



ICES

International Council for
the Exploration of the Sea

CIEM

Conseil International pour
l'Exploration de la Mer

Draft ICES Cooperative Research Report

Chemical aspects of ocean acidification monitoring in the ICES Marine area

Extracted sections relative to field monitoring of OA

- (1) The Ocean Acidification data set and meta-data
- (2) Draft OSPAR procedure for OA monitoring
- (3) Relevant monitoring in the OSPAR regions as attached xls sheet

Prepared by the ICES Marine Chemistry Working Group

David J. Hydes, NOC (UK)

Evin McGovern MI (Ireland)

Alberto V. Borges, ULg (Belgium)

Naomi Greenwood, CEFAS (UK)

Caroline Kivimae, NUIG (Ireland)

Klaus Nagel, IOW (Germany)

Solveig Olafsdottir, MRI (Iceland)

David Pearce, CEFAS (UK)

Elisabeth Sahlsten, SMHI (Sweden)

Carmen Rodriguez, IEO (Spain)

Carlos Borges, IH (Portugal)

Pamela Walsham MSS (UK)

Draft OSPAR MIME Monitoring Guidelines for Chemical Aspects of Ocean Acidification

(prepared by ICES-Marine Chemistry Working Group 24 Feb 2012)

Contents		
		page
1.	Introduction	1
2.	Purposes	1
3.	Quantitative objectives	1
4.	Sampling strategy	2
4.1	Monitoring for purposes 1 and 2	2
4.2	Monitoring for purpose 3	2
5.	Sampling equipment	3
5.1	Equipment	3
5.2	Contamination	3
6.	Storage and pre-treatment of samples	3
6.1	Storage	3
6.2	Pre-treatment	3
7.	Analytical procedures	3
8.	Analytical quality assurance	4
9.	Reporting requirements	5
10.	References	5

Monitoring Guidelines for Chemical Aspects of Ocean Acidification

1. Introduction

Ocean acidification is an unavoidable consequence of increased atmospheric concentrations of CO₂ and the partitioning of CO₂ into seawater. CO₂ reacts with seawater to produce carbonate, bicarbonate and hydrogen ions. Since the industrial revolution the concentration of hydrogen ions in seawater has increased by 30%. Ecosystems in certain seas such as Arctic waters are potentially more vulnerable to these changes as they will tend to become under saturated with respect to the carbonate minerals forming the shells of many organisms earlier than other areas (Gattuso and Hansson, 2011). Elsewhere it is important to consider that the concentration of hydrogen ions affects many biogeochemical processes such as the ratio of available ammonia to ammonium supporting primary production and the solubility of trace metals. Eutrophication may be closely linked to ocean acidification through the production of organic matter from CO₂ during primary production (Borges and Gypens, 2010; Provoost et al., 2010; Cai et al 2011). The degree of ocean acidification may be assessed through the measurement of carbonate species in solution and the calculation of the saturation states of the shell forming carbonate mineral aragonite and calcite. At present a recommendation cannot be made for a minimum reliable approach to monitoring (such as measurement of pH during late winter immediately prior to the spring bloom during eutrophication related surveys). This because data of sufficient accuracy and precision for the assessment of acidification status is generally absent. We are at a stage where the collection of baseline data to look at regional and temporal differences through the year should be encouraged. It should be noted that work on Ocean Acidification complements any the study and budgeting of marine CO₂ inventories and air-sea fluxes. Planning of the two activities should be coordinated.

2. Purposes

The measurement of carbonate species in seawater is carried out for the following purposes:

1. To monitor the spatial distribution of carbonate species concentrations within the maritime area to determine the anthropogenic influence on their distribution. (High quality marine observations should be coupled to regular monitoring of major river inputs^A, as changes in alkalinity in river inputs will influence changes in coastal seas.)
2. To assess trends in degree of ocean acidification by monitoring pH, other carbonate system parameters and carbonate mineral saturation, over periods of several years.
3. To provide information of sufficient spatial and temporal resolution to underpin the identification of biological impacts and future ecological risks.

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) of the marine areas concerned.

It is intended that the region-specific temporal trend-monitoring programme should have the power (e.g. 90%) to detect a change in concentration (e.g. 0.02 pH) over a selected period (e.g. 10 years). To clarify the situation and to help define objectives, Contracting Parties should collect and undertake statistical analyses of new baseline data sets collected (collection of new data should meet the quality criteria required for the monitoring of ocean acidification). The representative monitoring stations chosen for this should be selected on the basis of numerical modelling results and cover the range of environments from nutrient rich estuaries to deep ocean water and around cold water corals.

The spatial distribution of the monitoring programme should enable Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability in carbonate parameter concentrations. This would include a definition of the extent of the monitoring area and understanding of how monitoring by different Parties is complementary. This should be done to enable a full assessment which can be integrated across the whole OSPAR area.

4. Sampling strategy

Monitoring should consider all four measurable carbonate species (Dickson, 2010) measured as Total Dissolved Inorganic Carbon (DIC), Total Alkalinity (TA), Partial Pressure (of dissolved) Carbon Dioxide (pCO₂), and hydrogen ion concentration measured as pH^B (Dickson et al., 2007). The following supporting parameters are required for calculation of final individual concentrations of components of the carbonate system which are not measurable directly such as the concentration of carbonate ions (CO₃²⁻): temperature, salinity, silicate and phosphate.

The equilibrium chemistry of the carbonate system has been studied extensively (Dickson 2010) and the equilibria have been precisely quantified so that if two components of the system are measured the other two can be calculated with known level of error that varies with the choice of the pair and the concentration levels being worked at (Hydes et al., 2010). Well-tested software (e.g. CO2SYS and SEACARB^C) is available for carrying out the required calculation.

At the present state of development of analytical methods and supporting reference materials, the most reliable methods for work with samples are measurements of DIC and TA, which are supported by Reference Materials^D. For underway sampling high frequency (< 5 minutes) measurements with high precision and accuracy (< 1 ppm) can be achieved for the measurement of pCO₂ (measurements can be referenced against WMO approved gas standards^E). For assessment of ocean acidification, in some areas where only measurements of

pCO₂ are available they can be coupled to estimates of TA from salinity (Lee et al., 2006) to give a reliable calculation of pH.

Prior to establishing long term monitoring Parties should undertake wide ranging measurements to define the levels of variability across their marine areas before defining a minimum effective programme for observations in their areas. This should take into account and be coordinated with the plans of other Parties and their own existing programmes for monitoring other parameters (eutrophication being the likely most complementary activity).

Guidelines for monitoring are set out below in line with existing guidelines for the monitoring of eutrophication. For the parallel assessment of air-sea fluxes for the establishment of annual air-sea fluxes, year round monitoring of pCO₂ needs to be done with repeat visits sites on at least a monthly basis in representative areas (to be defined from numerical models).

4.1 Monitoring for purposes 1 and 2

In coastal seas monitoring of carbonate parameters should take place along salinity gradients in order to account for freshwater run-off from land to sea and as a measure to ensure consistency in treatment of the data for assessment.

Monitoring in shelf seas should be sufficiently extensive take account of inputs and the oceanographic characteristics of each region, particularly the in-flow of ocean water across the shelf break.

TA-salinity relationships for a coastal area can provide information about processes involved in regulating TA concentrations and the levels and variability of riverine inputs. A linear relationship indicates that physical mixing is the dominant process regulating the nutrient concentration, while non-linearity indicates the additional influence of chemical and/or biological processes. Several sources of freshwater or offshore water may add complexity to TA-salinity mixing diagrams, and temporal variability in the TA concentrations of the sources may contribute additional scatter and variability to the relationship. The temporal trend monitoring strategy should ensure that sufficient data are collected in order to confirm that maximum winter DIC concentrations was detected in given year.

Sufficient data should be collected so that a normalisation of the carbonate parameters to salinity (e.g. 34.5 for the North Sea) can be done and the precision of the normalisation defined statistically. pH and pCO₂ vary significantly with temperature therefore for assessments their values should be reported at agreed common temperature (e.g. 15.00 °C).

After sampling, the supporting parameters should be inspected to assess the level of algal activity at the time of sampling (e.g. chlorophyll a and dissolved oxygen) with respect to daily and annual cycles in production and decay to assess the error bar that should be attributed to data when included in temporal trend studies.

For Ocean Acidification monitoring in off shelf waters key areas include Arctic Seas and around cold-water corals because of their vulnerability to change. Measurements are required in subsurface waters as these can be used for calculation of the accumulation anthropogenic carbon in the water (e.g. Tanhua et al., 2007).

4.2 Monitoring for purpose 3

Monitoring for purpose 3 is intended to the address issues of where do decreased pH conditions affect ecosystem functions. For purpose 3, the sampling strategy for the carbonate system should be linked to appropriate biologically orientated surveys e.g. studies of corals, molluscs and embryonic life stages of certain groups of organisms. From a biological perspective there is a need to capture data on the spatial and temporal variation in the acidity of the waters surrounding the particular potentially sensitive organisms.

5. Sampling equipment

5.1 Equipment

Water samples for analysis of DIC/TA can be collected using a rosette frame or hydro-bottles clamped to a hydro-wire and lowered to the prescribed depth. Use of a rosette sampler combined with a profiling probe for measurement of temperature and salinity (a “CTD” profiler) is preferred. Additional sub-samples should be taken from water bottles and analysed for salinity, nutrients, dissolved oxygen and chlorophyll-a. Sampling from an underway water supply may also be possible but the procedure should be validated.

Samples for DIC/TA should be collected directly into Pyrex glass bottles with gas tight stoppers and the samples poisoned by the addition of Mercuric Chloride. For rosette sampling the priority for the order of drawing samples is - samples for DIC/TA should be taken after CFC and oxygen samples but before nutrient and salinity samples, to minimise the CO₂ exchange across the free surface that forms in the hydro-bottle as it drains.

5.2 Contamination

Sampling should be undertaken in such a way that any ship’s discharges are avoided. Sample bottles should remain closed when not in use.

Sample bottles should be thoroughly rinsed with sample before filling. A tube attached to hydro-bottle running to the base of the sample bottle should be used to minimise the possibility of gas exchange during sampling.

6. Storage and pre-treatment of samples

6.1 Storage

Bottles that are gas tight should be used for sample storage. Normally Pyrex bottles of 250 or 500 ml capacity are used and sealed with a greased ground glass stopper held in with a retaining band. Samples poisoned with Mercuric Chloride (Dickson *et al.*, 2007; SOP 1) can stable for at least one year if collected carefully.

It is recommended that laboratories should conduct systematic studies of the stability of their samples. As part of these tests exchange samples between laboratories should be done to separate errors due to degradation of samples from measuring errors.

6.2 Pre-treatment

Unnecessary manipulation of the samples should be avoided, however filtration with GF-F filters may be used for TA samples from turbid waters. No recommendation can be given for DIC samples. An accepted filtration method that minimises the gas exchange for DIC samples has not been published.

7. Analytical procedures

The methods for the determination of the four carbonate species are described in detail in Dickson *et al.* (2007). The preferred methods are (1) TA - acid base titration with the end point calculated by Gran fit; (2) DIC - addition of phosphoric acid with quantification of the evolved CO₂ by Coulometry; (3) pCO₂ underway samples - equilibration of gas stream with the surface water and determination of the equilibrated mole fraction of CO₂ in the gas stream by infra-red spectrometry at a known gas pressure; (4) No recommendation can presently (2012) be given on a technique for direct measurements of pH because both the equipment and methods of calibration are not at a mature stage of development.

8. Analytical quality assurance

The quality assurance programme should ensure that the data are fit for the purpose for which they have been collected, *i.e.* that they satisfy levels of precision and accuracy compatible with the objectives of the monitoring programme.

Regular collection of duplicate samples should be undertaken. Specific technical information on QA and QC is provided by Dickson et al (2007. SOPs 21, 22 and 23). Reference Materials (RM) are available for TA and DIC and reference gasses for pCO₂ (see above). Recommendations and Matlab tools for pCO₂ QC procedures were developed as part of the Surface Ocean CO₂ Atlas (SOCAT) project and are available at <http://www.socat.info/publications.html>. Quality assurance information should be reported as specified in Section 9.

When possible in addition to routine use of RMs, the data should be checked for cruise-to-cruise consistency by comparing samples from the deep ocean with near-steady CO₂ chemistry (> 2000 meters for instance), by comparing DIC-Salinity relationships, and/or relationships between DIC and nitrate, phosphate and oxygen (Tanhua *et al.*, 2010).

A system of regular inter-comparisons between the concerned laboratories should be organised.

Summary tables of total errors and biases for individual methods

Table 8.1 Generally accepted levels of error associated with each method based on Dickson (2010)

		Ref Method	State of art	Other
	Total dissolved inorganic carbon $\mu\text{mol kg}^{-1}$			
(A)	Acidification / vacuum extraction / manometric determination	1.0		
(B)	Acidification / gas stripping / coulometric determination		2-3	
(C)	Acidification / gas stripping / infrared detection			4
(D)	Closed-cell acidimetric titration			10+
(E)	Auto-analyser colorimetric			5+
	Total alkalinity $\mu\text{mol/kg}$			
(F)	Closed-cell acidimetric titration		2-3	
(G)	Open-cell acidimetric titration	1.2		
(H)	Other titration systems			2-10
	pH			
(I)	Electrometric determination with standard TRIS buffer.		0.005	0.01-0.03
(J)	Spectrophotometric determination using I. <i>m</i> -cresol purple	0.003		
	xCO₂ / pCO₂ μatm			
(K)	Direct - equilibrator infrared determination of xCO ₂		2	
(M)	Indirect - membrane colorimetric determination of xCO ₂			2-10
(L)	Direct - membrane infrared determination of xCO ₂			1-10

Table 8.2 Present status of Reference Materials for the quality control of oceanic carbon dioxide measurements based on Dickson (2010).

Analytical Measurement n	Desired Accuracy ¹	Uncertainty ²	Availability
DIC	$\pm 1 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$	since 1991 ³
TA	$\pm 1 \mu\text{mol kg}^{-1}$	$\pm 1 \mu\text{mol kg}^{-1}$	since 1996 ⁴
pH	± 0.002	± 0.003	since 2009 ⁵
Mole fraction of CO ₂ in dry air	$0.5 \mu\text{mol mole}^{-1}$	$\pm 0.1 \mu\text{mol mole}^{-1}$	since 1995 ⁶

1. Based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the CO₂ content of sea water that allow the increases due to the burning of fossil fuels to be observed. (SCOR. 1985. Oceanic CO₂ measurements. Report of the third meeting of the Working Group 75, Les Houches, France, October 1985.)

2. Estimated standard uncertainties for the Dickson SIO reference materials.

Sterilised natural seawater, certificated using a definitive method based on acidification, vacuum extraction, and manometric determination of the CO₂ released. Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

3. Certificated using a definitive method based on an open-cell acidimetric titration technique (Dickson *et al.*, 2003). Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>).

4. Standard buffer solutions based on TRIS in synthetic seawater (Nemzer & Dickson, 2005; DeVallis & Dickson, 1998). Available from UC San Diego (<http://andrew.ucsd.edu/co2qc/>). These now available, in at present limited quantities, from Dickson's laboratory for the validation of locally prepared buffers. Dickson *et al.*, 2007 - SOP 6a describes the preparation of buffers using 2-amino-2-hydroxy-1,3-propanediol (TRIS) and 2-aminopyridine (AMP) in synthetic sea water.

5. For calibration of continuous pCO₂ measurement systems, cylinders of air certificated on the basis of non-dispersive infrared spectrometry are available from NOAA/ESRL, (<http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html>).

9. Reporting requirements

Data reporting should be in accordance with the latest ICES reporting formats, together with information on methods used, detection limits, reference values and any other comments or information relevant to an ultimate assessment of the data. In order to establish the acceptability of the data, they should be reported together with and summary information from recent control charts, including dates, sample sizes, means and standard deviations. **For monitoring data only directly measured values should be reported.** This avoids any uncertainty about how calculated value was arrived at. During the subsequent assessment other parts of the carbonate system will be calculated. If this data is in its turn archived any derived values should be flagged to indicate how the values were arrived at. Pesant *et al* (2010) propose a system of secondary flagging for this purpose.

Data for TA and DIC should be reported in units of $\mu\text{mol kg}^{-1}$ and accompanied by a measurement of the in-situ temperature recorded with an error of less than ± 0.01 °C, salinity $< \pm 0.1$, phosphate $< \pm 0.1 \mu\text{mol kg}^{-1}$, silicate $< \pm 1.5 \mu\text{mol kg}^{-1}$.

10. References

- Blackford, J.C. & Gilbert, F.J., 2007. pH variability and CO₂ induced acidification in the North Sea. *Journal of Marine Systems*, 64: 229-241.
- Borges, A. V. & Gypens, N., 2010. Carbonate chemistry in the coastal zone responds more strongly to eutrophication than ocean acidification, *Limnol. Oceanogr.*, 55: 346–353. DOI: 10.4319/l.o.2010.55.1.0346..
- Cai, W. J. et al (2011) Acidification of subsurface coastal waters enhanced by eutrophication. *Nature Geosciences* DOI: 10.1038/NGEO1297
- DeVallis, T. A. & Dickson, A. G., 1998. The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ('tris') in synthetic sea water. *Deep-Sea Research I*, 45:1541-1554.
- Dickson, A.G., Afghan, J.D. & Anderson, G.C. 2003. Reference materials for oceanic CO₂ analysis: a method for the certification of total alkalinity. *Mar. Chem.*, 80: 185–197.
- Dickson A.G., 2010. The carbon dioxide system in seawater: equilibrium chemistry and measurements pp17 to 40 In Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.), 2010. Guide to best practices for ocean acidification research and data reporting, 260pp. Luxembourg: Publications Office of the European Union.
- Dickson, A. G., Sabine, C. L. & Christian, J. R., 2007. Guide to best practices for ocean CO₂ measurements, PICES Special Publication, 3, Sidney, Canada, 2007.
- Gattuso J.-P. & Hansson L., 2011. Ocean acidification: background and history. In: Gattuso J.-P. & Hansson L. (Eds.), *Ocean acidification*, pp. 1-20. Oxford: Oxford University Press.
- Hydes D.J., Loucaides S. & Tyrrell T., 2010. Report on a desk study to identify likely sources of error in the measurements of carbonate system parameters and related calculations, particularly with respect to coastal waters and ocean acidification experiments. Supplement to DEFRA contract ME4133 "DEFRApH monitoring project". Southampton, UK, National Oceanography Centre Southampton, 53pp. (National Oceanography Centre Southampton Research and Consultancy Report, 83. University of Southampton ePrint ID:164135
- Lee, K., Tong, L.T., Millero, F.J., Sabine, C. L., Dickson, A.G., Goyet, C., Park, G.H., Wanninkhof, R., Feely, R.A. & Key, R. M., 2006. Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans *Geophysical Research Letters*, 33: L19605, doi:10.1029/2006GL027207.
- Nemzer B. V. & Dickson A. G., 2005. The stability and reproducibility of Tris buffers in synthetic seawater. *Marine Chemistry* 96: 237-242.
- Pesant, S., Hook, L.A., Lowry, R., Moncoiffé, G., Nisumaa, A-M. & Pfeil, B. 2010. Safeguarding and sharing ocean acidification data, pp243-258, *In* Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.), 2010. Guide to best practices for ocean acidification research and data reporting, 260 p. Luxembourg: Publications Office of the European Union.
- Provoost, P., van Heuven, S., Soetaert, K., Laane, R., & Middelburg, J. J., 2010. Long-term record of pH in the Dutch coastal zone: a major role for eutrophication-induced changes, *Biogeosciences Discuss.*, 7: 4127-4152, doi:10.5194/bgd-7-4127-2010
- Tanhua. T., Koertzing. A., Friis, K., Waugh, D.W. & Wallace, D.W.R., 2007. An estimate of anthropogenic CO₂ inventory from decadal changes in oceanic carbon content. 104: 3037–3042. doi 10.1073 pnas.0606574104
- Tanhua, T. S., van Heuven, S., Key, R. M., Velo, A., Olsen, A. & Schirnick, C., 2010. Quality control procedures and methods of the CARINA database, *Earth System Science Data*, 2: 35-49.

Endnotes

^A River monitoring is needed for (1) understanding of the variability in river inputs and the drivers of this variability (2) to give better parameterisation of river inputs in numerical models of marine acidification (e.g. Blackford et al 2006).

^B Confusion can arise due to the existence of several different pH scales. pH is an operationally defined concept and there are four different scales (U.S. National Bureau of Standards (NBS), free scale, total hydrogen ion scale, seawater scale), which result in significantly different numerical values. The recommended scale for use in seawater related calculation is the total hydrogen ion scale. It is critical that the scale used is reported as part of the meta data when data are deposited in a data base.

^C CO₂ system calculation software can be down loaded from (1) <http://cdiac.ornl.gov/ftp/co2sys/> (2) Lavigne H. & Gattuso J.-P., 2011. seacarb: seawater carbonate chemistry with R. R package version 2.4. <http://CRAN.R-project.org/package=seacarb> (3) http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/

^D Dickson Lab <http://andrew.ucsd.edu/co2qc/>

^E NOAA Carbon Cycle Greenhouse Gases Group (CCGG <http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html>) is presently responsible for maintaining the World Meteorological Organization mole fraction scales for CO₂, CH₄, and CO.

ICES Marine Chemistry Working Group Extract

Data reporting

5.1 Data reporting and storage

In 2012 best practice for the reporting of data on ocean acidification to data centres is still evolving. In the EPOCA Guide to Best Practice in Ocean Acidification Research, Pesant et al (2010) discuss in detail why improved practice is needed in data reporting and how this can be achieved. The sections below follows the ideas developed by Pesant et al (2010), following on is a recommended meta data listing, which is based on that developed for reporting nutrient data and recommended in the GO-SHIP manual (Hydes et al., 2010). All available data and meta data need to be lodged in accessible data bases at appropriate data centres. This should be done in such a way that when it is retrieved from the data centre the data is actually useful to others.

5.1.2 Meta data requirements

We recommend that data and meta data be prepared and submitted together.

Best practices requires the meta data are made informative when names, titles and descriptions are assigned. Descriptions should be consistent and refer to well-recognised vocabulary registers for the parameters, equipment and sensors, etc.

Meta data should include the following information (a detailed list is given in the Appendix at the end of this section):

Dataset identity: [Its name] title, summary, date created and last updated, lead scientist contact details (last name, first name, e-mail, institution name, address and description), and reference to related research project (name and UUID^A).

Sampling details: [Information regarding the cruise or laboratory (eg. mesocosm) study] event name (code), Fieldwork/experiment name, research infrastructure name (e.g. ship, mesocosm, laboratory), responsible data producer's name and contact details, sampling device name, sampling device method, sample preservation and storage.

Parameter details: parameter name, parameter short name (often used in data tables where values are reported), details of reporting units (e.g. micro-mole/kg).

Measurement method: method name and method (description or citation)

Quality Control data: Summary of precision of analyses by batch (provider determined) including control charts where available.

Sample UUID and measured value: [plus appropriate location data Lat and Long or time]

Calculated value: For carbonate experimental studies where a complete data set from an experiment is being recorded such data sets are likely to include calculated values of carbonate system components for example values of pH calculated from measurements of TA and DIC. Pesant et al. (2010) suggested a flagging method (and set of appropriate flag codes) for identifying the calculation method used and the measurements used for the calculation.

5.1.3 Specific meta data requirements for seawater carbonate chemistry and ancillary parameters

In the study of seawater carbonate chemistry, the composition of the whole carbonate system can be calculated when two of the four measurable components have been measured. For accurate calculations data on water temperature, salinity and concentrations of phosphate and silicate are also required. An error in the measurement of DIC or TA generates an error in the calculated pH of ~ 0.003 pH units. Measurements of temperature, salinity, phosphate and silicate to precisions 0.1 °C, 0.1 psu, 1 micro-mole/kg and 15 micro-mole/kg respectively, each also shift the calculated pH by ~ 0.002 units when pH is

calculated from measurements of from DIC and TA. Ideally therefore target precisions for reporting in-situ temperatures should be with an error of less than ± 0.01 °C, similarly salinity $< \pm 0.1$, phosphate $< \pm 0.1 \mu\text{mol kg}^{-1}$, silicate $< \pm 1.5 \mu\text{mol kg}^{-1}$.

For the carbonate components the following metadata information is needed:

Dissolved inorganic carbon - DIC concentration (micro-mole/kg): information about sample replication, sample volume and head space, poisoning (poison volumes), analysis method (technique description, reference), CRM information (correction magnitude, batch number, analysis log), overall precision, and accuracy.

Total alkalinity - TA (micro-mole/kg): type of titration and cell type (with reference), sample volume curve fitting method (with reference), CRM information (correction magnitude, batch number, analysis log), overall precision, and accuracy.

Carbon dioxide partial pressure – pCO₂ (micro-atmosphere): analytical method (technique description, reference and equipment used), in situ temperature, temperature during measurement, temperature normalisation, temperature correction method, variable reported (xCO₂, pCO₂ or fCO₂), gas, standard gas concentrations, frequency of standardisation, overall precision and accuracy (Pierrot et al., 2009).

pH: pH scale, analytical method (technique description including, when appropriate, probes, buffer names and reference), in situ temperature, temperature during measurement, temperature normalisation/correction method, in situ pressure, calibration method, overall precision and accuracy.

The software packages Seacarb (Lavigne & Gattuso, 2010), CO₂sys (Lewis & Wallace, 1998), SWCO₂ (Hunter, 2012) can be used to compute a complete and consistent sets of carbonate chemistry parameters, using in situ values of temperature and salinity, and any pair of the carbonate chemistry parameters listed above (see Hydes et al., 2010). For the most accurate calculation of the individual components contributing to the total alkalinity TA, concentrations of silicate and phosphate need also to be included in the calculations and therefore need to be made available as part of the reported data set. The Seacarb software uses flags to specify which pair of seawater carbonate chemistry parameters are used for computations. Pesant et al (2010) recommended that “these “Carbonate Chemistry Computation” flags (CCC flags) are used when archiving computations from Seacarb (Lavigne & Gattuso, 2010) and/or CO₂SYS (Lewis & Wallace, 1998), and that the method of calculation and the appropriate flag be written out fully in the metadata. For example with pH, “pH was computed on the total scale using Seacarb (Lavigne & Gattuso, 2010) from DIC and total alkalinity. DIC was first calculated with CO₂SYS (Lewis & Wallace, 1998) using pH (other scale) and total alkalinity as input parameters (CCC flag 29)”. It is essential that a table explaining the CCC flags is provided to the data centres.”

Data may be dispersed in a range of national and international projects (e.g. CARBOOCEAN, EPOCA) data centres. Data should be reported to both the Carbon Dioxide Information Analysis Center (CDIAC - <http://cdiac.ornl.gov/oceans/home.html>) and to the ICES data repository. Reporting data to the ICES data repository enables it to be linked to many related additional datasets e.g. nutrients and integrated ecosystem data. Globally most research groups measuring carbonate parameters submit data to CDIAC. CDIAC has established reporting formats for these data and metadata, and has worked with the community to develop systems for effective data access and review particularly the Surface Ocean CO₂ Atlas (SOCAT, 2012). ICES should consider how data reporting would evolve so that relevant data is available and accessible to both databases without replicating reporting requirements. Harmonised data vocabularies and meta-data reporting requirements need to be elaborated.

References

SOCAT, 2012

Lavigne, H. and Gattuso, J.-P. (2010) seacarb: seawater carbonate chemistry with R. R package version 2.3.4. <http://cran-project.org/package=seacarb>.

- Pesant, S., Hook, L.A., Lowry, R., Moncoiffé, G., Nisumaa, A-M. and Pfeil, B. (2010) Safeguarding and sharing ocean acidification data, pp243-258, *In* Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.), 2010. Guide to best practices for ocean acidification research and data reporting, 260 p. Luxembourg: Publications Office of the European Union.
- Pierrot, D. E. Lewis, and D. W. R. Wallace. 2006. CO2SYS_calc_XLS: *MS Excel Program Developed for CO₂ System Calculations*. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee.
- Pierrot, D., C. Neill, K. Sullivan, R. Castle, R. Wanninkhof, H. Lueger, T. Johannessen, A. Olsen, R.A. Feely, C.E. Cosca, 2009. Recommendations for autonomous underway pCO₂ measuring systems and data-reduction routines. *Deep-Sea Research II* 56, 512–522
- Lewis, E., and D. W. R. Wallace. 1998. Program Developed for CO₂ System Calculations. ORNL/CDIAC-105. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee (cdiac.ornl.gov/ftp/co2sys/)
- Hydes, D.J., Loucaides, S. and Tyrrell, T. (2010) Report on a desk study to identify likely sources of error in the measurements of carbonate system parameters and related calculations, particularly with respect to coastal waters and ocean acidification experiments. Supplement to DEFRA contract ME4133 “DEFRApH monitoring project”. Southampton, UK, National Oceanography Centre Southampton, 53pp. (National Oceanography Centre Southampton Research and Consultancy Report, 83) <http://eprints.soton.ac.uk/170235/>
- Hunter, K. (2012) http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2
- Hydes, D. J., M. Aoyama, A. Aminot, K. Bakker, S. Becker, S. Coverly, A. Daniel, A. G. Dickson, O. Grosso, R. Kerouel, J. van Ooijen, K. Sato, T. Tanhua, E. M. S. Woodward, J. Z. Zhang (2010) Determination Of Dissolved Nutrients (N, P, Si) In Seawater With High Precision And Inter-Comparability Using Gas-Segmented Continuous Flow Analysers The GO-SHIP Repeat Hydrography Manual: A Collection of Expert Reports and Guidelines IOCCP report N.14, ICPO Publication Series N. No.134, Version 1, 2010

Footnote^A

Universally Unique Identifiers (UUIDs including DOIs, URLs, URNs or LSIDs) are now widely used by scientific journals to cite their papers. Similarly, information systems such as the Publishing Network for Geoscientific and Environmental Data (PANGAEA®) are automatically registering every dataset with persistent Digital Object Identifiers (DOIs) that are used to cite data. Like most UUIDs, DOIs are used in web browsers to get online access to metadata and data (although sometimes restricted), which considerably helps identifying intellectual property. Several data centres (e.g. CDIAC) are tagging their datasets with UUIDs. Peer-reviewed and indexed journals such as Earth System Science Data (ESSD; <http://www.earth-system-science-data.net/>) allow researchers to rapidly publish data prior to their full analysis and thereby obtain public recognition of their generation of the data.

Annexe 3

Metadata for reporting on carbonate system measurements

A3.1 Information required

General Information:

Cruise information:

1. Vessel (name; country; vessel ID)
2. Principal Scientist for cruise
3. Date and Port of departure
4. Date and Port of arrival
5. Cruise ID (EXPOCODE)
6. Name of experiment (e.g. P16 or M60/5)
7. Leg
8. Geographical coverage (e.g. North Atlantic; 30°N to 50°N and 60°W to 10°W)
9. Number of CTD stations
10. Number of surface (underway) samples

Mesocosm or laboratory information

1. Name of supporting programme (e.g. EPOCA)
2. Principal Scientist for study
3. Scientist reporting data
4. Name of individual process study
5. Mesocosm/laboratory location
6. Start and end dates of study
7. Name of experiment (e.g. Svalbard 2010)
8. Number of systems and samples measured
9. Brief description of environmental modifications to carbonate saturation state

Carbonate measurements:

PI and analysts carrying out analyses

1. Name project PI reporting data (e.g. Toby Tyrrell)
2. Name analytical service PI (e.g. Eric Achterberg)
3. Name senior analyst (e.g. Cynthia Dumousseaud)
4. Organization: (e.g. UKOA Carbonate Analytical Service)
5. Address
6. Phone
7. Email

Variables descriptions:

1. Variable names (e.g. xCO₂ or pCO₂ at say 25 °C or in-situ temperature)
2. Data base parameter codes
3. Reporting units

Dates of:

1. Collection
2. Reception by analytical service
3. Measurement

Sampling procedures and storage:

1. Sampling containers (e.g. 500 ml Schott Glass Duran clear glass). Grease for the stopper.
2. Processing of sampling during collection (e.g. Filtering of alkalinity samples – method e.g. vacuum filter size e.g. GF/F).
3. Poisoning of samples (e.g. 100 micro-litre saturated HgCl₂)
4. Storage (e.g. in dark refrigerated 4 °C)

Method description (separate details for each method DIC/TA/pCO₂/pH):

1. Instrument: - instrumentation used for the measurements. (For instance: VINDTA 3C.)

- Method for each measured parameter, and appropriate reference. (For instance: Dickson et al., (2007) SOP 6
- Note deviations in your set-up from the reference method or any modification from the standard instrument.
- Note temperature control and variability during analysis for sample, acid, volumetric burettes.
- Note electrode slope and stability if titrations are used

Reagents:

- Brands and stock information of the reagents/salts used.
- Where the solutions prepared on the ship, or pre-made in the lab prior to cruise
- Which medium was used for the reagents (e.g. MilliQ, NaCl solution)

Standardisation:

- How were your stock solutions prepared (initial salts, medium), + method (volumetric; mass)
- How were the stock solutions diluted to working concentrations (medium) + method (volumetric; mass)
- How were stock solutions standardised (i.e. coulometric standardization of acid titrant)
- Blank measurements (medium)
- Which pipettes were used? State calibration information of the pipettes.

Reference material:

- Certified reference materials used (state batch numbers, producer etc.).
- pCO₂ calibration gasses and reference gasses used for calibration of working standard gasses.
- State calibration method used for coulometer (gas loops) and how often calibration is performed.
- State when and how often reference materials are used for QC during a run.
- State how precision and stability is tested.

Quantification procedures:

- Mathematical formula used for the calculation of concentration (e.g. Alkalinity – Gran plot/Curve fitting; e.g. pCO₂ – Pierrot et al (2009)
- Calibration curves/ranges (e.g. pCO₂ number of standard gasses and concentration)
- Blank corrections
- Recalculation of run

Data quality: Best estimate of accuracy and precision

- State how these numbers were obtained (e.g. by measurements of n duplicates and by running n number of CRM samples).
- Number of samples/duplicates measured
- Provide relevant control charts (see Dickson et al., (2007) SOP 22)

Flagging used

- Data should be flagged following the WOCE codes as first step by the analyst and then by the project scientist before reporting the data to e.g. CDIAC; following the SOCAT procedure: 2 (good), 3 (questionable) or 4 (bad).
- When calculated values are reported the flagging scheme suggested by Pesant et al 2010) should be followed, and an additional column added to the data file. See Pesant et al. CCC flags Table 15.1, example below.

CCC flag	Computation software	Input parameters (in addition to temperature, salinity, pressure Si and PO ₄)
1	seacarb	pH (total scale) and CO ₂
2	seacarb	CO ₂ and HCO ₃ ⁻
3	seacarb	CO ₂ and CO ₃ ²⁻

Notes

- A significant part of the information required above are specific for the carbonate system measurements and will be generic for a particular lab, i.e. will only have to filled out once by each

lab; variations to the standard procedures can then easily be edited in for each cruise, mesocosm and/or process study.

2. "Accuracy" is the closeness of agreement between a measured value and the true quantitative value of the measurand. It can only be quantified in situations where measurements can be made of a measurand for which an agreed value exists such as a certified reference material.
3. "Precision" is the closeness of agreement of replicate measurements of the same property under specified conditions. It can be quantified by a measure such as standard deviation.

Definitions follow VIM (International Vocabulary of Metrology);
http://www.bipm.org/utis/common/documents/jcgm/JCGM_200_2008.pdf