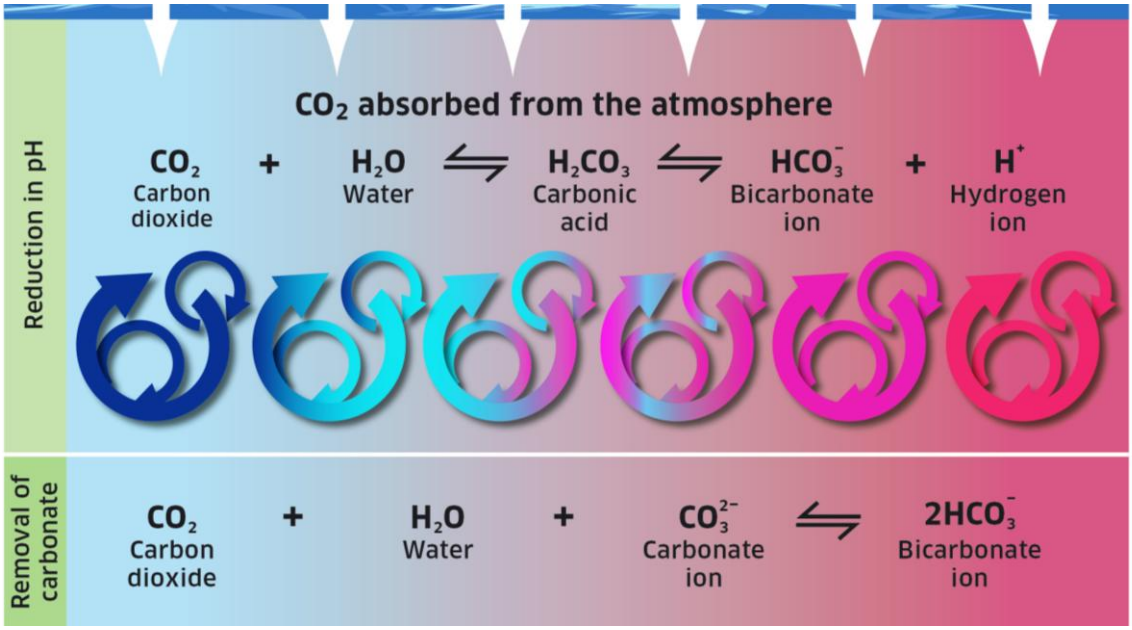

Figure 1: The carbonate system of seawater and the potential impact as a result of atmospheric absorption of CO2. Source: Baxter et al (2011). This is a 'litmus paper' diagram; the colour changes from blue to red as more CO2 is absorbed and the carbonate equilibria shift to release more hydrogen ions.

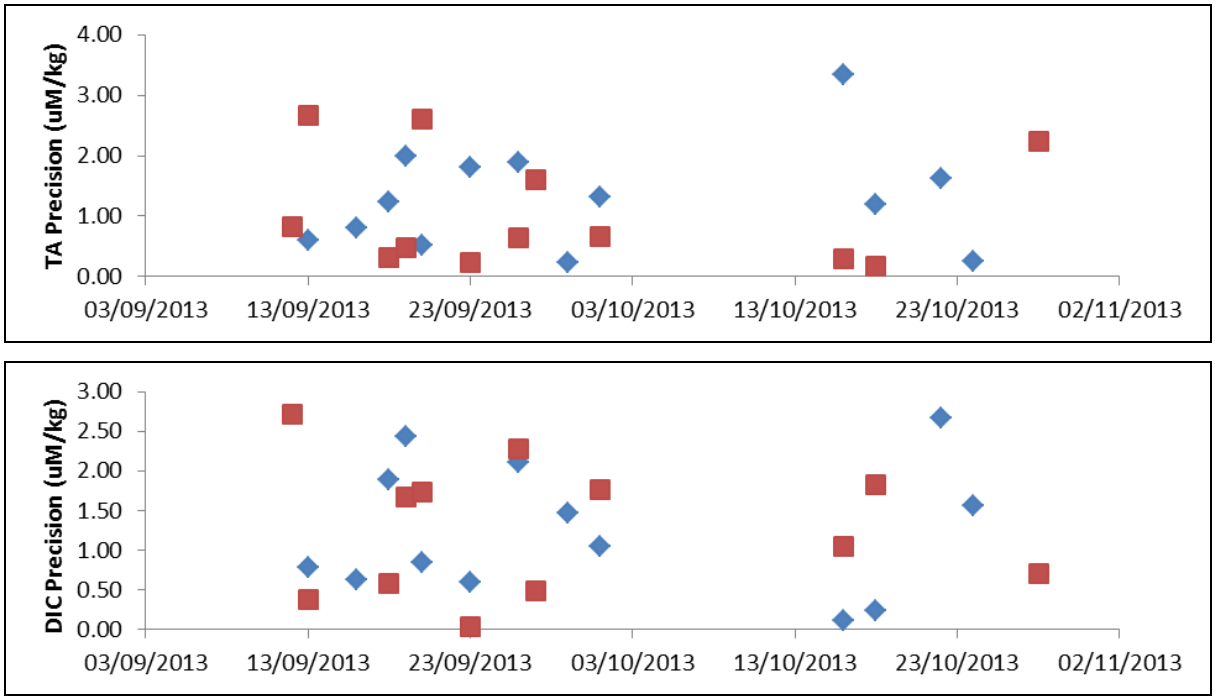

Figure 2: Precision of the DIC and TA analysis, for Vindta 11 (blue diamond) and Vindta 24 (red square), assessed using three previously analysed standards at the start of each day of analysis.

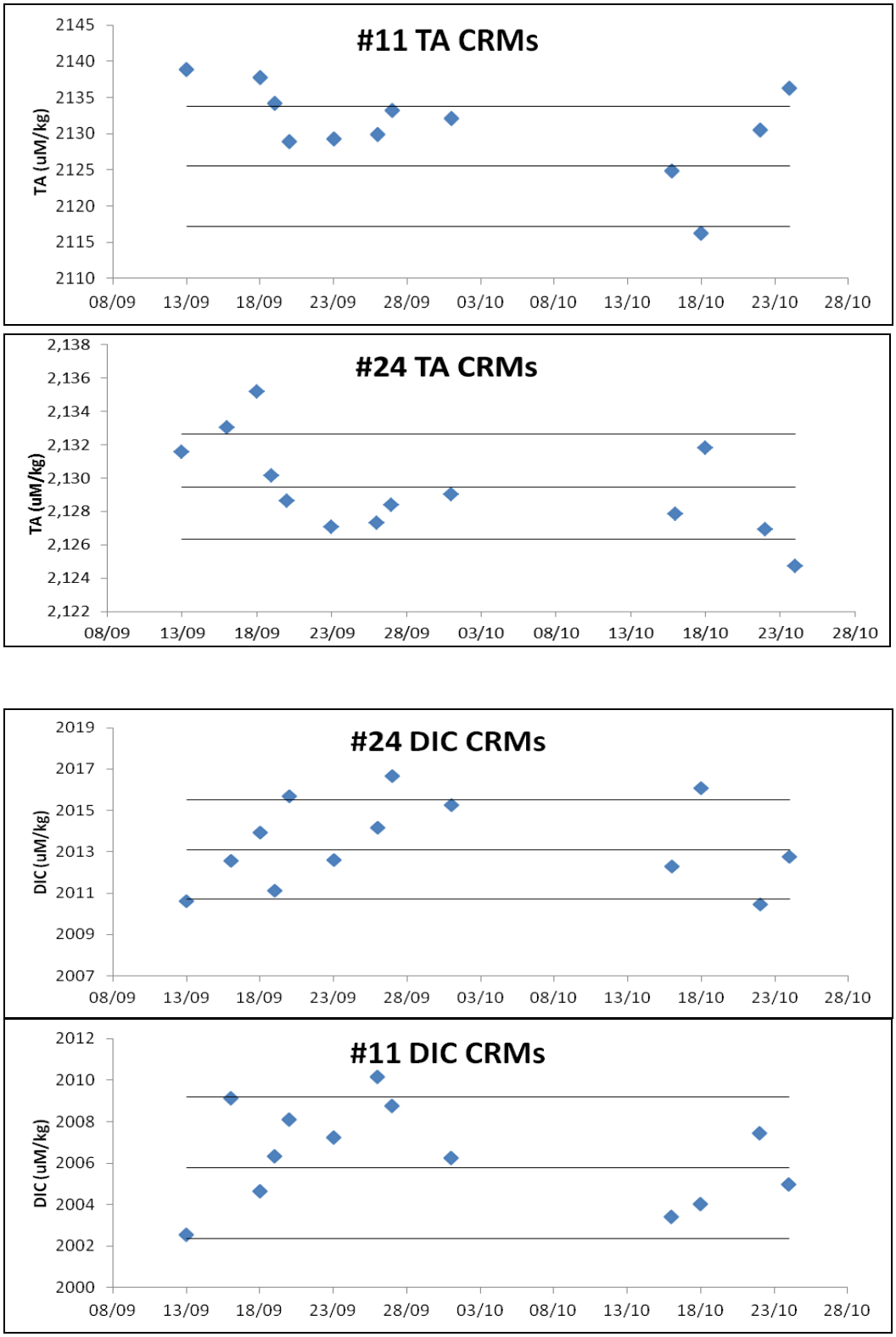

Figure 3: The first reference material analysed each day was used to calculate the sample correction value for DIC and TA. The three lines correspond to mean concentration (centre line) and +/- 1SD of the mean.

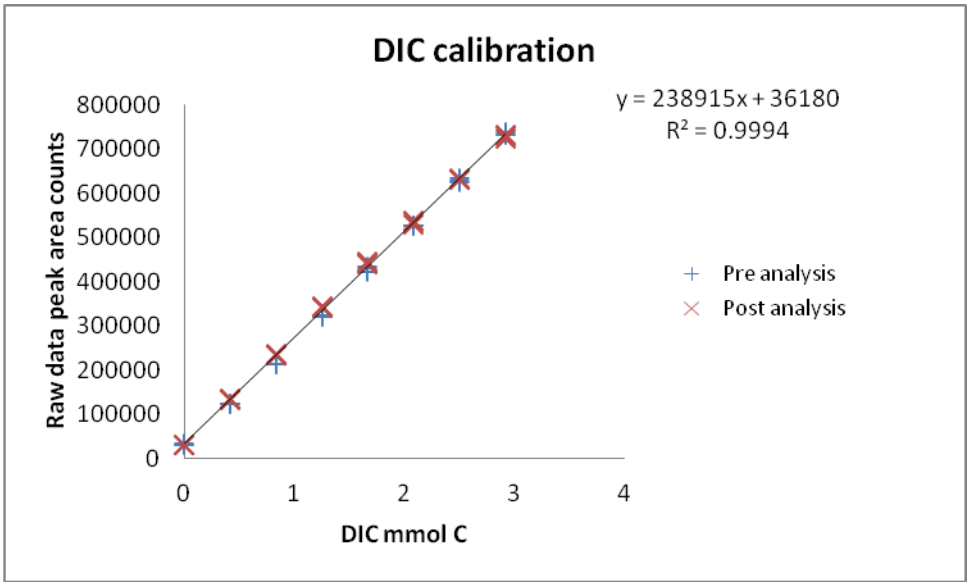

Figure 4: Feasibility studies - Combined pre and post calibration data used to determine DIC concentrations in discrete and moored samples.

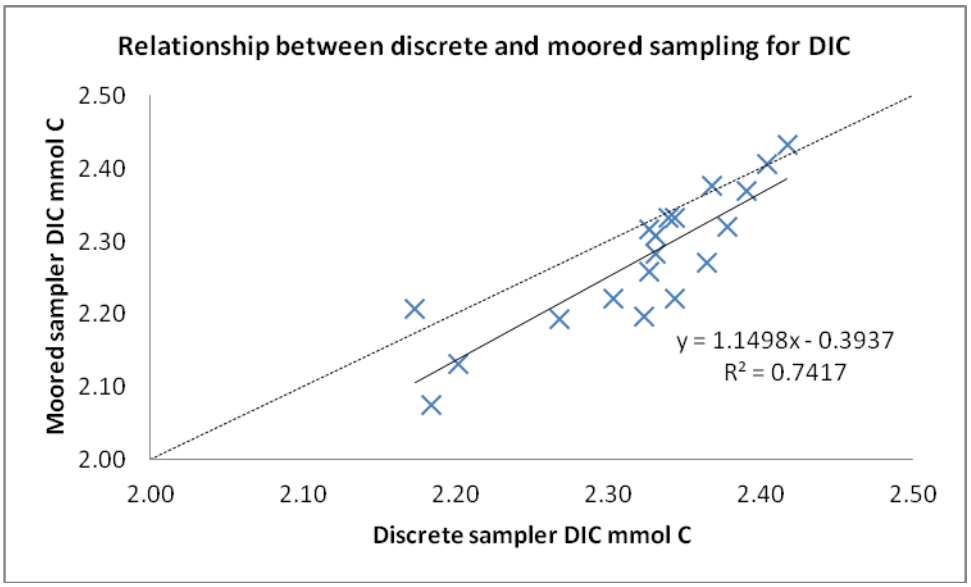

Figure 5: Feasbility study - Relationship between discrete and moored sampling for DIC. The dashed line represents a 1:1 comparison and the solid black line is the regression slope fitted to both data sets.

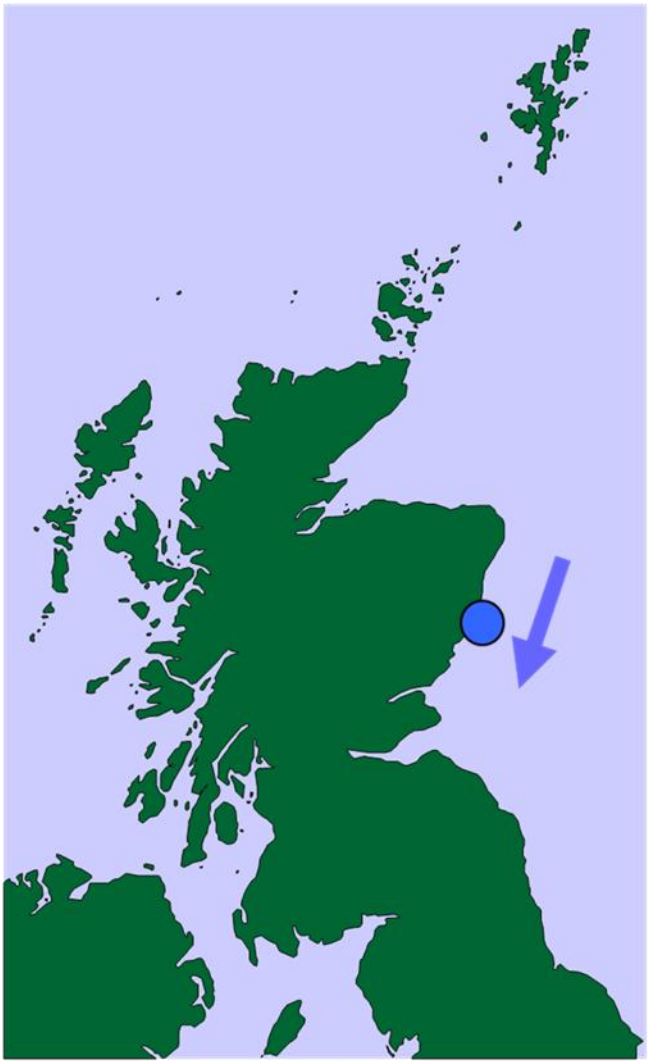

Figure 6: Stonehaven sampling site located ~25 Km south of Aberdeen and 5 Km offshore. The water depth at the site is ~ 50 m with a southerly current.

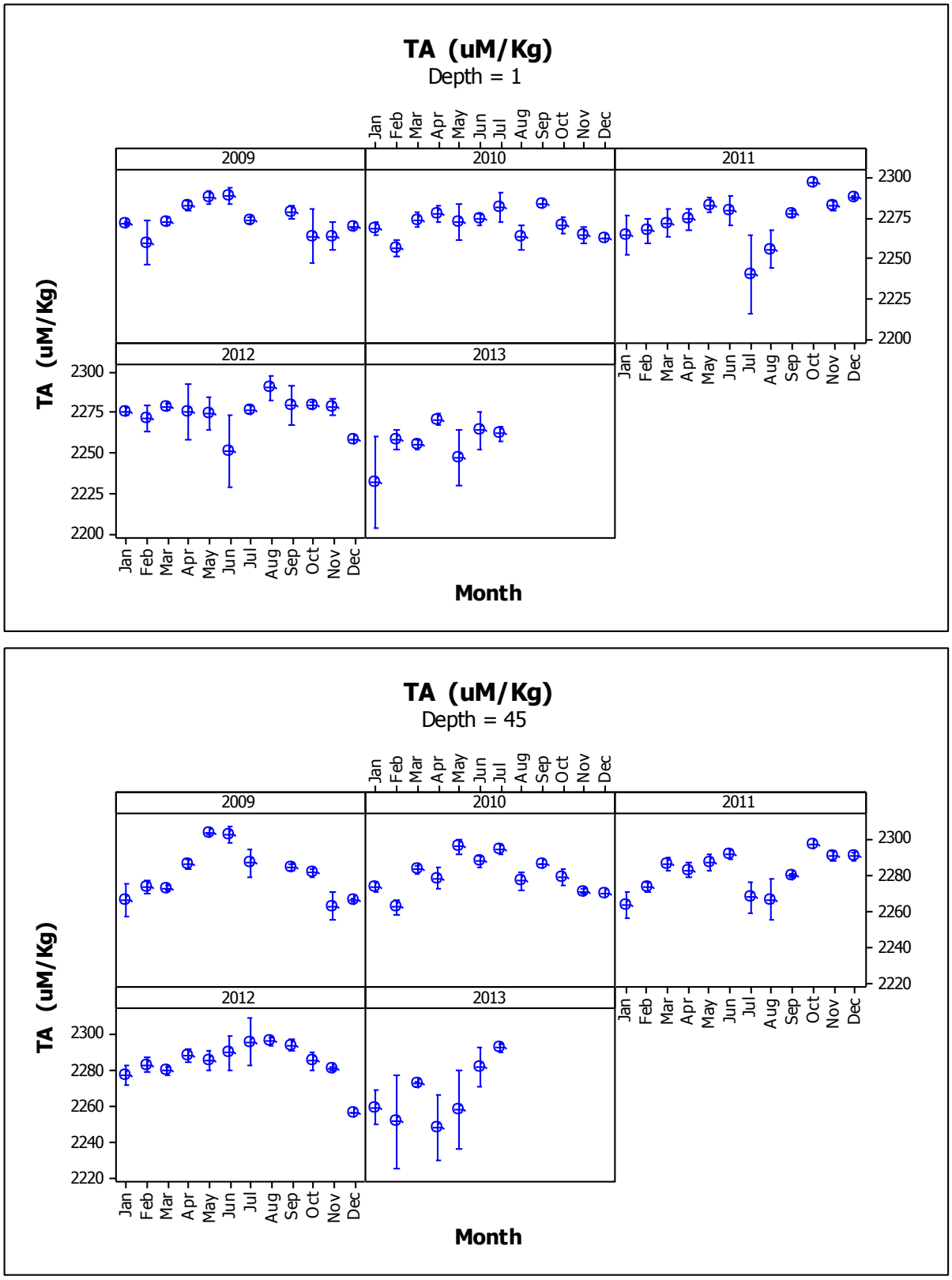

Figure 7: Total Alkalinity (TA) plot of Stonehaven dataset (2009-2013) from samples collected at the surface (1m) and just above the seabed (45 m). The error bars correspond to 1 standard error of the mean. A strong seasonal cycle was observed until 2012 when increase in TA concentration was observed.

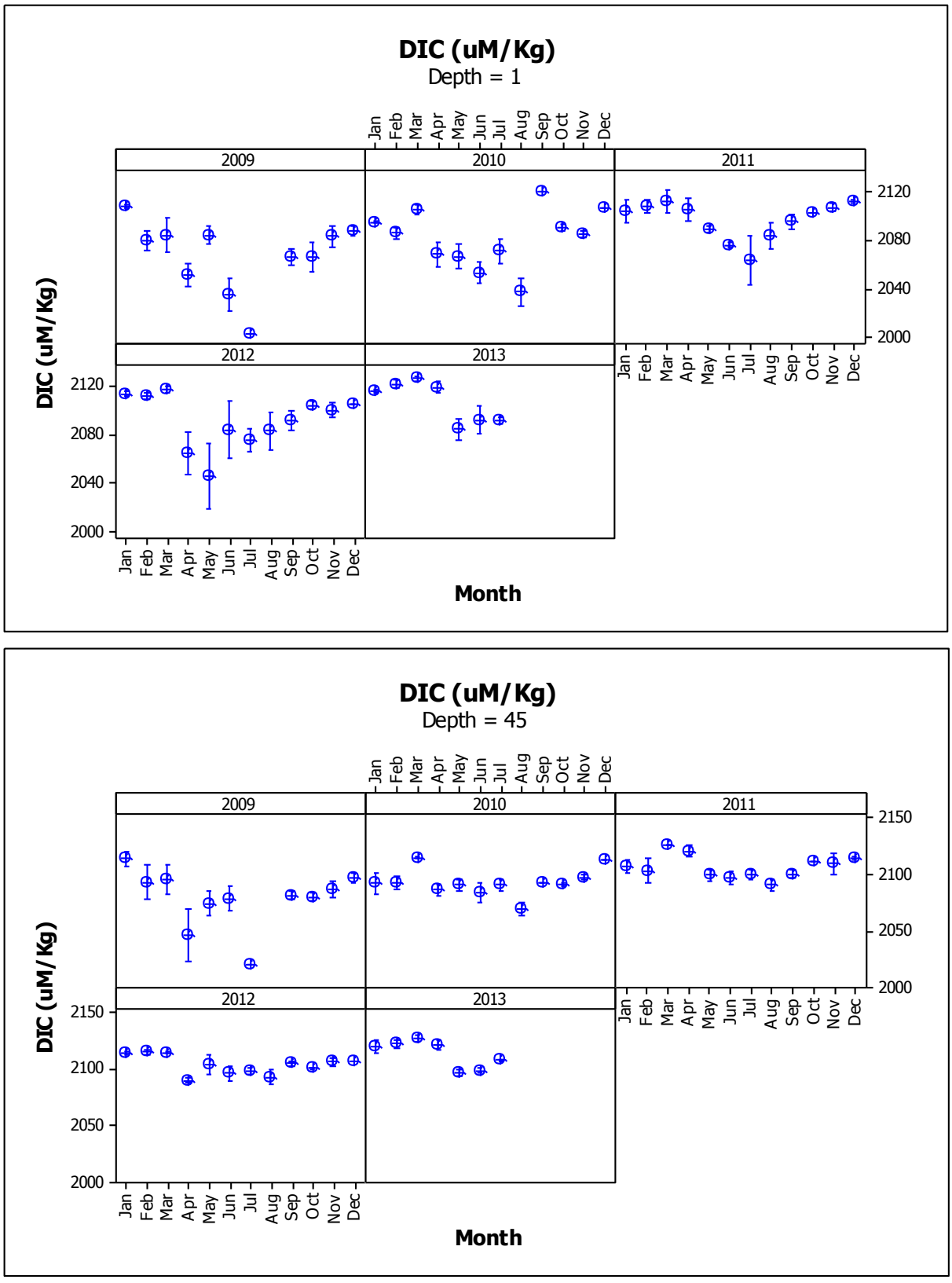

Figure 8: Dissolved inorganic carbon (DIC) plot of Stonehaven dataset (2009-2013) from samples collected at the surface (1 m) and just above the seabed (45 m). The error bars correspond to one standard error of the mean.

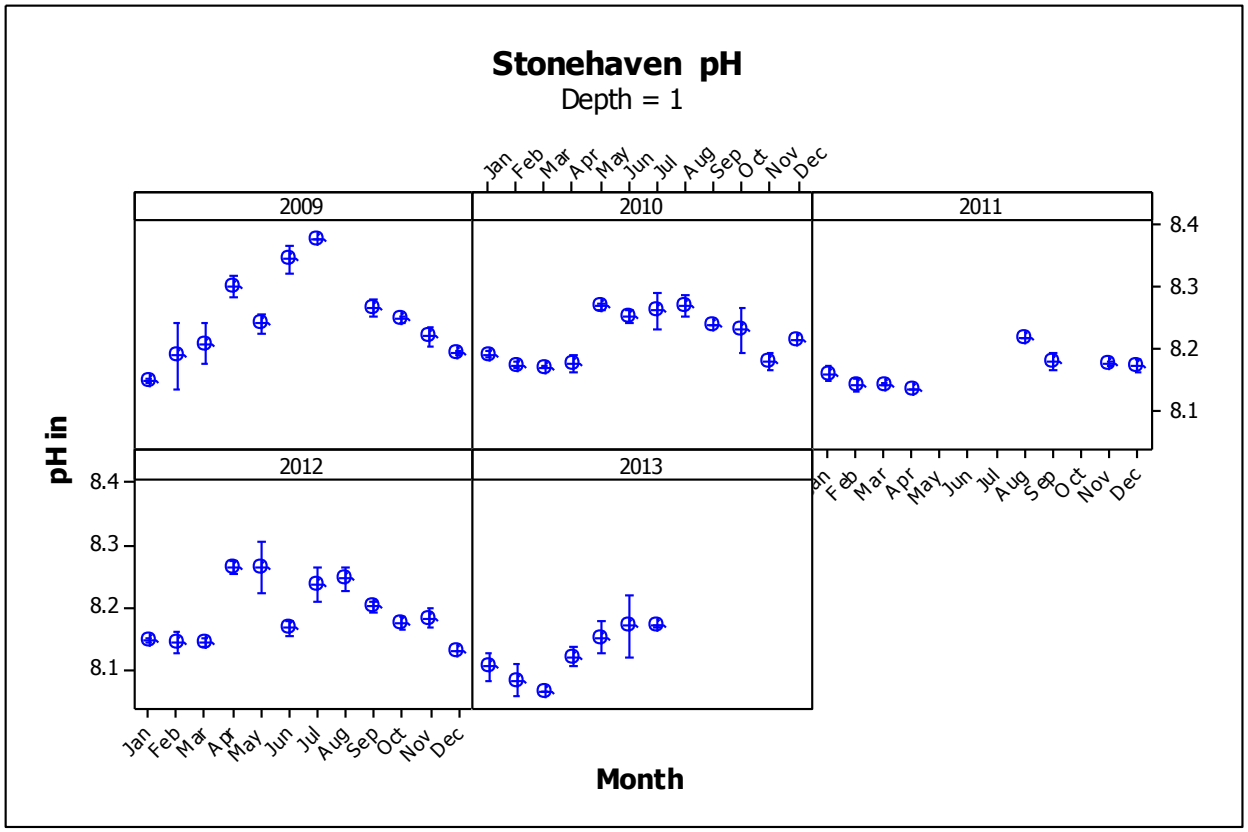

Figure 9: pH at Stonehaven (2009-2013) from samples collected at the surface (1 m). The pH was calculated using CO_2SYS (version 2.1).

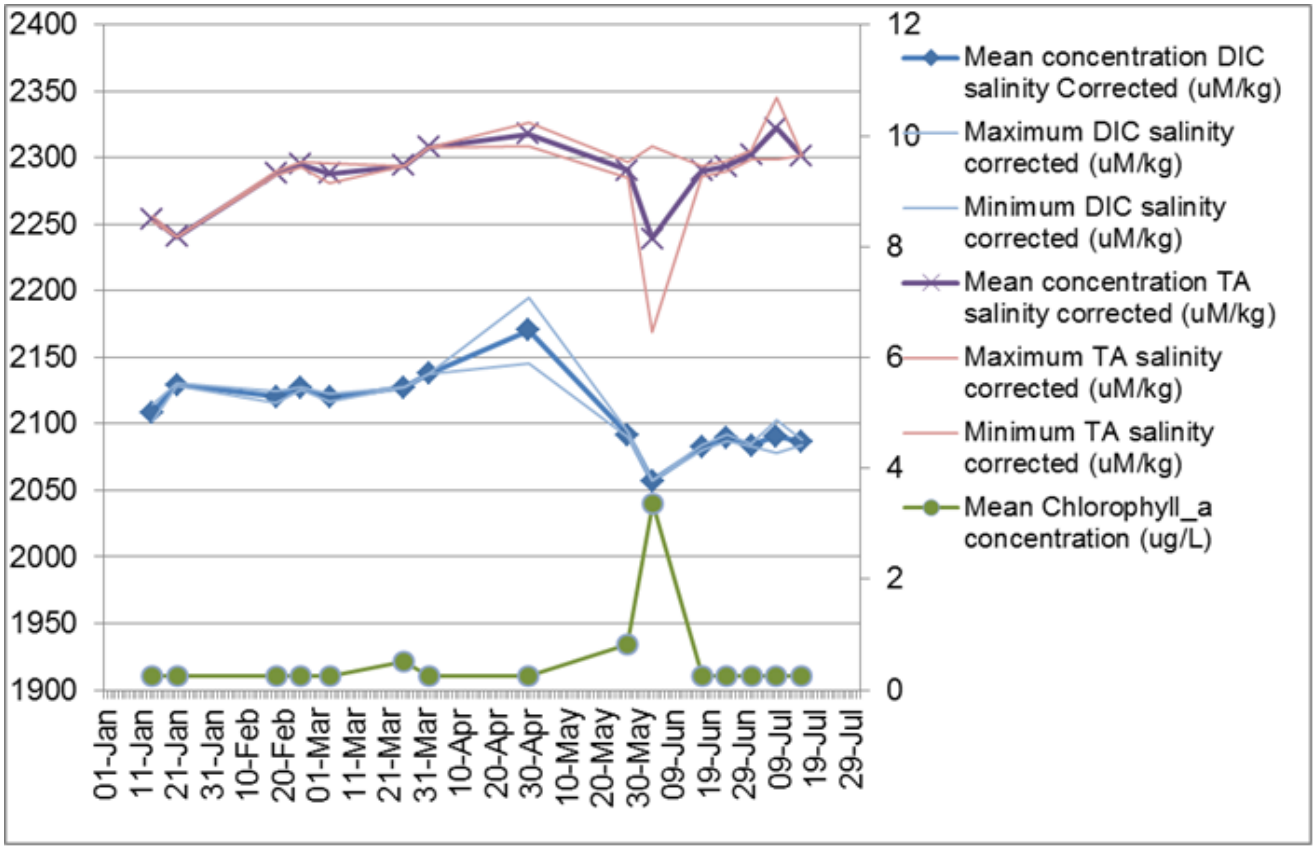

Figure 10: Dissolved inorganic carbon (DIC, blue) and total alkalinity (TA, red) concentrations (µM/kg) for the Minch North for the first half of 2013. Also plotted chlorophyll-a (Chl_a, green), in µg/L.

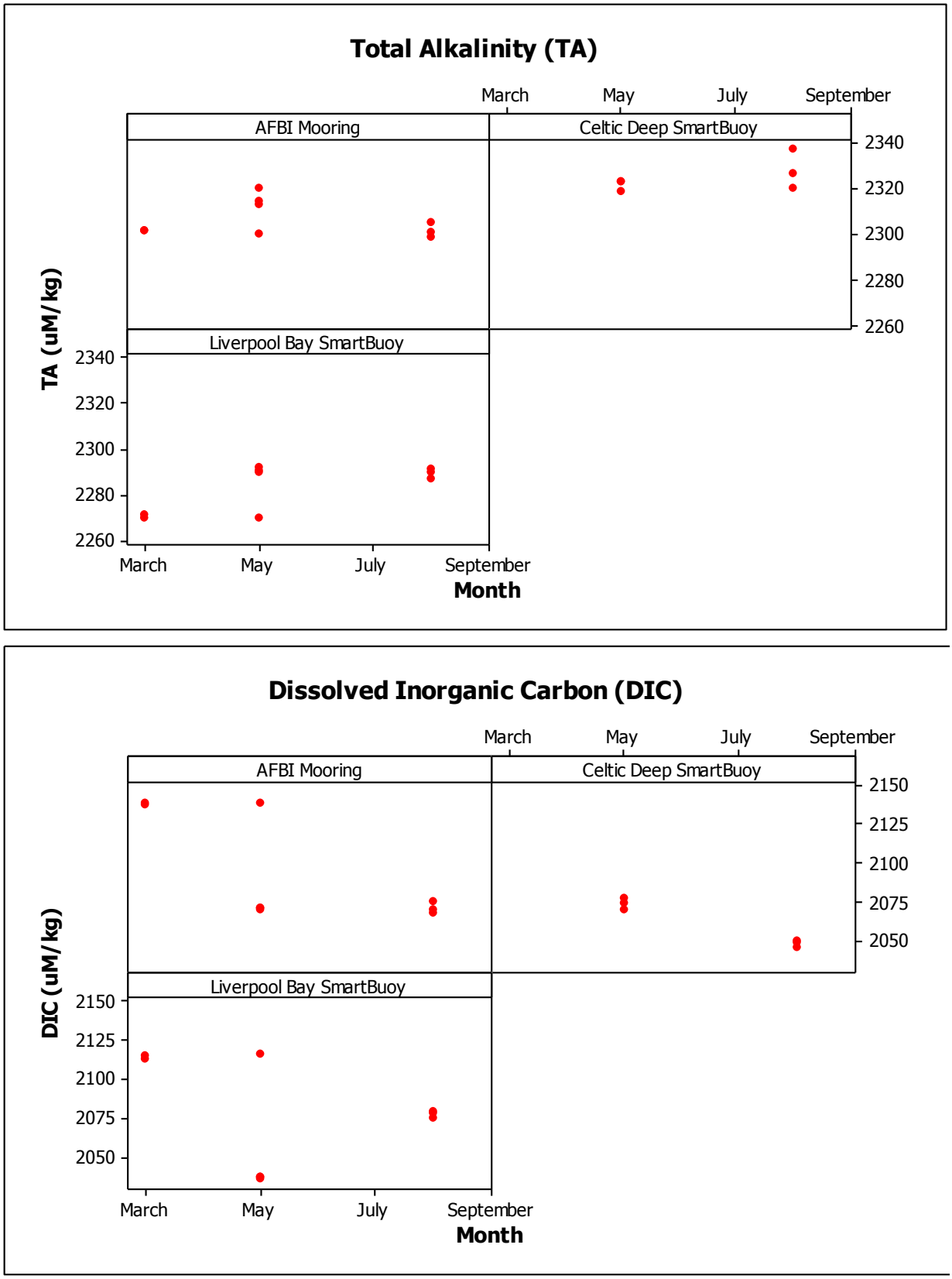

Figure 11: Dissolved inorganic carbon and Total Alkalinity from discrete water samples collected at three buoy sites (AFBI, Celtic Deeps and Liverpool Bay) during the first half of 2013.

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