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Chemical aspects of ocean acidification monitoring in the ICES marine area

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Editors

David J. Hydes ● Evin McGovern ● Pamela Walsham

Authors

Alberto V. Borges ● Carlos Borges ● Naomi Greenwood ● Susan E. Hartman
David J. Hydes ● Caroline Kivimae ● Evin McGovern ● Klaus Nagel
Solveig Olafsdottir ● David Pearce ● Elisabeth Sahlsten
Carmen Rodriguez ● Pamela Walsham ● Lynda Webster

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H. C. Andersens Boulevard 44–46
DK-1553 Copenhagen V
Denmark
Telephone (+45) 33 38 67 00
Telefax (+45) 33 93 42 15
www.ices.dk
info@ices.dk

Contents

Acknowledgements

Executive summary

It is estimated that oceans absorb approximately a quarter of the total anthropogenic releases of carbon dioxide to the atmosphere each year. This is leading to acidification of the oceans, which has already been observed through direct measurements. These changes in the ocean carbon system are a cause for concern for the future health of marine ecosystems. A coordinated ocean acidification (OA) monitoring programme is needed that integrates physical, biogeochemical, and biological measurements to concurrently observe the variability and trends in ocean carbon chemistry and evaluate species and ecosystems response to these changes. This report arises from an OSPAR request to ICES for advice on this matter. It considers the approach and tools available to achieve coordinated monitoring of changes in the carbon system in the ICES marine area, i.e. the Northeast Atlantic and Baltic Sea.

An objective is to measure long-term changes in pH, carbonate parameters, and saturation states (Ωaragonite and Ωcalcite) in support of assessment of risks to and impacts on marine ecosystems. Painstaking and sensitive methods are necessary to measure changes in the ocean carbonate system over a long period of time (decades) against a background of high natural variability. Information on this variability is detailed in this report. Monitoring needs to start with a research phase, which assesses the scale of short-term variability in different regions. Measurements need to cover a range of waters from estuaries and coastal waters, shelf seas and ocean-mode waters, and abyssal waters where sensitive ecosystems may be present. Emphasis should be placed on key areas at risk, for example high latitudes where ocean acidification will be most rapid, and areas identified as containing ecosystems and habitats that may be vulnerable, e.g. cold-water corals. In nearshore environments, increased production resulting from eutrophication has probably driven larger changes in acidity than CO_2 uptake. Although the cause is different, data are equally required from these regions to assess potential ecosystem impact.

Analytical methods to support coordinated monitoring are in place. Monitoring of at least two of the four carbonate system parameters (dissolved inorganic carbon (DIC), total alkalinity (TA), pCO_2, and pH) alongside other parameters is sufficient to describe the carbon system. There are technological limitations to direct measurement of pH at present, which is likely to change in the next five years. DIC and TA are the most widely measured parameters in discrete samples. The parameter pCO_2 is the most common measurement made underway. Widely accepted procedures are available, although further development of quality assurance tools (e.g. proficiency testing) is required.

Monitoring is foreseen as a combination of low-frequency, repeat, ship-based surveys enabling collection of extended high quality datasets on horizontal and vertical scales, and high-frequency autonomous measurements for more limited parameter sets using instrumentation deployed on ships of opportunity and moorings. Monitoring of ocean acidification can build on existing activities summarized in this report, e.g. OSPAR eutrophication monitoring. This would be a cost-effective approach to monitoring, although a commitment to sustained funding is required.

Data should be reported to the ICES data repository as the primary data centre for OSPAR and HELCOM, thus enabling linkages to other related datasets, e.g. nutrients and integrated ecosystem data. The global ocean carbon measurement community reports to the Carbon Dioxide Information Analysis Center (CDIAC), and it is imperative that monitoring data are also reported to this database. Dialogue between data centres to facilitate an efficient "Report-Once" system is necessary.

1 Background information and monitoring objectives

1.1 Scope of the report

Largely because of the burning of fossil fuels, the concentration of carbon dioxide (CO_2) in the earth's atmosphere is rising year on year (Raupach *et al.*, 2008). Each year, the ocean absorbs about one quarter of this extra CO_2 (Le Quéré *et al.*, 2009). This is making the ocean progressively more acidic, a process commonly referred to as "ocean acidification" (Caldeira and Wickett, 2003). There are concerns about the potential effects on marine ecosystems that may result from ocean acidification (Royal Society, 2005; Turley *et al.*, 2009). This challenges organizations charged with addressing these concerns to develop monitoring programmes that can provide reliable information on changes in the acidity of the ocean and coastal seas. Coordinated monitoring, such as implemented under the OSPAR and HELCOM regional sea conventions, implies a degree of harmonization of monitoring methodologies and reporting to ensure availability of comparable data and facilitate wide-scale geographical and temporal assessments. In 2010, ICES provided detailed information to the OSPAR Commission in response to a request for advice on monitoring methodologies for ocean acidification. The Marine Chemistry Working Group (MCWG) of ICES contributed advice on the chemical aspects of monitoring. The MCWG is of the opinion that the guidance produced for OSPAR would have wide interest and should be made easily accessible as a CRR; this report is based on the advice provided to OSPAR. It considers an overall framework for monitoring and specifically reviews the status of methodologies for measuring the carbonate system, including emerging technologies. Annex 5 summarizes current and recent activities to determine the carbonate system in the Northeast Atlantic and Baltic Sea. This identifies activities, which may provide a basis on which to build future monitoring programmes, within the areas of the ocean regulated by OSPAR and HELCOM (see Figure 1.1).
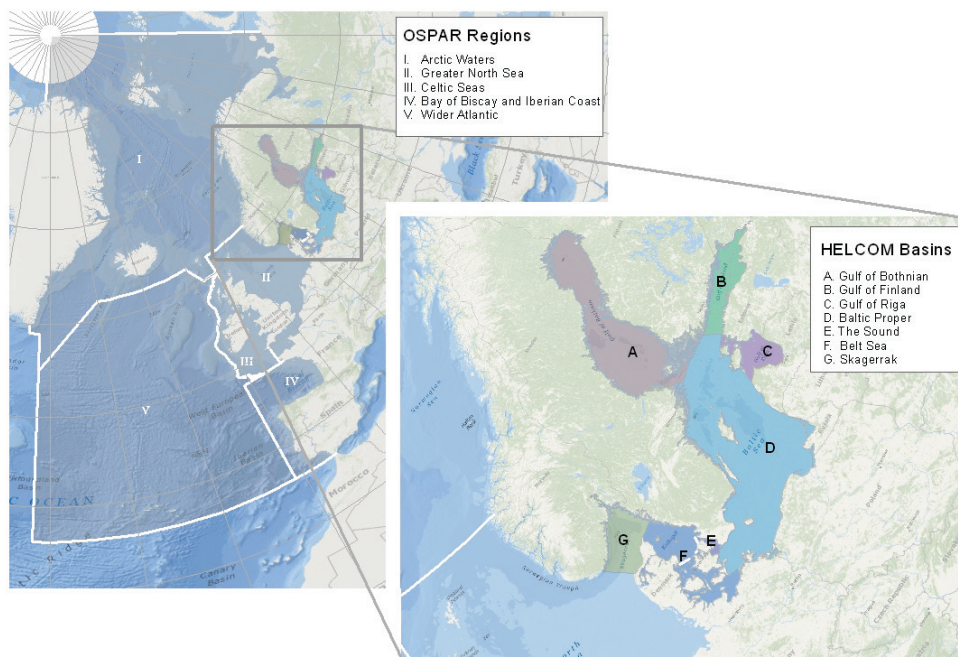

Figure 1.1. Map showing the areas covered by OSPAR and HELCOM.

1.2 Ocean acidification

Recent reports have identified ocean acidification resulting from the absorption of anthropogenic CO_2 by the oceans as a major concern because of its potential effects on marine biogeochemistry and ecosystems and the lack of appropriate information for assessing the risks (e.g. Royal Society, 2005; Gattuso and Hansson, 2011). Acidification (measured as a reduction in pH) is a certain consequence of the rise in atmospheric concentrations of CO_2 (carbon dioxide) and the resulting net oceanic CO_2 uptake (Figure 1.2).

Ocean acidification and potential climate change from the increase in concentration of the greenhouse gas CO_2 in the atmosphere share the same cause. 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. The transfer of CO_2 between the atmosphere and the ocean is governed by the difference in fugacity of CO_2 between the two phases and the transfer velocity. It is influenced by a number of conditions, particularly water temperature and windspeed. CO_2 reacts with water to form carbonic acid (H_2CO_3). H_2CO_3 dissociates to carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydrogen ions (H^+). CO_3^{2-} reacts further with the H^+ to form additional HCO_3^- ions. The total of dissolved inorganic carbon (DIC) in seawater is the sum of about ~90% HCO_3^-, ~9% CO_3^{2-}, and ~1% as dissolved CO_2 and H_2CO_3. As the concentration of CO_2 increases in the atmosphere, DIC will increase in the sea, and the balance (chemical equilibrium) between the different carbonate components will shift to maintain the same pCO_2 in the water as in the atmosphere; concentrations of HCO_3^- and CO_2 will increase while concentrations of CO_3^{2-} and pH will decrease (Zeebe and Wolf-Gladrow, 2001). This reduction in concentration of CO_3^{2-} will result in lowered saturation states of $CaCO_3$ solid phases, leading to reduced saturation depths of marine carbonates such as aragonite, calcite, and magnesian calcites. Surface water is currently super saturated with respect to the carbonate solid phase, but in deeper water as pressure increases, the balance shifts to undersaturation (Feely *et al.*, 2004; Rost *et al.*, 2008). In addition to alterations to the carbonate system, ocean acidification will alter other aspects of the inorganic and organic chemistry of seawater; however, there is limited research in this area. A decrease in pH can affect the speciation of elements such as key nutrients (N, P, Si) and metals (e.g. Fe; Millero *et al.*, 2009). There are only limited data available to assess the vulnerability of different areas to change and to understand the spatial and interannual variability of uptake of CO_2 by the ocean that has been observed (e.g. Schuster *et al.*, 2009a). Compared to changes in the ocean, changes in concentrations of CO_2 in the atmosphere are small. Consequently, local differences in conditions in the ocean are important in determining the rate of uptake of CO_2 in different regions of the ocean. Some marine regions will be more rapidly affected than others. Ultimately, all marine regions will be affected (Orr *et al.*, 2005). The susceptibility of water to change depends on its chemical composition and temperature. The average global rate of decrease in pH is (ca. 0.002 pH units year^{-1}). However, local processes have already been observed to cause more intense changes than expected (Thomas *et al*. 2007, 2009; Feely *et al*., 2008; Wooton *et al*., 2008; Borges and Gypens, 2010; Cai *et al*., 2011; Mucci *et al*., 2011). This raises questions about the degree to which such changes will be sustained, or if not, the extent to which the underlying processes causing these changes will continue to produce additive effects in conjunction with the ongoing progressive increase in acidification.
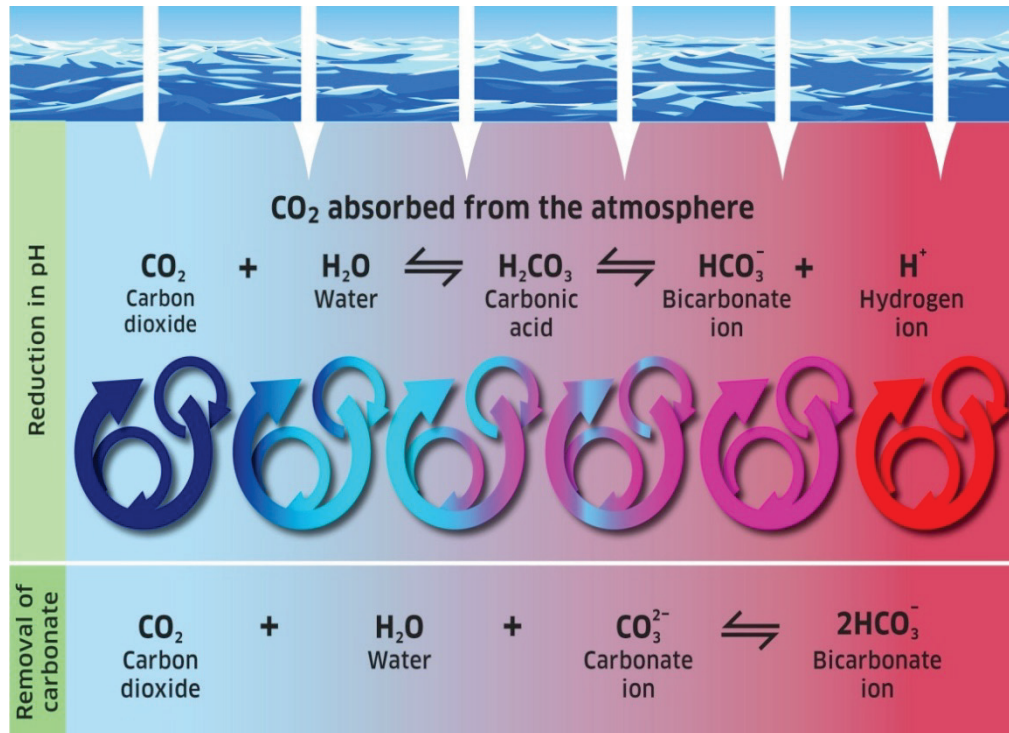
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Figure 1.2. The carbonate system of seawater and the potential impact as a result of atmospheric absorption of CO₂. Source: Baxter *et al.* (2011). This is a "litmus paper" diagram; the colour changes from blue to red as more CO₂ is absorbed and the carbonate equilibria shift to release more hydrogen ions.

At temperate latitudes, the natural annual cycles and interannual fluctuations in temperature and biological production result in a natural cycle and interannual fluctuations in pH that are large compared to the likely net annual rate of decrease (Blackford and Gilbert, 2007; Section 2 of this document). Consequently, a long-term monitoring programme must be designed to discern between the long- and short-term fluctuations. Waters where there is enhanced production due to nutrient enrichment will have a larger cycle in biological production and respiration and, consequently, a greater-than-natural range in acidity through a year (Blackford and Gilbert, 2007).

The seas of the northwestern European shelf area may be flushed by ocean water at such a rate (Holt and Proctor, 2008) that it is the change in carbonate chemistry of the ocean water that may be the primary determinant of the underlying long-term rate of change in pH of these shelf seas. In turn, the rate of increase in acidity in ocean waters will vary from year to year in line with changes in the amount of uptake of atmospheric CO₂. Variations in uptake are a result of variations in temperature, biological activity, and mixing between surface and deeper waters. Many potentially relevant processes in shelf seas are poorly described at present, such as inputs from rivers producing enhanced production and respiration (Borges and Gypens, 2010; Provoost *et al.*, 2010; Mucci *et al.*, 2011), factors influencing TA and reactions with the benthos (LeBrato *et al.*, 2010; Hu and Cai, 2011). Both monitoring and process studies in shelf seas are required so that a distinction can be made between ocean control and control by local processes.

1.3 Carbonate system components

pH is defined using four different scales (see Section 1.4). The reason for the existence of four pH scales stems from the practical considerations around preparing buffer solutions for the calibration of pH electrodes (see Annex 1).

Total alkalinity (TA) = $[HCO_3^-]$ + $2[CO_3^{2-}]$ + $[B(OH)_4^-]$ + $[OH^-]$ − $[H_3O^+]$ plus other minor components.

Total dissolved inorganic CO$_2$ (DIC) = the sum of the concentrations of dissolved CO_2 (CO_2 + H_2CO_3) and the bicarbonate and carbonate ions DIC = $[CO_2]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$.

Partial pressure – pCO$_2$ (Fugacity fCO$_2$) of CO$_2$ in solution: The partial pressure of CO_2 (pCO_2) is the pressure that CO_2 dissolved in a water sample exerts on the overlying air. The pCO_2 is defined to be in wet (100% water-saturated) air and is a function of the solubility of the gas and the concentration of dissolved CO_2. The fugacity of CO_2 (fCO$_2$) is pCO_2 corrected for the non-ideal behaviour of the gas. The fugacity is about 0.3–0.4% lower than the partial pressure over the range of interest in natural waters. If values of fCO$_2$ are reported, it is important that the method of adjusting pCO_2 to fCO$_2$ is also reported (see Zeebe and Wolf-Gladrow, 2001, p. 248 for an introduction to the relationship between activity and fugacity).

As the concentration and partial pressure of CO_2 rises in the atmosphere, a fraction of that CO_2 will tend to dissolve in the ocean until the partial pressure of CO_2 in the ocean matches that in the atmosphere. This process of CO_2 exchange between ocean and atmosphere is described as being controlled by Henry's Law—the <u>solubility</u> of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

$$pCO_{2(gas)} = pCO_{2(aqueous)} = [CO_2]_{(aqueous)} / K_0(T,S)$$

where K_0 (T, S) is the temperature-dependent solubility (or Henry's Law) constant.

Interrelationship of carbonate system components: TA and DIC are independent of temperature and pressure; while pCO_2 and pH are not.

Measurements of two of these variables (along with the temperature, salinity, pressure, and concentrations of phosphate and silicate) will allow the calculation of the other two, because the relevant equilibrium constants (K1 and K2) for equilibria 1 and 2 below are well established (Zeebe and Wolf-Gladrow, 2001).

$$CO_2 + 2H_2O = H_3O^+ + HCO_3^- \qquad 1$$

$$HCO_3^- + H_2O = H_3O^+ + CO_3^{2-} \qquad 2$$
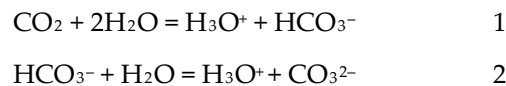
The accuracy and precision obtainable in such calculations have been considered in a number of papers (e.g. McElligot *et al.*, 1998). Some work has gone into the estimation of the second parameter where only one has been measured. Estimations are most reliable for alkalinity, which tends to follow a near-conservative relationship with salinity in ocean waters (e.g. Lee *et al.*, 2006).

Complications with use of data for pH arise because there are <u>four different definitions of the pH scale</u> [see Section 1.4] in current usage. This presents some uncertainty when dealing with data reported in the literature and with datasets where the scale used has not been defined. This makes the data worthless for the study of ocean acidification. There are several different formulations of K1 and K2 arising from how an equation was fitted to the observed data (e.g. Dickson and Millero, 1987). Again, it is critical that the formulation used is reported as part of any derived dataset.

1.4   Definition of pH and pH scales

The activity of a species i is defined as the difference between the chemical potential of the species in the sample solution and its chemical potential in a reference state, referred to as standard state:

$$\mu_i - \mu_i{}^\circ = RT \ln (a_i) = RT \ln (c_i\, \gamma_i) \qquad\qquad (1)$$

where μ_i and $\mu_i{}^\circ$ are the chemical potentials (J mol^{-1}) of species i in the actual and standard states, respectively, a_i is the activity of species i, R is the gas constant (in J Kmol^{-1}), T is temperature (in degrees Kelvin), c_i is concentration on an appropriate concentration scale, and γ_i is the activity coefficient. The activity coefficient is, by definition, unity in the standard state ($\gamma_i \rightarrow 1$ in pure water). The activity coefficient of most ions is less than 1 in seawater, but dissolved CO_2 has an activity coefficient greater than 1.

The pH is defined from the activity of the hydrogen ion:

$$pH = -\log_{10} (a_{H+}) \qquad\qquad (2)$$

As a solution with zero ionic strength (corresponding to the standard state) cannot be prepared, and because single ion activity coefficients cannot be determined, it is not possible to measure pH as defined in equation (2). Therefore, an operational definition based on potentiometric measurements and an activity coefficient convention has been introduced. It uses buffers with assigned pH values that are close to the best estimates of $-\log_{10} (a_{H+})$. This scale is known as the NBS pH scale.

For seawater measurements, the low-ionic-strength-NBS buffers cause significant changes in the liquid junction potential between calibration and sample measurements when using an electrode system. Unless the change is carefully characterized for each electrode system, the error introduced is larger than the precision and accuracy required for the assessment of ocean acidification (Wedborg *et al.*, 1999).

The situation has been greatly improved by the introduction of pH buffers based on synthetic seawater, which have a composition close to that of the sample, thereby reducing the liquid junction potential changes between calibration and sample measurement.

The seawater pH scales are based on the adoption of seawater as the standard state (thus setting $\gamma_i = 1$ in seawater), with concentration and activity being identical [see equation (1)]. Three different seawater pH scales have been defined, based on different ways of defining the hydrogen concentrations. The free-hydrogen-ion scale [pH(F)] uses the concentration of free hydrogen ions to define the hydrogen ion activity (Bates and Culberson, 1977):

$$a_{H+}(F) = [H^+] \qquad\qquad (3)$$

$$pH(F) = -\log_{10} [a_{H+} (F)] \qquad\qquad (4)$$

As a proportion of acid added to seawater is bound to sulphate and fluoride ions, the concentration of free hydrogen ions cannot be determined analytically. As fluoride forms a minor component of seawater, fluoride-free synthetic seawater was adopted by Hansson (1973). This approach provides the total hydrogen scale [pH(T)]:

$$a_{H+}(T) = [H^+] + [HSO_4^-] = [H^+] \{1 + K_{HSO4} [SO_4]_{tot}\} \quad (5)$$

where

$$K_{HSO4} = [HSO_4^-]/([H^+][SO_4^{2-}])$$

$$pH(T) = - \log_{10} [a_{H+} (T)] \qquad (6)$$

Dickson and Riley (1979) and Dickson and Millero (1987) proposed inclusion of fluoride in the buffer, and this yielded the seawater-hydrogen-ion-concentration scale [pH(SWS)]:

$$a_{H+}(SWS) = [H^+] + [HSO_4^-] + [HF]$$

$$= [H^+] \{1 + K_{HSO4-}[SO_4]_{tot} + K_{HF}[F]_{tot}\} \qquad (7)$$

where

$$K_{HF} = [HF]/([H^+][F^-])$$

$$pH(SWS) = -\log_{10} [a_{H+} (SWS)] \qquad (8)$$

For work in seawater, the pH(T) scale is the most commonly used scale and the recommended scale for monitoring activities (DOE, 1994). An important advantage in the use of this scale is that problems associated with the uncertainties in the stability constants for HF are avoided, and the preparation of appropriate buffer solutions is simplified.

Biogeochemical and physical processes influencing the acidity of seawater.

Based on the existing literature, the processes likely to determine the acidity in different regions of the marine environment at different times of year are:

1.　　**Atmospheric CO_2 concentration:** Increasing anthropogenic emissions of CO_2 have increased atmospheric CO_2 concentrations from 280 ppm in 1800 to close to 400 ppm at present. The atmospheric concentration is rising by about 2 ppm per year—twice the rate of increase in the 1960s.

2.　　**Ocean uptake**: About 50% of the CO_2 produced and emitted to the atmosphere (500 Giga (10^9) tonnes CO_2) over the last 200 years has been taken up by the oceans, resulting in a decrease in the pH from 8.2 to 8.1 (Sabine *et al.* 2004; Le Quéré *et al.*, 2009). Predictions indicate that the global ocean pH will decline by a further 0.3–0.4 by 2100 and by 0.6 by 2300 in the business-as-usual IPCC scenario used by Calderia and Wickett (2003).

3.　　**"CO_2 pumps"**: Each year, there are large natural annual fluxes of CO_2 between the ocean and the atmosphere of about 90 Gt C. The uptake of new athropogenic carbon each year is a small fraction of this, with a net flux of 2 Gt C into the ocean. Pre-1800, it is believed that these large fluxes were in balance, with a net flux from ocean to the atmosphere of about 0.6 Gt C year^{-1} that balanced the supply of dissolved inorganic carbon to the oceans from rivers (Sarmiento and Sundquist, 1992). The large influxes and effluxes are controlled by a combination of marine productivity, respiration, and sinking of organic matter (**the biological pump**) and ocean circulation (**the solubility pump**). Most anthropogenic CO_2 is thought to be taken up by the solubility pump in regions such as the Northeast Atlantic and Arctic oceans (Takahashi *et al.*, 2009).

4.　　**$CaCO_3$ dissolution and $CaCO_3$ precipitation:** A long-term (1000 to 10 000 years) sink for anthropogenic CO_2 is absorption in the oceans and reaction with carbonate sediments. As the oceans turn over ("acidic" surface waters move into the depths of the ocean), the excess CO_2 in these waters will react with calcium carbonate in deep-ocean sediments, and this will reduce the acidity of the water. This process will take several thousand years (Archer *et al.*, 1997).

5. **Seawater temperature and warming seas:** The warmer the water, the higher its pCO_2 and lower its pH; consequently, global warming has the potential to reduce the ocean's ability to absorb CO_2.

6. **Ocean circulation and upwelling of deep water:** The controls of alkalinity and DIC of deep-ocean waters are respiration of organic matter and dissolution of $CaCO_3$. Thus, deep water is rich in CO_2, and when this upwells, it carries CO_2 to surface waters and, therefore, reduces pH.

7. **Riverine input:** Freshwater input from estuaries is a direct input of DIC and alkalinity and can have a significant effect on pH in shelf seas.

8. **Nutrients:** Photosynthesis and respiration change the carbonate chemistry of water by removing and adding CO_2. Due to changes in nutrient inputs, the eutrophication status of some regions is changing, and this has the potential to change the carbonate chemistry more than uptake of CO_2 from the atmosphere.

9. **Other anthropogenic gas emissions:** In some regions, there are large fluxes of nitrogen oxides and sulphur dioxide to the atmosphere. The majority of this acid deposition occurs on or close to land and can amplify acidification in coastal regions.

10. **Methane hydrate releases:** Increasing global temperatures may release methane from melting tundra and sediment-bound methane hydrates. As well as being a strong greenhouse gas, methane is oxidized in the atmosphere, resulting in further increases to atmospheric CO_2 concentrations.

11. **Volcanic vents and seeps:** CO_2 vents and seeps can affect ocean pH in local waters where seepages occur (e.g. off Sicily).

2 Variability of the carbonate system across the OSPAR area

In most areas, projected rates of change in ocean acidity are small (0.002 pH units year^{-1}) compared both to present measurement capability and variation through the year and between areas (e.g. Blackford and Gilbert, 2007; Hofmann *et al.*, 2011). As a consequence, to avoid aliasing the interpretation of results from long-term monitoring, any programme of long-term monitoring has to be designed to take into account shorter-term variability in the system. The current state of knowledge of the variability of the system is summarized in this section.

Figure 2.1 provides information on cross-system variability and the range of spatial and temporal variability of seawater carbonate chemistry variables. In general, the dynamic range of pH tracks that of pCO_2. The dynamic ranges of pCO_2 and pH are more intense in estuarine environments and decrease towards marginal seas, showing intermediate dynamic range in nearshore and coastal upwelling systems. Estuaries show the largest dynamic range in TA, followed by nearshore ecosystems (due to the influence of run-off) and then marginal seas (related to strong gradients in the Arctic Ocean also due to the influence of run-off).

Table 2.1 summarizes available information on the temporal variability of seawater carbonate chemistry variables in the OSPAR regions from daily to interannual timescales. The daily variability due to the night–day cycle of biological activity (photosynthesis and respiration) is relatively uniform across the OSPAR regions, and two–tenfold lower than the seasonal amplitude. Note that these studies were carried out during the most productive periods of the year, typically in spring. During other less productive seasons (undocumented to our best knowledge), the daily variability is expected to be lower or even below detection levels. Pelagic calcification seems to be at cellular level coupled to photosynthesis; hence, it is also expected to follow a day–night cycle. Based on field studies (e.g. Robertson *et al.*, 1994; Harlay *et al.*, 2010; Suykens *et al.*, 2010), the maximal drawdown of TA during blooms of pelagic calcifiers is ~30 µmol kg^{-1} for a characteristic time-scale typically of 15 d (roughly equating at a drawdown of TA of ~2 µmol kg^{-1} d^{-1}). Thus, the impact of pelagic calcification at the daily scale on seawater carbonate chemistry is expected to be close to or below detection limits. In regions of strong horizontal salinity gradients (nearshore coastal environments such as the Irish Sea, English Channel, and southern bight of the North Sea), the tidal displacement of water masses leads to subdaily variability of seawater chemistry that is equivalent to or higher than the daily variability due to the day–night cycle of biological activity. For instance, tidal variations in TA and pCO_2 of, respectively, 50 µmol kg^{-1} and 50 µatm, have been reported in the southern bight of the North Sea (Borges and Frankignoulle, 1999).

Seasonal variations in seawater carbonate variables are mainly related to biological activity (organic carbon production and degradation, $CaCO_3$ production and dissolution), to the physical structure of the water column (mixing and stratification), and to the thermodynamic effect of seasonal temperature changes for pCO_2 and pH. The amplitude of the seasonal variations in seawater carbonate variables is strongest in OSPAR Region II (North Sea) and more or less equivalent in the other four OSPAR regions (Table 2.1).

Interannual variability in seawater carbonate variables is strongest in OSPAR Region II (North Sea) and roughly equivalent in OSPAR Regions III (Celtic seas), IV (Bay of Biscay and Iberian Coast), and V (Wider Atlantic) and lowest in OSPAR Region I (Arctic waters) (Table 2.1). Except for OSPAR Region I, interannual variations are

equivalent to the amplitude of seasonal variations. Table 2.1 shows the maximum interannual variations that are typically observed during the most productive season (spring). Interannual variability in seawater carbonate variables is usually lower during the other periods of the year (Schiettecatte et al., 2007; Omar et al., 2010 for the North Sea). Interannual variability in the seawater carbonate variables is related to variable river inputs in nearshore ecosystems (Borges et al., 2008a), to biological activity in nearshore and offshore ecosystems (Borges et al., 2008a; Omar et al., 2010), to vertical mixing (Borges et al., 2008a, 2008b; Dumousseaud et al., 2009), and to changes in temperature (Dumousseaud et al., 2009; Omar et al., 2010). These drivers of interannual variations interact; for instance, milder and warmer years will be characterized by lower winter mixing that will lead to a lower seasonal replenishment of nutrients and lower primary production, but also a lower vertical input of DIC (Borges et al., 2008b).

Spatial gradients in seawater carbonate variables can be related to the heterogeneity of water masses and will, to some extent, track the spatial gradients in salinity or in temperature. Spatial gradients in seawater carbonate variables can also be related to the more-or-less marked patchiness of biological activity. The spatial gradients in seawater carbonate variables are strongest in the Iberian upwelling region of OSPAR Region IV (Bay of Biscay and Iberian Coast), followed by OSPAR Region II (Greater North Sea) (Table 2.2). Note that Table 2.2 reports the large-scale (at basin-scale) spatial gradients, but mesoscale spatial gradients can be much more intense, such as across frontal structures (Borges and Frankignoulle, 2003) or across river plumes (Borges and Frankignoulle, 1999).

Long-term changes in pH are poorly documented, and most available information on long-term changes in seawater carbonate variables is based on the analysis of seawater pCO_2 data. In all OSPAR regions, the reported rate of increase in pCO_2 in seawater is equivalent to or higher than the increase in atmospheric CO_2 (Table 2.3). The fact that pCO_2 could be increasing faster in surface waters than in the atmosphere has been attributed to changes in circulation both through vertical mixing (Corbière et al., 2007) and through horizontal distribution of water masses (Thomas et al., 2008), or to the decrease in buffering capacity of seawater (Thomas et al., 2007). In nearshore regions influenced by river inputs, such as the southern bight of the North Sea, the decadal changes in seawater carbonate variables due to changes in nutrient inputs have been evaluated by model simulations to be more intense than expected from the response to ocean acidification (Gypens et al., 2009; Borges and Gypens, 2010). The effect of eutrophication on carbon cycling could counter the effect of ocean acidification on the carbonate chemistry of surface waters. But changes in river nutrient delivery due to watershed management could also lead to stronger changes in carbonate chemistry than ocean acidification. Whether antagonistic or synergistic, the response of carbonate chemistry to changes in nutrient delivery to the coastal zone (increase or decrease, respectively) could be stronger than ocean acidification (Borges and Gypens, 2010).

Note that the long-term yearly rates of change in pCO2 and pH are close to the sensitivity of the analytical methods to detect this change. Also, the long-term yearly rates of change in pCO2 and pH are between three- and tenfold lower than the typical interannual variability in these quantities in the OSPAR regions (Table 2.1). This implies that to detect long-term changes in seawater carbonate variables, sustained monitoring of more than 10 years is required to obtain a signal that is analytically significant and to discern the long-term trend from natural interannual variability.
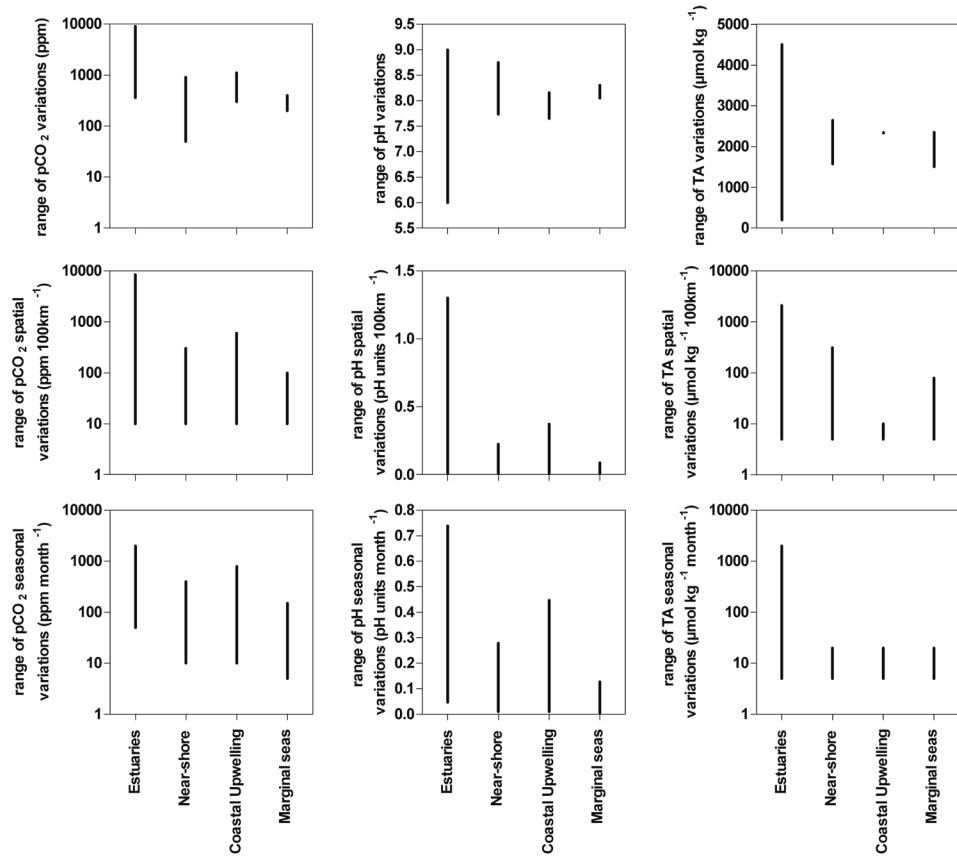
Figure 2.1. Range of spatio-temporal variability across different coastal environments of the partial pressure of CO_2 (pCO$_2$), pH, and total alkalinity (TA). Adapted from Borges (2011).

Table 2.1. Amplitude of daily and seasonal variations and interannual variability in the partial pressure of CO2 (pCO2), total alkalinity (TA), pH, and dissolved inorganic carbon (DIC) in the OSPAR regions (I, Arctic waters; II, Greater North Sea; III, Celtic seas; IV, Bay of Biscay and Iberian Coast; and V, Wider Atlantic). The variations in pH and DIC were computed from pCO2 and TA and were broken down into changes due to pCO2 (ΔpCO2) and due to TA (ΔTA).

OSPAR REGION	pCO_2 (μATM)	TA (μMOL KG^{-1})	pH		DIC (μMOL KG^{-1})	
			ΔpCO_2	ΔTA	ΔpCO_2	ΔTA
Amplitude of daily variations (maximum, i.e. most productive period)						
I	20 [a]	~0	0.020	~0	10	~0
II	20 [b]	~0	0.020	~0	10	~0
III	15 [b]	~0	0.015	~0	7	~0
IV	15 [b]	~0	0.015	~0	7	~0
V	20 [a,c]	~0	0.020	~0	10	~0
Amplitude of seasonal variations						
I	45 [d]	20 [h]	0.047	0.003	23	17
II	220 [e]	60 [i]	0.309	0.010	175	52
III	70 [b]	50 [b,j]	0.075	0.008	37	43
IV	30 [f]	20 [k]	0.031	0.003	15	17
V	60 [g]	20 [h]	0.064	0.003	31	17
Interannual variability						
I	5 [l]	?	0.005	?	2	?
II	150 [e]	?	0.183	?	96	?
III	50 [k]	20 [b]	0.052	0.003	25	17
IV	50 [k]	10 [k]	0.052	0.002	25	9
V	20 [m]	?	0.020	?	10	?

[a] Robertson *et al.* (1993); [b] Frankignoulle and Borges (2001b); [c] Frankignoulle and Borges(2001a); [d] Olsen *et al.* (2008); [e] Omar *et al.* (2010); [f] Borges and Frankignoulle (2002); [g] Schuster and Watson (2007); [h] Robertson *et al.* (1994); [i] Thomas *et al.* (2009); [j] Harlay *et al.* (2010); [k] Dumousseaud *et al.* (2009); [l] Nakaoka *et al.* (2006); [m] Santana-Casiano *et al.* (2007).

Table 2.2. Typical spatial gradients at basin-scale (per 100 km) of the partial pressure of CO_2 (pCO_2), total alkalinity (TA), pH, and dissolved inorganic carbon (DIC) in the OSPAR regions (I, Arctic waters; II, Greater North Sea; III, Celtic seas; IV, Bay of Biscay and Iberian Coast; and V, Wider Atlantic). The variations in pH and DIC were computed from pCO_2 and TA and were broken down into changes due to pCO_2 (ΔpCO_2) and due to TA (ΔTA).

OSPAR REGION	pCO_2 (μATM 100 KM^{-1})	TA (μMOL KG^{-1} 100 KM^{-1})	pH (pH UNITS 100 KM^{-1})		DIC (μMOL KG^{-1} 100 KM^{-1})	
			ΔpCO_2	ΔTA	ΔpCO_2	ΔTA
I	2[a]	8[g]	0.002	0.001	1	7
II	20 [b,c,d]	20[h]	0.020	0.003	10	17
III	10[b]	5[b,i]	0.010	0.001	5	4
IV	10[b] to 50[e]	5[e,i]	0.010–0.052	0.001	5–26	4
V	2[f]	5[f]	0.002	0.001	1	4

[a] Olsen *et al.* (2008); [b] Frankignoulle and Borges (2001b); [c] Thomas *et al.* (2004); [d] Omar *et al.* (2010); [e] Borges and Frankignoulle (2002); [f] Schuster and Watson (2007); [g] based on salinity gradients from Olsen *et al.* (2008) ; [h] Thomas *et al.* (2009) ; [i] Dumousseaud *et al.* (2009).

Table 2.3. Long-term changes in surface waters of the partial pressure of CO_2 (pCO_2) and pH in the OSPAR regions (I, Arctic waters; II, Greater North Sea; III, Celtic seas; IV, Bay of Biscay and Iberian Coast; and V, Wider Atlantic). The changes in pH were computed from those of pCO_2 assuming a constant total alkalinity.

OSPAR REGION	pCO_2 (μATM YEAR^{-1})	pH (pH UNITS YEAR^{-1})
I	1.5–3.0 [a]	−0.0015 to −0.0030
I	2.1 ± 0.2 [d]	−0.0024 ± 0.002
II	4.4 [b]	−0.0044
III	3.2 [c]	−0.0032
IV	3.2 [c]	−0.0032
V	1.9–4.9 [c]	−0.0019 to −0.0049
V		−0.002e

[a] Omar and Olsen (2006); [b] Thomas *et al.* (2007); [c] Schuster *et al.* (2009a), [d] Olafsson *et al.* (2009), [e] McGrath *et al.* (2012).

3   Monitoring framework

Research into ocean acidification can be considered to cover three areas of observation and experiment:

1. Observation of change in the chemical composition of seawater focusing on changes in carbonate system chemistry.

2. Observation of effects of those changes on the concentrations of other chemical components of seawater.

3. Observations and experiments to determine the impact of chemical changes on the functioning of marine ecosystems.

This report is focused on the first area-monitoring of changes in the chemical composition of seawater. Coordinated monitoring requires that the minimum set of data to be measured in the field samples is defined and that a harmonized approach is developed for collection of the data. A plan should encompass the collection of sufficient ancillary data so that the likely causes of change in carbonate chemistry can be reliably identified.

Any programme that is developed on a national basis will need to take into account the requirements of Regional Sea Conventions and European Framework directives. While ocean acidification is not a specific pressure listed under the Marine Strategy Framework Directive (MSFD) (EC, 2008), it is a stressor that, over time, may affect ecosystem functioning and resilience and compromise achievement of good environmental status (GES). It is necessary to understand the impacts of climate change (including increased temperatures) and acidification alongside the impacts of other pressures such as pollution and harvesting the oceans biological resources. pH, pCO_2 profiles, or equivalent information used to measure marine acidification is one of the elements listed under physical and chemical feature under Table A3.1 of Annex III of the MSFD. Member States are required to establish and implement coordinated monitoring for assessment of environmental status of their marine waters on the basis of the indicative lists of elements set out in Annexes III and V of the MSFD.

Regional monitoring should also tie into and be consistent with other extant and planned global monitoring, modelling, assessment, and research activities (see Annex 6). For instance, monitoring should also link into ongoing and developing complementary activities focused on quantifying annual fluxes of CO_2 from the atmosphere into the North Atlantic (e.g. the Surface Ocean CO_2 Atlas (SOCAT) and the Integrated Carbon Observation System (ICOS)).

3.1   Objectives of chemical monitoring

An ocean acidification monitoring programme must have access to information on the processes controlling the chemistry of carbon dioxide in seawater—the physical and biological oceanographic contexts of the observations (e.g. advection of water masses; stage in the plankton production/decay cycle).

Key stages and objectives for a coordinated monitoring programme for the ICES maritime area are:

i)   Assembly of baseline datasets against which longer-term ocean acidification monitoring can be judged. To ensure that results are not aliased by short-term variability, a monitoring programme assessing long-term trends will need to be scientifically and statistically robust (see tables in Section 2).

ii) Assessment of medium- to long-term temporal variations in carbonate chemistry in surface, mode, and deep waters with respect to, for example:

A) variation in the extent of deep winter mixing that controls the properties of the carbonate system in the surface layer of the ocean;

B) temporal changes to saturation state in deeper waters which will affect ecosystems such as cold-water corals (e.g. track the aragonite and calcite saturation horizons).

iii) Providing information appropriate for validation and improvement of numerical models to obtain better forecasts of environmental perturbations and ecological risks.

iv) Providing data to assist groups gathering evidence of ecological status and impacts.

v) Providing information to national and international policymakers on the impacts of increased global CO_2 concentrations and underpin the need for international agreements to reduce CO_2 emissions.

3.2 Sampling strategies and target areas

At present, we lack reliable knowledge of how ocean acidification is likely to progress in different areas. Available information suggests that the rate of change is variable with both time and location. Observations need to document current variability in the full spectrum of areas covered by OSPAR and HELCOM from the open Atlantic and Arctic oceans, shelf seas, and Baltic Sea into estuarine regions and abyssal waters. It is essential that we have knowledge of the daily, seasonal, and interannual variations in each area. This knowledge is required for the design of a long-term monitoring programme that will avoid aliasing assessments due to poor knowledge of short-term variability. Relevant recent and planned activities in the OSPAR and HELCOM areas are listed in Annex 5. Particular emphasis should be placed on key areas at risk within these areas, for example high latitudes where ocean acidification will be most rapid, and areas identified as containing ecosystems and habitats that may be particularly vulnerable, e.g. cold-water corals.

Representative monitoring is thus required for the following areas:

(i) The Arctic Ocean (OSPAR Region I) because its waters are potentially most sensitive to change (Steinacher *et al.*, 2009).

(ii) The Atlantic Ocean – surface waters (OSPAR Region V): This provides the source waters to the shelf seas and is already known to show more variability than is predicted by numerical models (Olafsson *et al.*, 2009).

(iii) Intermediate water masses in contact with sensitive cold-water coral habitats.

(iv) Shelf sea and coastal waters (all OSPAR regions and HELCOM). In nearshore environments, increased production resulting from eutrophication has probably driven larger changes in acidity than CO_2 uptake. Inclusion of carbonate parameters in riverine input monitoring is required to support assessments of coastal water.

Much of the required monitoring can be done in conjunction with existing activities carried out by operational agencies and scientific groups making sustained observa-

tions. For example, incorporation of carbonate system parameters into current eutrophication monitoring and riverine input monitoring, such as the OSPAR Riverine Input and Direct Discharge (RID) programme, would provide a cost-effective approach to delivering shelf and coastal monitoring. Work will need to be done using a range of platforms (research ships, moorings, etc. described in Section 3.5). High repeat-rate (less than daily–monthly) observations will be necessary at some locations in the first phase to define the scale of intra-annual variability. For offshelf work, coordination is required with regular hydrographic cruises, which are being under taken at least once a year, such as IEO's cruises in the Bay of Biscay, UK NERC "Ellett Line" cruise between Scotland and Iceland, and UK Marine Scotland Science cruises in the Faroe–Shetland Channel.

3.3   Required information

Assessment of the status of the marine carbonate system requires measurements of more than pH alone. In addition to quantifying the dissolved carbonate species, the saturation state of the biogenic mineral phases that contain carbonate (aragonite and calcite) should also be calculable from the measurements. Changes in the saturation state provide information about the potential effects on calcium carbonate-shelled organisms.

The four measurable parameters of the carbonate system are total alkalinity (TA), total dissolved inorganic carbon (DIC), partial pressure of carbon dioxide (pCO_2), and pH. The chemical equilibria connecting these species in solutions have been extensively quantified for seawater. Consequently, measurements of any two components allow the concentration of the other two to be calculated. However, the precision of this assessment varies with the pair chosen. There is no optimal choice of parameters, and each has advantages and disadvantages (Dickson, 2010). For these calculations, measurements of temperature and salinity are required, with precisions of better than 0.05°C for temperature and 0.1 for salinity to achieve 0.001 precision in the calculation of pH. Concentrations of nitrate, phosphate, and silicate need to be known. Standard protocols for nutrients in seawater are available (Hydes *et al.*, 2010a; ICES, 2012[1]). To achieve a pH precision of 0.001, precisions of 0.3 μmol kg^{-1} and 15 μmol kg^{-1} for phosphate and silicate are required, respectively.

- TA and DIC is the preferred pair to measure for calculation of pH and pCO_2, if these are not measured directly.

- TA, DIC, and pH together provide full coverage of the inorganic carbon system and also allow checking of the internal consistency.

- The assessment of change in the carbonate system is greatly assisted when ancillary data are available on hydrography, concentrations of nutrients, dissolved oxygen, and biomass.

Further details can be found in the EPOCA project's handbook on acidification research (Dickson *et al.*, 2007; Riebesell *et al.*, 2010).

3.4   Minimum dataset

An ocean acidification dataset is one of defined data quality, which contains data that can be used to assess the status or impact of ocean acidification and includes a quanti-

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[1] Proposed revision of JAMP Eutrophication Monitoring Guidelines: Nutrients (OSPAR, 1997).

fication of carbonate chemistry. For field-measured data, measurements must include temperature, salinity, and two inorganic carbon variables and measurements of nitrate, phosphate, and silicate.

For monitoring of ocean acidification, the MCWG suggests the following minimum set of variables are reported (required accuracy in brackets).

Carbonate system chemistry

<u>All of</u>

1) Sample water temperature (0.01°C)

2) Sample salinity (0.01 g kg^{-1})

3) Concentration of phosphate (0.3 µmol kg^{-1}) (as contribution to measured total alkalinity)

4) Concentration of silicate (15 µmol kg^{-1}) (as contribution to measured total alkalinity)

5) Concentration of nitrate (1 µmol kg^{-1}) (for assessment of potential alkalinity)

<u>Two out of</u>

1) Total alkalinity: for closed cell, ±3 µmol kg^{-1}; for open cell, ±1.0 µmol kg^{-1}

2) Total dissolved inorganic carbon: DIC (±2 µmol kg^{-1})

3) pH: spectrophotometrically, ±0.001 pH units; glass electrode, 0.003 pH units

4) pCO_2: (1–2 microatmosphere)

Ancillary data

Data on the carbonate system have to be set in the context of the water mass from which the sample was taken, particularly its history of biological activity. The context can be set from historical data when carbonate studies are being added to an existing time-series of observations. Where a new time-series is being established, wider-area data should be sought to assess the likely changes. This might come from inspection of related numerical modelling in the area and satellite observations. If a site is within an estuary (one where the salinity range varies rapidly with time and local processes may be important, e.g. Abril *et al.,* 2003), then along estuary surveys may be critical. In shelf waters, the likely influence of river inputs again needs to be assessed (Raymond and Cole, 2003; Cai *et al.,* 2010; Hydes and Hartman, 2011). Similarly, benthic calcification and denitrification rates may significantly affect the concentration of alkalinity of shallow shelf seas, but information is currently limited to a few areas (Thomas *et al.*, 2009; LeBrato *et al.*, 2010). When dealing with deeper-water masses below the winter mixed layer, data on the age of the water mass is invaluable, and measurement of CFCs is recommended. These concerns make minimum ancillary data hard to define. However, as datasets grow, they will begin to indicate where extra studies are needed to allow the data to be interpreted. It is therefore suggested to start with a minimum ancillary dataset that includes:

(i) location: latitude, longitude, and time of sampling;

(ii) sample depth;

(iii) a measure of plankton biomass: chlorophyll *a* and/or dissolved oxygen anomaly;

(iv) concentration of nitrate (1 μmol kg⁻¹) (for assessment of potential alkalinity).

Where the air–sea exchange contribution is to be assessed, data on pCO_2 in the water and in the air are needed along with information on windspeed.

3.5   Sampling and sampling platforms

Ocean acidification monitoring will require a combination of traditional hydrographic surveys and autonomous measurement of key parameters using instruments deployed on a variety of platforms (Feely *et al.*, 2010). A key requirement is the collection of data at set locations on interannual and intra-annual variability to set against the background of underlying long-term change. Such data are difficult to collect from research vessels. Newer platforms such as instrumented ships of opportunity (Ferryboxes) and moorings can provide the needed increase in spatial and as well as temporal coverage.

Ships of opportunity (SOO) and Ferryboxes: The activities are coordinated globally by the IOC-sponsored IOCCP (International Ocean Carbon Coordination Project, www.ioccp.org). The extent of global coverage can be seen via the CDIAC webpage http://cdiac.ornl.gov/oceans/VOS_Program/VOS_home.html. These have been used successfully (Watson *et al.*, 2009) for monitoring the surface water pCO_2 values. pCO_2 is closely related to the pH of the water. pH can be calculated successfully (±0.002) from direct measurements of pCO_2 (±1 μatm) and estimating the TA of the water from the salinity (Lee *et al.*, 2006) in many areas. The regions in which this is possible are being extended by the addition of the routine collection of water samples for measurements of TA on the SOO ships in addition to automated underway measurements of pCO_2. Much of the effort of the International Ocean Carbon Coordination Programme (IOCCP) project focuses on the oceans. Within northwestern European shelf seas, additional systems are fitted in a number of Ferrybox systems. The Ferrybox webpages (www.FerryBox.org) provide information on lines in operation and equipment being used. Additionally, developments in sensors and instruments for use in SOO systems were reviewed by Schuster *et al.* (2009b), Borges *et al.* (2010), and Byrne *et al.* (2010).

Buoy/moorings: Instrumented buoys and moorings also provide platforms for the collection of detailed time-series data (see http://cdiac.ornl.gov/oceans/ Moorings/moorings.html and http://www.eurosites.info/). Several different strategies are being employed in the development of reliable instrumentation and sensors. The Batelle pCO_2 buoy systems, developed by the National Oceanic and Atmospheric Administration (NOAA) and Monterey Bay Aquarium Research Institute (MBARI), are currently used operationally in the US for open-ocean and shelf-sea monitoring systems, with more than 20 systems deployed to date (http://www.battelle.org/seaology/). Other systems are deployed at the EuroSites locations, the European station for time-series in the ocean (ESTOC), and Porcupine Abyssal Plain (PAP), for example.

Evaluations of likely systems have been and are being carried out by the Alliance for Coastal Technologies (ACT), and evaluation reports have been published (www.act-us.info), including a test of *in-situ* pH sensors in autumn 2012.

Argo floats: A new generation of Argo floats is being tested using pH sensors (Juranek *et al.*, 2011). Widespread use rather than use as part of specific research will

require that the new sensors are compatible with the required long life (up to four years) of the floats in the global monitoring network, and that the extension to biogeochemical measurements does not run foul of the restrictions placed by some states on access to their water under the Convention on the Law of the Sea.

<u>Hydrographic cruises:</u> Traditionally, most marine research and monitoring surveys have been conducted using research vessels. These still provide the only mechanism by which subsurface samples can be collected over large areas and which allows for the collection of high-quality data for a much broader range of parameters than can be acquired using, for example, ships of opportunity. Monitoring of ocean acidification requires regular hydrographic cruises to measure the accumulation of anthropogenic DIC in mode waters and in deep waters in the region of sensitive ecosystems such as cold-water corals. For work on ocean acidification, consideration needs to be given to large spatial scales because the input of atmospheric CO_2 is diffuse over the oceans. This is in contrast to much other monitoring in relation to the MSFD, such as that for eutrophication, which can focus on the coastal zone because contaminants are entering the ocean from rivers. The location of monitoring can and should be guided by numerical models that provide an indication of sensitive areas (Orr *et al.*, 2005; Orr, 2011). The major scientific programme studying the hydrography of deep ocean water (GO-SHIP) (Hood *et al.*, 2010) and the World Ocean Circulation Experiment (WOCE) have set a standard of sampling through the water column, which is a spacing of 30 nautical miles for physical measurements, with higher resolutions in regions of steep topography and boundary currents. When carbon and tracer measurements are made in these programmes, the spacing has tended to be extended to 60 nautical miles because of the extra workload involved in collecting and processing the samples during a cruise.

4 Measurement methods and quality assurance

4.1 Procedures

Work on ocean acidification will build on the research and development activities that have already gone into precise studies of carbonate chemistry and the air–sea exchange of CO_2. Current best practice for the analyses has been carefully described by Dickson *et al.* (2007) in a series of standard operating procedures that cover both the methods and the basic quality control procedures. The Dickson manual is available online at http://cdiac.ornl.gov/oceans/Handbook_2007.html. Further relevant information was also compiled by the EPOCA project and is available at www.epoca-project.eu (Dickson, 2010).

The basic methods in common use are:

(i)   TA: potentiometric titration (open or closed cell).

(ii)   DIC: acidification followed by infrared detection or coulometric titration.

(iii)   pH: spectrophotometric detection or potentiometric using a glass electrode.

(iv) pCO_2: seawater in equilibration with air and infrared detection.

Details of the equipment available to carry out the analyses and current suppliers of the equipment can be found on the IOCCP webpages at: http://www.ioccp.org/Sensors.html.
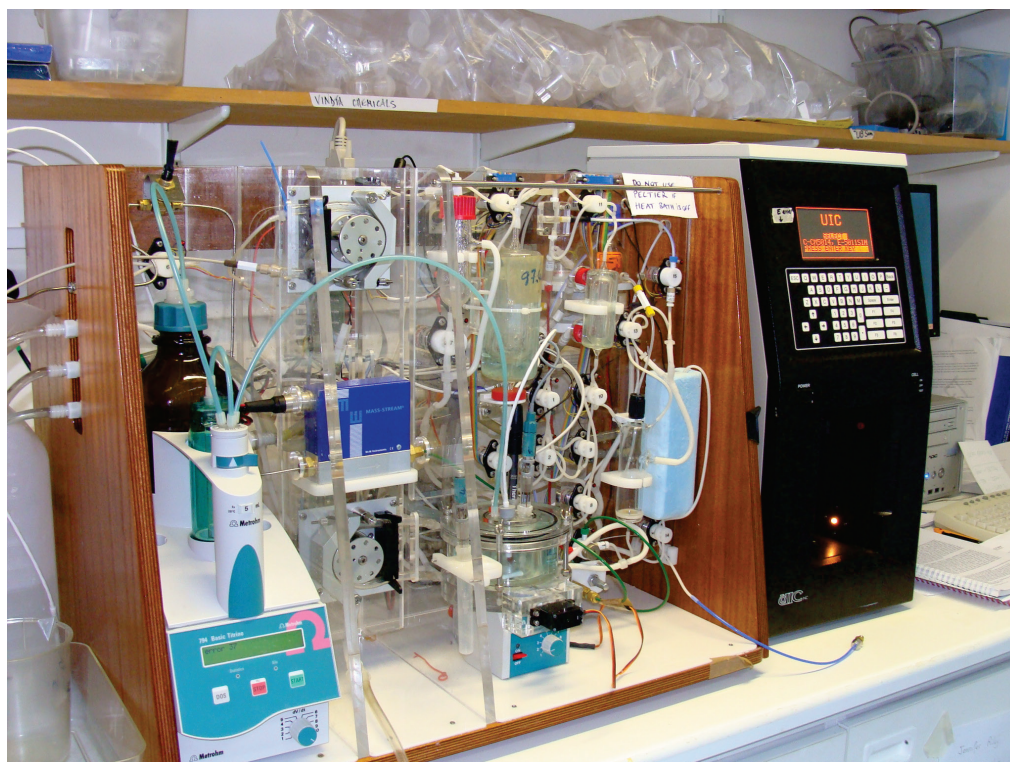
Figure 4.1. VINDTA 3C system for semi-automated measurement of DIC and TA. Photo: Pamela Walsham.

Methods for the determination of DIC and TA in discrete water samples are well established. However, measurements of DIC and TA are relatively time-consuming, with throughput of only three measurements per hour when using the VINDTA system (http://www.marianda.com). There are obvious advantages to speeding up processing, and methods should be developed that can be operated as part of autonomous systems. Measurements of pH using glass electrodes are a cause of concern because of problems with both the stability of electrodes and the production of suitable buffer solutions. Recent developments on both fronts have led to reassessment of the approach, and further work is continuing in this area. Colorimetric methods for measuring pH on cruises work well for some laboratories (Clayton and Byrne, 1993; Vázquez-Rodríguez *et al.*, 2012). Colorimetry has been used in experimental underway systems on research cruises (Bellerby *et al.*, 1995; Friis *et al.*, 2004), and this has led to a number of development projects to produce instruments that can be operated reliably as part of underway systems.

Following best practice, it is considered that experienced laboratories should be able to attain the following precisions when making direct measurements of particular variable (Dickson, 2010):

(i)   TA: for closed cell, ± 3 µmol kg^{-1}; for open cell, ± 1.0 µmol kg^{-1}.

(ii)   DIC: ± 1.5 µmol kg^{-1}.

(iii)   pH: spectrophotometrically, ± 0.001 pH units; glass electrode, 0.003 pH units;

(iv) pCO_2: ± 1–2 µatm.
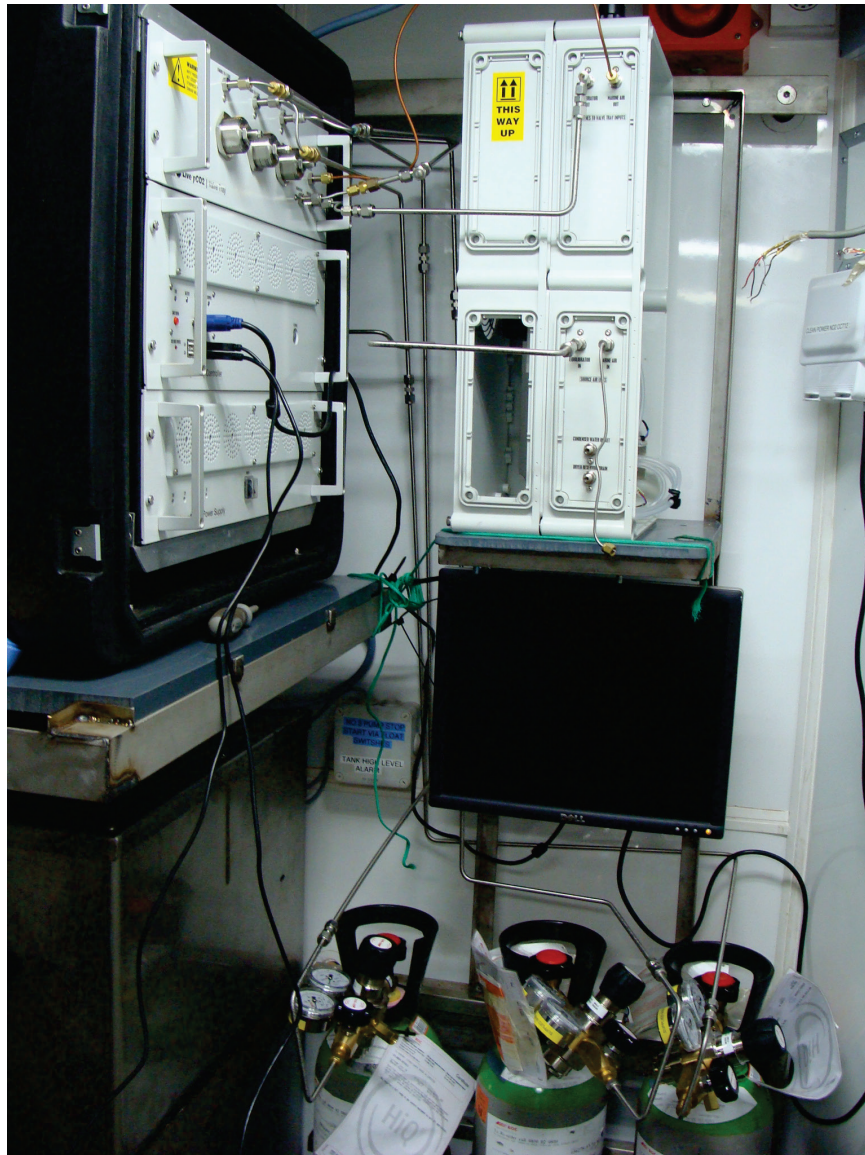
Figure 4.2. Dartcom underway pCO₂ system installed on RV "Scotia". Photo: Pamela Walsham.

4.2   Calibration and quality control

4.2.1   DIC and TA

To assess accuracy of measurements, reference materials (RM) are available for DIC and TA analysis. The carbonate analysis community has set up a reference material supply service provided by Andrew Dickson's laboratory at the Scripps Research Institute (University of California). This operation is partially funded by the US National Science Foundation (NSF) and runs on a not-for-profit basis. These reference materials consist of natural seawater sterilized by a combination of filtration, ultraviolet radiation, and addition of mercuric chloride. They are bottled in 500 ml borosilicate glass bottles sealed with greased ground glass stoppers. Samples from each batch prepared are analysed for salinity, total DIC, and TA, using the best available methodologies, by the Scripps Institute (http://andrew.ucsd.edu/co2qc/index.html).

Currently, these are produced on a limited scale ("cottage industry") in Andrew Dickson's laboratory. Increased research into ocean acidification has the potential to increase the demand for reference materials beyond the capacity of this laboratory. Dickson is working with Akihiko Murata (JAMSTEC, Japan) and others to develop an

alternative and larger source of supply.

Additionally, to aid long-term monitoring work in an increasing number of laboratories, there is a need for a proficiency-testing scheme for carbonate parameters, similar to that offered by Quasimeme for other parameters ("Quality Assurance of Information for Marine Environmental Monitoring in Europe" – www.QUASIMEME.org).

4.2.2 pCO_2

The NOAA Carbon Cycle Greenhouse Gases Group (CCGG – http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html) is currently responsible for maintaining the World Meteorological Organization mole fraction scales for CO_2, CH_4, and CO, with the mission of propagating this scale for data intercomparison.

The CCGG can fill and calibrate compressed gas cylinders for use as standard reference gases by other laboratories for measurements of CO_2, CH_4, CO, and the stable isotopes of CO_2 (^{13}C and ^{18}O). These gases form the basis of calibration of the nondispersive infrared (NDIR) analysers that are used as the detector in most underway pCO_2 systems. Recently, high-resolution, cavity-enhanced, direct-absorption spectroscopy CO_2 analysers have been made commercially available and are deployed by some laboratories coupled to equilibrators (Gülzow *et al.*, 2012). Depending on the design of the system, two to four different concentrations of gas are used to provide regular calibrations. This permits accuracies of better than 1 µatm CO_2 to be achieved by some systems. Intercomparisons of systems using equilibrators have been carried out, and these have revealed inadequacies in some systems, leading to improvements in design.

4.2.3   pH

There are currently two methods in routine use for measuring the pH of seawater. These are the (i) potentiometric determination with standards based on TRIS and AMP buffers using hydrogen ion/reference electrodes and more recently ISFET-based systems (ion-selective, field-effect transistors; Martz *et al.*, 2010) and (ii) spectrophotometric determination using *m*-cresol purple (Clayton and Byrne, 1993) (see Annex 1 for greater details on the direct determination of pH).

For work on the carbonate system, the "total scale" (see Section 1.4) is generally used for reporting pH data. It should be noted that the numerical values output by the different scales are significantly different. For example, at T = 25°C and salinity = 35, pH (free scale) is ~0.11 higher than pH (total), while the difference between pH (total scale) and pH (seawater scale) is < 0.01. In every case, the pH scale used must be reported, together with salinity, temperature, and pressure, which will allow conversion between scales to be calculated if necessary. When making measurements of pH in high ionic-strength seawater, the use of NBS buffers is not recommended; changes in the liquid junction potential of the reference electrode can introduce systematic errors of more than ± 0.1 pH (Whitfield *et al.*, 1985; Covington *et al.*, 1988). For work in seawater, the measurement system needs to be calibrated with buffer solutions made up in water of similar ionic strength to the seawater being measured. The buffer compound used is "TRIS" (2-amino-2-hydroxymethyl-1,3-propanediol). Carefully prepared solutions have a high level of stability, with a drift rate typically ≤ 0.0005 pH units per year (Nemzer and Dickson, 2005). The uncertainties arising from the preparation of such buffers is typically less than 0.002 in pH.

5 Data reporting and assessment

5.1 Data reporting

Best practice for the reporting of data on ocean acidification to data centres is still evolving. Data are dispersed in a range of national and international projects (e.g. CARBOOCEAN, CARBOCHANGE, EPOCA, COCOS) and related data centres. Co-ordinated monitoring requires common data reporting. ICES is the primary repository for OSPAR and HELCOM monitoring data. Contracting Parties (CPs) to these conventions should be encouraged to submit their acidification monitoring data to the ICES oceanographic or environmental database, according to latest ICES formats. This has the obvious advantages of simplifying reporting where carbonate parameters are collected alongside other monitoring activities (e.g. eutrophication) and allows it to be linked with other related physical, chemical, and ecosystem data held by ICES.

Globally, most research groups measuring carbonate parameters submit data to the Carbon Dioxide Information Analysis Center (CDIAC – http://cdiac.ornl.gov/oceans/home.html). The global carbon dioxide community established reporting formats for these data and related metadata (IOCCP, 2004). Data should also be reported to CDIAC, and it is recommended that ICES develop data-exchange protocols with other international data centres that hold relevant OA data, particularly CDIAC, to facilitate single reporting requirements for monitoring agencies.

The community initiated the Surface Ocean CO_2 Atlas (SOCAT – http://www.socat.info) project in 2007. SOCAT follows the community-agreed reporting formats for data and metadata and gives access to global surface CO_2 data in a uniform format database for the first time (Bakker *et al.*, 2012; Pfeil *et al.*, 2012). The SOCAT product is an international effort based on a database developed by the University of Bergen's Bjerknes Centre for Climate Research. Within SOCAT, systems for effective data access and review were developed (Pfeil *et al.*, 2012). ICES should consider how data reporting would evolve so that relevant data are available and accessible to both databases without replicating reporting requirements. Harmonized data vocabularies and metadata reporting requirements need to be elaborated.

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. This should be done in such a way that any data are "metadata documented" and are in a uniform format. The section below follows the ideas developed by Pesant *et al.* (2010). In Annex 4, we provide a set of suggestions for the metadata that should be recorded to make measurements fully traceable. This list is based on that developed for reporting nutrient data and recommended in the GO-SHIP manual (Hydes *et al.*, 2010a). All available data and metadata need to be archived in accessible databases at appropriate data centres.

5.2 Metadata requirements

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

Best practice requires that metadata are made informative when names, titles, and descriptions are assigned. Descriptions should be consistent and refer to well-recognized vocabulary registers for the parameters, equipment, and sensors.

Metadata should include the following information (a detailed list is given in Annex 4, based on reporting requirements in the GO-SHIP manual; Hydes *et al.*, 2010a):

- 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[2]).

- Sampling details: [information regarding the cruise or laboratory (e.g. 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. $\mu mol\ kg^{-1}$).

- 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 (latitude and longitude) or time].

- Calculated value: for carbonate, where more than three components are measured, a cross-check on the data can be obtained by calculation, e.g. pCO_2 measured and 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.

5.3 Specific metadata requirements for seawater carbonate chemistry and ancillary parameters

For the carbonate components, the following metadata information should be recorded:

- Dissolved inorganic carbon (DIC concentration ($\mu mol\ kg^{-1}$): information about sample replication, sample volume and head space, poisoning (poison volumes), analysis method (technique description, reference), RM information (correction magnitude, batch number, analysis log), overall precision, and accuracy.

- Total alkalinity TA ($\mu mol\ kg^{-1}$): type of titration and cell type (with reference), sample volume curve fitting method (with reference), RM infor-

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[2] Universally Unique IDentifiers (UUIDs including DOIs, URLs, URNs, and 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.

mation (correction magnitude, batch number, analysis log), overall precision, and accuracy.

- Carbon dioxide partial pressure (pCO$_2$ (microatmosphere): analytical method (technique description, reference, and equipment used), *in situ* temperature, temperature during measurement, atmospheric pressure, pressure at equilibration, temperature normalization, temperature correction method, variable reported (xCO$_2$, pCO$_2$, or fCO$_2$), gas, standard gas concentrations, frequency of standardization, 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 normalization/correction method, *in situ* pressure, calibration method, overall precision, and accuracy.

Three software packages, Seacarb (Lavigne and Gattuso, 2010), CO2SYS (Lewis and Wallace, 1998), and SWCO$_2$ (Hunter, 2012), are currently commonly used to compute 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.*, 2010a). For the most accurate calculation of the individual components contributing to the total alkalinity, concentrations of silicate and phosphate also need to be included in the calculations and, therefore, need to be made available as part of the reported dataset. 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 and Gattuso, 2010) and/or CO2SYS (Lewis and 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 and Gattuso, 2010) from DIC and total alkalinity. DIC was first calculated with CO2SYS (Lewis and 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."

5.4 Assessment

Information gathered from *in situ* monitoring and sample measurements are essential to assess the dynamics of the specific sites monitored and to study the driving processes. To quantify variability and potential vulnerability on a broader scale and at the ecosystem level, the observed data need to be linked to assessments based on the output from numerical models. Models provide a methodology to simulate a comprehensive range of physical, chemical, and biological processes at a variety of spatial (point to global) and temporal (subseasonal to century) scales. Models have limitations, as they are simplified representations of reality, for example, aggregating biological diversity to a limited number of functional types. Although they are generally incapable of exact replication of specific observations and are dependent on functional concepts and attendant parameterizations that are often uncertain, their skill lies in revealing quantitative links and spatial gradients between processes and their effects over short to long time-scales. Harmonized assessment requires programmes of both nationally and internationally coordinated monitoring measurements linked to schemes for assessment that include the use of numerical models.

Various approaches are used for thematic assessments under the OSPAR Joint Assessment and Monitoring Programme. For instance, a lead country collating data and undertaking an assessment on behalf of all CPs; countries carrying out assessments of their own waters according to harmonized protocols (e.g. the common procedure for identification of the eutrophication status of the OSPAR maritime area), or joint assessments by expert working groups, such as the annual assessments of hazardous substances. Ultimately, assessments of the chemical aspects of ocean acidification should be designed to inform policy-makers of status, trends, and outlook for ocean acidification in the maritime area. Specifically assessments should:

- describe the spatial variability across the regional area;

- identify trends and temporal variability over the medium and long term;

- assess the causes of the variability (e.g. influence of riverine inputs for coastal waters);

- highlight specific areas where there is greatest risk (e.g. rate of acidification, vulnerable ecosystems);

- provide information to fine-tune ongoing monitoring;

- provide products that can communicate the outputs to policy-makers and the public.

Examples of approaches are MCCIP (UK) Report Cards (e.g. Turley *et al.*, 2009), Indicator fact sheets (e.g. HELCOM), and contributions to holistic assessments such as OSPAR's Quality Status Report (e.g. OSPAR, 2010).

6 Findings and recommendations

Coordinated observations of the carbonate system in the ICES maritime area are feasible. These should be started as soon as possible to establish a long-term ocean acidification dataseries.

Monitoring is foreseen as a combination of low-frequency, repeat, ship-based surveys enabling collection of extended high-quality datasets on horizontal and vertical scales, and high-frequency autonomous measurements for more a limited parameter set using instrumentation deployed on ships of opportunity, moorings, and other platforms as the technology develops.

There are several national and international projects that have been and are currently active in the Northeast Atlantic and Baltic areas making sustained measurements using a variety of platforms. These can be used as a basis for the development of the required monitoring programme. Building relevant measurements into other related programmes will support cost-effective monitoring, e.g. incorporation of carbonate parameters into OSPAR eutrophication monitoring programmes.

Monitoring requires a long-term commitment to both observation and methods (technological) development. Present methods are slow and require high skill levels. Improvements in the methods should be sought to improve their ease and speed of use. Monitoring will need to adapt to these changes.

6.1 Parameters, protocols, and quality assurance

- There are four parameters that describe the carbonate system: (i) hydrogen ion concentration (pH), (ii) total alkalinity (TA), (iii) total dissolved inorganic carbon (DIC), and (iv) partial pressure of carbon dioxide pCO_2. A minimum of two must be determined to derive the other two. If three of the variables are determined, this allows verification of the computed value. DIC and TA are the most widely measured for discrete samples, while pCO_2 is the most common for underway measurement.

- At present, there are practical and technological limitations to pH measurements, but since pH is of primary concern, this parameter should be measured when possible in the future.

- Necessary parameters to be measured alongside the carbonate parameters are temperature, salinity, dissolved phosphate, and silicate, as these are required for carbonate system calculations. It is strongly recommended that dissolved oxygen and nitrate also be measured to provide information on the timing of the data relative to the seasonal production/respiration cycle.

- To achieve consistency, the widely accepted procedures outlined in the handbook by Dickson *et al.* (2007) must be followed.

- To obtain reliable and consistent datasets, it is essential that a high level of quality assurance be established from the outset of the programme. This can be based on the reference materials (RMs) for DIC and TA, which are available from Prof. Andrew Dickson (Scripps Research Institute, USA), and reference gases for pCO_2 measurement are available from NOAA. (Certified buffer solutions for use in the measurement of pH are currently under development).

- There is a need for laboratory proficiency testing schemes for carbonate parameters (TA and DIC) to be initiated to support monitoring (e.g. QUASIMEME).

6.2   Approach and coverage for monitoring

- The design of a monitoring programme should be staged.

- An initial research phase with more widely dispersed and more frequent measurements is necessary to provide the information required to design a statistically robust long-term monitoring programme. Information from ecosystem models should be used to aid the design.

- Measurements need to cover the range of waters from estuaries, shelf seas and ocean mode waters, and abyssal waters where sensitive ecosystems may be present.

- Particular emphasis should be placed on key areas at risk within the OSPAR area, for example, high latitudes where ocean acidification will be most rapid and areas identified as containing ecosystems and habitats that may be particularly vulnerable, e.g. cold-water corals.

- River monitoring programmes should include carbonate parameters to elucidate the influence on coastal waters.

6.3   Reporting

- Data should be reported to both the ICES data repository (http://www.ices.dk/marine-data/guidelines-and-policy/Pages/Submitting-data-and-meta-data.aspx) and the Carbon Dioxide Information Analysis Center (CDIAC – http://cdiac.ornl.gov/oceans/home.html).

- Reporting data to the ICES data repository enables it to be linked to many related OSPAR/HELCOM datasets, e.g. nutrients and integrated ecosystem data.

- Globally, most research groups measuring carbonate parameters submit data to CDIAC. The global carbon dioxide community established reporting formats for these data and related metadata (IOCCP, 2004).

- The Surface Ocean CO_2 Atlas (SOCAT – http://www.socat.info) gives access to global surface CO_2 data in a uniform format database.

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ANNEX 1: Direct measurement of pH

In this annex is described the current state of development with respect to the direct measurement of pH. A number of laboratories around the world are developing systems for the reliable and automated measurement of pH that can achieve levels of precision and accuracy required for work on monitoring ocean acidification (±0.001 pH units). Much of this work is being done with colorimetric and fluorometric chemistry. A critical step will be the transfer of these methods into equipment and procedures that can be used by non-specialist laboratories, allowing them to achieve the accuracies and precisions now being obtained by specialist groups. Glass pH electrodes are still widely used for the measurement of pH. However, their use has major limitations and it is important that workers in this field are aware of them. Therefore, the use of electrodes is discussed first below. Newer potentiometric methods using field-effect transistor technology may offer a robust way of making reliable measurements for many laboratories in the near future. While for laboratories with the required skills, the method of choice will be spectrophotometry using a purified indicator dye.

Potentiometric (electrode) methods

For ocean acidification (OA) monitoring, pH may appear to be the ideal parameter to measure. However, the direct measurement of accurate pH values in the marine environment is still challenging. The use of glass electrodes is discussed first. Some of the problems discussed, particularly with respect to calibration, are common to all methods.

Electrode calibration

As electrodes need regular calibration, the first requirement for using pH electrodes is the availability and use of suitable buffers that span the range of pH to be measured. In the marine environment, these are pH buffers based on TRIS [tris-(hydroxymethyl) aminomethane] and AMP (2-aminophenol) and made up in artificial seawater of known salinity. The pH of these buffers is dependent on salinity and temperature, and empirical equations are used to assign the pH. The current state-of-the-art method is described in SOP 6a "Determination of the pH of seawater using a glass/reference electrode cell" of Dickson *et al.* (2007). Dickson advises that pH electrodes should only be used to analyse field-collected samples under well-controlled laboratory conditions. Following current best practice, the top reference laboratories should obtain an accuracy of 0.003 in pH when the salinity of the buffer is matched to that of the sample seawater.

A high level of analytical expertise is required for making up seawater buffers, and it is important to regularly check them against reference materials obtained from a trusted source. Small quantities of prototype reference TRIS buffers are now available from Andrew Dickson's laboratory at the Scripps Research Institute (University of California) for this purpose. This means that the routine use of electrode measurements should be capable of producing data with better "traceability" than previously. However, at present, there is no source for the second required buffer, AMP. A good supply of both buffers would reduce the uncertainty in the measurement of marine pH. Information on the shelf life of these reference buffers (sealed and once opened) is required together with recommendations on storage.

Choice of electrodes

The next requirement concerns the choice of electrodes (hydrogen ion and reference)

and measurement systems. There is a wide range of hydrogen electrodes available from a number of manufacturers. Conventional electrodes use glass membranes, which, provided they are treated with care, will provide reliable measurements. Before use (and at regular intervals thereafter), it is important to check that the slope of the electrode is within 1% of the theoretical Nernstian slope. Although using two buffers will allow the calibration of the pH cell, a reduction in the theoretical slope will reduce maximum accuracy and may indicate a potential fault with the electrode.

Although the selection of the hydrogen electrode is important, the choice of the reference electrode is critical to the accuracy and stability of the pH measurements. Generally, the reference electrode is of the Ag/AgCl type. When designing a reference electrode, the main concern is the junction between this electrode and the seawater being measured. Various designs of junction are available, including glass frit, single junction, double junction, PTFE ring, and free-diffusion liquid junction. Ideally, the junction should afford a fixed reference potential regardless of the sample's temperature, salinity, and other physical and chemical properties. However, this is not the case, and the selection of the reference electrode is generally a compromise between ease of use and accuracy desired; no "best buy" can been recommended. Typical laboratory-based systems use a double-junction reference electrode. Butler *et al.* (1985) and Whitfield *et al.* (1985) introduced the concept of a capillary free-diffusion liquid junction, which consisted of a potassium chloride (KCl) salt bridge solution in a capillary between the reference electrode and the hydrogen electrode cell. Changes in seawater sample composition had negligible effect on the reference electrode, and the liquid junction in the capillary could be reformed reproducibly. To obtain the highest accuracy, the seawater buffers used should match the seawater salinity as closely as possible and certainly within about 5 salinity units. The use of a sodium glass electrode as the reference in the pH measurement cell avoids the issues discussed for a conventional reference electrode (Tishchenko *et al.*, 2011). The calculation of pH uses a Pitzer model and requires sample salinity and temperature to be measured at the same time as the cell voltage. This approach may offer the potential for improving longer-term stability and lower measurement drift when using a glass hydrogen electrode in the marine environment, especially in regions of rapidly changing salinity such as estuarine waters. However, it still requires more research and development before it could be considered a routine method for pH measurement.

New type of electrode

Other types of hydrogen electrodes are currently in development, e.g. ISFETs. These alternative electrodes may afford advantages in the future for robustness and stability Martz *et al.* (2010). A sensor based on this technology (Hofmann *et al.*, 2011) is now available as a commercial product: the SeaFET from Satlantic (Annex 4). However, Satlantic currently describes it as a research tool, and further development and testing are required before it can be recommended for routine monitoring.

Instrument design

The final requirement is for the electronics and pH cell design. The hydrogen ion electrode requires a very high impedance input to the voltage measurement system to ensure that the current flowing through the glass membrane is extremely low. However, under these conditions, glass electrodes act as antenna for potentiomagnetic interference, and extreme care must be taken with design of analogue electronics, screening, and earthing. A standard pH meter generally measures to 0.1 mV (equivalent to 0.002 pH). However, to be certain of obtaining accuracies approaching 0.003 pH, it is strongly advised to measure the voltage to 0.01 mV (approximately

tenfold higher resolution in voltage than required for the target pH precision). In the laboratory, it is recommended to use a high-accuracy, calibrated digital voltmeter (5 and 1/2 digit) fitted with very high impedance input specifically designed for use with pH and glass electrodes. For an autonomous or field-based system, expert design of analogue electronics, screening, and earthing should be undertaken. Add to these the choice of hydrogen and reference electrodes and issues with electrode measurement stability on *in situ* samples, and this suggests why it is difficult to take field measurements at accuracies >0.02 pH.

One system that has attempted to minimize these issues is the estuarine pH system described by Pearce and Wood (1997). This vessel-fitted, flow-through system used the free-diffusion, liquid-junction design, where the reference electrode was maintained at a fixed temperature (±0.1 K), and the capillary connection to the hydrogen electrode measurement cell contained 3.5 M KCl. The system used 20 ppt TRIS buffer. An accuracy of 0.02 pH was obtained for estuarine water of salinity from about 5 to 35. The electronics were designed to ensure good quality voltage measurements with minimal noise and no voltage offset. During use, the system refreshed the liquid junction automatically at a programmed interval, and electrode calibrations were carried out before and after a survey and every 4–6 h during a survey. Improvements in the accuracy of such a system should be possible by the additional use of AMP buffers and closer matching of salinity to the ambient conditions.

Currently, there is no recognized, recommended standard pH electrode-based system (including electrodes, buffers, electronics, and software) for autonomous or shipboard continuous flow measurements. The development of an automated calibration regime (based on TRIS- and AMP-based buffers of suitable salinities) is required for long-term stability in autonomous systems. Flow-injection systems using ISFET-based electrodes and requiring small quantities of buffers may afford cost-effective, reliable systems with satisfactory accuracy.

Sources of errors

From the preceding discussion, it is clear that there are several sources of errors in the potentiometric determination of pH. The combination of these errors, especially for autonomous measurements, contributes to lower accuracies obtainable in the field than under controlled laboratory conditions. Such sources of error include:

- reference electrode selection and use (changes in liquid-junction potential affecting measured cell voltage), although this could be mitigated to some extent by using a cell without a liquid junction;

- seawater buffer pH uncertainties (absolute values and drift);

- hydrogen electrode selection and use (including Nernstian response checks);

- noise and voltage offsets brought about by poor earthing and/or electronics design.

Conclusions and recommendations

The direct measurement of accurate (> ±0.003) pH values using potentiometric techniques in the marine environment is extremely challenging. To improve the accuracy of *in situ* and other autonomous measurements of pH using potentiometric techniques, development work is required to overcome the many issues highlighted. The following recommendations are made:

(i) Electrodes are not currently recommended for autonomous use on moorings, and ship flow through systems where data accuracy greater than about 0.02 pH is required.

(ii) Only with extreme care and training is it possible to obtain accuracies approaching 0.005 pH, when field-collected seawater samples (salinity ca. 35) that are subsequently analysed in the laboratory. An enhanced and more detailed version of SOP 6a would improve this situation, increasing the confidence in measurements made in non-reference laboratories.

(iii) There is a requirement for increased quantities of certified reference buffers (TRIS and AMP) to help improve confidence in electrode-based pH measurements.

(iv) Further developments are required before reliable, accurate autonomous measurements can be made. The use of ISFET-based sensors and cells without a liquid junction should be further assessed. The aim should be to produce recommended, accredited electrodes and electronics/software systems to ensure intercomparability between monitoring organizations.

(v) Interlaboratory (QUASIMEME-type exercise) checks with reference seawater solutions of known pH would ensure reliability and accuracy of these measurements.

Spectrophotometric and fluorometric methods

Highly accurate spectrophotometric methods based on the indicator m-cresol purple or phenol red (Clayton and Byrne, 1993; Chierici *et al.,* 1999) are available that provide a precision of about ±0.001 pH units (compared to ±0.01 using a classic pH electrode) in oceanic waters. Once the indicator pK values have been determined as a function of temperature and salinity, the calibration resides in the indicator itself, rather than relying on the preparation of TRIS seawater buffers. The main concern has been the varying purity of the commercially available indicators; however, Liu *et al.* (2011) have shown that the meta-cresol purple indicator can be purified by HPLC, assuring a reliable source of indicator for pH measurements. Adapting this method to low-salinity water demands knowledge of the indicator stability constants at the relevant salinities. Project work is ongoing with the aim to adjust the method to minimize the effects in low-salinity water. Lower-salinity waters also tend to be in dynamic coastal and estuarine regions where turbidity is likely to be high. So similarly, potential errors from suspended solids entering the sample stream will also need to be assessed as automation begins to be applied to spectrophotometric methods of measuring pH.

Several laboratories are working on the automation of the spectrophotometric method. The colorimetric method is described in SOP 6b "Determination of the pH of seawater using the indicator dye *m*-cresol purple" of Dickson *et al.* (2007). The manual method has been used successfully over a number of years by some laboratories (Perez *et al.,* 2010). To obtain accurate data, biases due to contamination of the dye need to be taken into account (Yao *et al.,* 2007). The method has been automated (e.g. Friis *et al.,* 2004; Assman *et al.,* 2011), but work is ongoing in a number of laboratories to produce reliable systems that can be run autonomously. A system is available from Sunburst Sensors (http://www.sunburstsensors.com/, Seidel *et al.,* 2008). Wang *et al.* (2007) reported on an autonomous multiparameter flow-through CO_2 system meas-

uring surface seawater pH, carbon dioxide fugacity (fCO$_2$), and total dissolved inorganic carbon (DIC). All three measurements are based on spectrophotometric determinations of solution pH at multiple wavelengths using sulfonephthalein indicators. The field precisions were reported to be 0.0008 units for pH, 0.9 μatm for fCO$_2$, and 2.4 mol kg^{-1} for DIC.

Ideally, instruments in a flow-through system should be robust, yet deliver high precision and accuracy. A new promising fluorometric approach is being developed (Hulth *et al.*, 2002; Hakonen and Hulth, 2008, 2010; Hakonen *et al.*, 2010) to determine pH in a continuous mode. This involves immobilization of a fluorescent dye on a film that is exposed to a continuous flow of seawater, and the resulting fluorescence emission is recorded with a CCD camera. Due to the size of the film, a large number of spectra can be recorded per time interval, each having an individual calibration. With this system, problems of low buffering capacity (and other confounding factors such as humic substances) are minimized.

Hakonen and Hulth (2008) have successfully implemented a time-dependent, non-linear calibration protocol on ratiometric fluorescence from the pH-sensitive fluorophore 8-hydroxypyrene-1,3,6-trisulfonic acid. Due to the significantly reduced photoacidity of HPTS immobilized in the ethyl-cellulose sensing membrane, a dual excitation/dual emission ($F$1, ex/em: 405/440nm and $F$2, ex/em: 465/510 nm) ratiometric (RF1,F2 = $F$1/$F$2) sensing scheme was utilized to amplify sensor response. Using the dual emission-sensing scheme, the signal-to-noise ratio was enhanced by 400%. Sensor performance, including the time-dependent, non-linear calibration procedure, was limited by the electrode used for standardization. The apparent pKa of the sensor ranged from 6.74 to 8.50, mainly determined by the immobilization procedure of HPTS. Principles and mechanisms of the ratiometric-fluorosensor, implementing non-linear calibration protocols for drift compensation, can be applied for pH measurements in a variety of environments. Complex sampling environments include e.g. soils and aquatic sediments, and bioanalytical applications for cells and cell-signalling networks. In principle, the non-linear calibration protocols for drift compensation presented in this study are likely to be general and applicable on optical sensors that show a sigmoidal response that demonstrates an explicit linear drift.

ANNEX 2: Possible sources of error related to calculations

Inconsistencies in the calculation of carbonate system variables

Seawater carbon measurements are not straightforward, and the accuracy of a particular measurement is difficult to determine, although reproducibility can be assessed. If appropriate estimates of the overall uncertainty (bias and precision) are not available, the existence of "discrepancies" is moot. Similarly, other information that is used to compute (for example) carbonate ion concentration is based on experimental measurements with associated uncertainties. Meaningful attempts to assess the propagation of errors need to take this into account. Additionally, other errors caused by an incomplete (or incorrect) model of the acid–base chemistry may be associated with particular samples, such as those caused by the presence of organic bases and acids in waters with high concentrations of biomass (Koeve and Oschlies, 2012). A paper by Hoppe *et al.* (2010) raised serious concerns over how well the pCO_2 concentration could be determined in experimental systems working at high levels of pCO_2 (>1000 ppm). Consequently, work to study the potential effects of ocean acidification (OA) on ecosystems faces two challenges:

1) Marine chemists must ascertain if their understanding of the marine carbonate system, gained largely in the deep sea, is adequate for work in coastal waters and experimental systems with high levels of organic matter and CO_2.

2) Experimentalists must carry out their experiments and analyses with sufficient rigor that the carbonate chemistry of their systems can be replicated in future validation experiments.

In 2010, Hydes *et al.* (2010b), as part of a study of baseline measurements of the carbonate system in UK waters (DEFRApH), carried out a desk study of the potential problems with the consistency of the software currently available for cross calculation of carbonate system components and possible sources of problems arising from how carbonate alkalinity is determined.

Their findings were:

1) Three of the four components of the carbonate system—DIC (total dissolved inorganic carbon), pCO_2, and pH—can be measured by direct techniques, so that uncertainty in the quantity measured is limited only by experimental error.

2) Carbonate alkalinity is arrived at indirectly by calculation based on the measurement of total alkalinity. Four independent studies (Hernandez-Ayon *et al.*, 2007; Muller and Bliei, 2008; Kim and Lee, 2009; and, more recently, Koeve and Oschlies, 2012) show titrateable organic matter can be present in samples from coastal waters and mesocosms at levels equivalent to a few tens of $\mu M\ kg^{-1}$ of alkalinity. Because of non-linearity in the equations, when such quantities of organic alkalinity are present, equivalent errors of tens of % will occur in the values of pCO_2 calculated from measurements of total alkalinity.

3) The three main different software packages (CO2SYSS, CO_2SW, and Seacarb) available for the calculation of CO_2 system variables give identical results when calculations are done with the same input parameters. At a

pCO$_2$ of 1000 µatm, a maximum sensitivity of only 5% was found to be the choice of constants.

4) Calculations of pCO$_2$ and [CO$_3^{2-}$] from a measurement paired with pH were found to be more sensitive to errors in pH than errors in the other measurement. Accurate pH measurements will thus yield accurate determinations of parameters of interest to OA, whereas poor pH measurements can only yield inaccurate and misleading determinations of OA-relevant parameters. With TRIS buffers, an accuracy of 0.005 pH units may be achievable by experienced analysts using the best techniques, equivalent to an error in pCO$_2$ of 10 µatm at a pCO$_2$ level of 1000 µatm, when pCO$_2$ is calculated from measurements of pH and DIC.

They considered:

1) Further work should be carried out using state-of-the-art techniques in a range of environments—coastal water to laboratory experiments—to determine the locations and scale of the contribution of organic material to measured total alkalinity.

2) Where possible, the carbonate system should be overdetermined to provide evidence of problems. The simplest way to do this is by measuring three or all four carbonate variables. Measurements of TA and DIC are commonly made in most laboratories carrying out high quality carbonate system measurements. Now that reference materials are available, measurement of pH can potentially provide the needed third determinand.

3) To assist with the development of high quality pH measurements outside the core community of carbonate chemists, a more closely specified standard operating procedure (SOP) than the current CO$_2$-SOP-6a (Dickson *et al.*, 2007) for the electrode-based measurements of pH is recommended. This should be based on experience already available in the community on the most appropriate pH electrodes and temperature sensors to use and the appropriate design of a measurement cell.

Appropriate metadata for all measurements of carbonate data in natural waters and experimental systems should be recorded. This is to enable carbonate system errors to be assessed and experiments replicated within known limits of reproducibility (Annex 4).

Validity of calculations in brackish waters

There are concerns about the accuracy of calculation procedures, such as the commonly used CO2SYS program (Lewis and Wallace, 1998; Pierrot *et al.*, 2006), at lower salinities. The limitations arise due to the degree to which the various dissociation constants for carbonic acid have been measured over the whole range of salinities of interest. The choice of dissociation constants of carbonic acid used in the calculations needs to be appropriate. The Mehrbach *et al*. (1973) constants, as refitted by Dickson and Millero (1987), are assumed to be the better choice to use in calculations based on ocean waters (Wanninkhof *et al*., 1999; Lee *et al*., 2000). However, they are only valid down to a salinity of 15, so they cannot be used reliably in estuarine waters or the Baltic. Millero *et al*. (2006) published dissociation constants of carbonic acid in seawater as a function of salinity and temperature, which extend over the whole salinity range. They have been included in version 14 of the CO2SYS excel version (http://www.ecy.wa.gov/programs/eap/models.html) software so awareness of the version being used is important. The latest version (2.3.3) of Seacarb

(http://CRAN.R-project.org/package=seacarb) includes the most up-to-date dissociation constants for K_1 and K_2 of Millero *et al*. (2006) and Millero (2010).

From the purely analytical point of view, methods described by Dickson *et al*. (2007) are valid in estuaries for TA and DIC if used appropriately. Where pCO_2, is measured directly using an equilibrator-based system, problems have been identified in turbid estuarine waters, so that an appropriately designed equilibrator needs to be used (e.g. Frankignoulle *et al*., 2001). Additionally, in estuaries, a major uncertainty arises with the choice of scales for pH and related buffers. Frankignoulle and Borges (2001a) have shown that consistent data for pH can be achieved over the full range of estuarine salinities if the data are referenced to the NBS scale. The limitation of using TRIS buffer values and the total scale is that values for TRIS buffers have only been determined for salinities >5 (DelValls and Dickson, 1998), and the data for the AMP buffer value is only established at salinity 35. Hence, the Nernstian behaviour of pH electrodes can only be checked at this salinity.

Reporting of values of the fugacity or partial pressure of dissolved CO_2

Comment based on note from Taro Takahashi (21 February 2012) on reporting of CO_2 data

When the concentration of CO_2 in solution is presented in terms of its partial pressure (pCO_2) and then used in calculations of air–sea exchange fluxes, an incorrect assumption has been made that CO_2 is an ideal gas. An ideal gas behaves as if the molecules are "hard balls" without stickiness or extra repulsion. On the other hand, when the concentration is expressed in terms of the fugacity (fCO_2), it is assumed that corrections for non-ideality arising from stickiness between molecules and asymmetry of molecular shapes have been correctly taken into account. Consequently, the gas-exchange fluxes can be calculated more accurately than if the directly measurable pCO_2 values were used.

In the case of CO_2, CO_2–CO_2 interactions and CO_2–H_2O interactions are considered to be the source of non-ideality. However, some groups consider only the non-ideality arising from the CO_2–CO_2 interaction, while others compute the fugacity including the CO_2–CO_2 and CO_2–H_2O interactions. Problems occur when values of fCO_2 are reported, but the corrections made to compute fugacity (fCO_2) from pCO_2 are not clearly stated in the metadata.

The second problem is that it is not clear that the information needed to make the corrections as accurately as is sometimes assumed possible is actually available at the present time. This second problem arises in that the fugacity formulation by Weiss (1974) is based on the solubility experiment by Murray and Riley (1971). The Murray

and Riley measurements were made using pure CO_2 gas saturated with water vapour at the respective temperatures. This means that the effects of CO_2–H_2O interactions are already included in the results. In some cases the CO_2–H_2O corrections are applied using a formula proposed by Weiss and Price (1980), which was deduced from the Spitzer's systematic relationships. Takahashi considers that this is a double correction for the non-ideality induced by CO_2–H_2O molecular interactions. The magnitude of the double correction is not known because of the difference in the proportion of H_2O and CO_2 molecules in the Murray and Riley experiment compared to natural air in an equilibrator-based measurement system. In the former, CO_2 is the predominant molecule, whereas in the latter (air equilibrated with seawater), H_2O is the predominant molecule relative to CO_2. Consequently, Takahashi *et al.* (2009) pointed out the ambiguities in the reporting of fCO_2 values and that, consequently, it is currently essential that the more directly measured value of pCO_2 should be reported.

ANNEX 3: Draft OSPAR Monitoring Guidelines for Chemical Aspects of Ocean Acidification

1. Introduction

Ocean acidification is an unavoidable consequence of increased atmospheric concentrations of CO_2 and the partitioning of CO_2 into seawater. CO_2 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 undersaturated with respect to the carbonate minerals forming the shells of many organisms earlier than other areas. A range of other biological processes and functions are also likely to be affected by changes in pH (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 CO_2 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 is because data of sufficient accuracy and precision for the assessment of acidification status are generally absent. At the present stage 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 the study and budgeting of marine CO_2 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) monitor the spatial distribution of carbonate species concentrations within the maritime area. (In coastal areas, high quality marine observations may need to be coupled to regular monitoring of major river inputs[3]);

2) assess trends in the degree of ocean acidification due to anthropogenic influences by monitoring pH, other carbonate system parameters, and carbonate mineral saturation over periods of several years;

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3. River monitoring is needed for (i) understanding of the variability of river inputs and the drivers of this variability, and (ii) to give better parameterization of river inputs in numerical models of marine acidification (e.g. Blackford and Gilbert, 2007).

3)   provide information of sufficient spatial and temporal resolution to underpin the identification of biological impacts and future ecological risks through direct observation and the use of numerical models.

3. Quantitative objectives

The quantitative objectives must take into account the characteristics (e.g. variability) in 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. ten years). To clarify the situation and to help define objectives, Contracting Parties should collect and undertake statistical analyses of new baseline datasets 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 allow Contracting Parties to determine the representativeness of their monitoring stations with regard to spatial variability of 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 that 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 (pCO_2), and hydrogen ion concentration measured as pH[4] (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 (CO_3^{2-}): temperature, salinity, silicate, and phosphate.

The equilibrium chemistry of the carbonate system has been studied extensively (see 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[5]) 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

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4. Confusion can arise due to the existence of several different pH scales. pH is an operationally defined concept, and there are four different scales (US 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 metadata when data are deposited in a database.

5. CO_2 system calculation software can be downloaded from (i) http://cdiac.ornl.gov/ftp/co2sys/, (ii) Lavigne and Gattuso (2011), and (iii)

http://neon.otago.ac.nz/research/mfc/people/keith_hunter/software/swco2/.

and TA, which are supported by reference materials[6]. For underway sampling, high-frequency (< 5 min) measurements with high precision and accuracy (< 2 µatm) can be achieved for the measurement of pCO_2 (measurements can be referenced against WMO-approved gas standards[7]). For assessment of ocean acidification, in some areas where only measurements of pCO_2 are available, they can be coupled to estimates of TA from salinity (Lee *et al.*, 2006) to give an estimation of pH. In such cases, the relationship between salinity and TA for that area should be established.

Prior to establishing long-term monitoring, Contracting 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 Contracting 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 pCO_2 needs to be done with repeat-visit 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 determine the scale of local influences resulting from variations in riverine inputs of carbonate species. Equally, monitoring in shelf seas should be sufficiently extensive to 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 internal and external processes involved in regulating TA concentrations, such as variability of riverine inputs and denitrification. A linear relationship indicates that physical mixing is the dominant process regulating the TA 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 of 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 the maximum winter DIC concentrations were detected in a given year.

All carbonate data should be reported with accompanying data for the salinity and *in situ* temperature of the sample because the values *in situ* pCO_2 and pH are sensitive, particularly to changes in temperature. Normalization of data to a particular salinity can help in identifying if a change in concentrations is related to change in water mass properties.

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6. Dickson Lab http://andrew.ucsd.edu/co2qc/.

7. NOAA Carbon Cycle Greenhouse Gases Group (CCGG; http://www.esrl.noaa.gov/gmd/ccgg/refgases/stdgases.html) is currently responsible for maintaining the World Meteorological Organization mole fraction scales for CO_2, CH_4, and CO.

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 offshelf waters, key areas include Arctic seas and vulnerable habitats, such as cold-water coral reefs.

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 identify where biological effects due to ocean acidification occur. 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 carbonate system 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 hydrobottles clamped to a hydrowire and lowered to the prescribed depth. Use of a rosette sampler is preferred, combined with an accurate and precise profiling probe for measurement of temperature (±0.05), salinity (±0.005), and pressure (a "CTD" profiler). Additional subsamples 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, leaving a 1% headspace, and the samples poisoned by the addition of mercuric chloride if the samples are to be stored (Dickson *et al.*, 2007; SOP 1). For rosette sampling, the priority for the order of drawing samples is as follows: samples for DIC/TA should be taken after CFC, oxygen, and pH samples, but before nutrient and salinity samples, to minimize the CO_2 exchange across the free surface that forms in the hydrobottle as it drains.

5.2 Contamination

Sampling should be undertaken in such a way that any ship discharges are avoided. Sampling bottles on the rosette and sample storage bottles should remain closed when not in use.

Sample storage bottles should be thoroughly rinsed with sample before filling. A tube attached to the sample collection bottle running to the base of the sample storage bottle should be used to minimize 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) should be stored in a cool and dark environment. Samples can be 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 Pretreatment

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 minimizes the gas exchange for DIC samples has not been published.

7. Analytical procedures

Methods for the determination of the four carbonate species are described in detail in Dickson *et al.* (2007). The preferred methods are: (i) TA: acid–base titration with the endpoint calculated by Gran fit; (ii) DIC: addition of phosphoric acid with quantification of the evolved CO_2 by coulometry; (iii) pCO_2 underway samples: equilibration of gas stream with the surface water and determination of the equilibrated mole fraction of CO_2 in the gas stream by infrared spectrometry at a known gas pressure; and (iv) no recommendation can currently (2012) be given on a technique for direct measurements of pH, and laboratories using direct measurements of pH should validate that the measurements obtained are fit for purpose for their target sampling area.

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, DIC, pH (TRIS), and reference gases for pCO_2 (see above). Recommendations and Matlab tools for pCO_2 QC procedures have been developed as part of the Surface Ocean CO_2 Atlas (SOCAT) and CARINA projects and are available at http://www.socat.info/publications.html (see Olsen and Pierrot, 2010, Matlab routines to aid QC of SOCAT data).

When possible in addition to routine use of RMs, the data should be checked for cruise-to-cruise consistency, where possible, by comparing samples from the deep ocean with near-steady CO_2 chemistry (e.g. >2000 m), by comparing DIC/TA relationships to salinity, and/or relationships between DIC and nitrate, phosphate, and oxygen (Tanhua *et al.*, 2010; http://cdiac.ornl.gov/oceans/2nd_QC_Tool/).

A system of regular intercomparisons between the concerned laboratories should be organized.

9. Reporting requirements

Data for TA and DIC should be reported in units of μmol kg^{-1}. Data for CO_2 should be reported as the partial pressure pCO_2 in units of microatmospheres. Data for pH should be reported with details of the pH scale to which the measurement is referenced; normally, this should be the total scale (Dickson, 2010).

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 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 the derivation of a calculated value. During the subsequent assessment, other parts of the carbonate system will be calculated. If these data are, in turn, archived, any derived values should be flagged to indicate how the values were calculated. Pesant *et al.* (2010) propose a system of secondary flagging for this purpose.

10. Summary tables

Table A3.1. Generally accepted levels of error associated with each method based on Dickson (2010).

		REF METHOD	STATE OF ART	OTHER
	Total dissolved inorganic carbon μmol 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 μmol kg^{-1}			
(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 *m*-cresol purple	0.003		

		REF METHOD	STATE OF ART	OTHER
	pCO$_2$ μatm			
(K)	Direct – equilibrator infrared determination of pCO$_2$		2	
(L)	Indirect – membrane colorimetric determination of pCO$_2$			2–10
(M)	Direct – membrane infrared determination of pCO$_2$			1–10

Table A3.2. Availability of reference materials for the quality control of carbon dioxide measurements in seawater (Dickson, 2010).

ANALYTICAL MEASUREMENT N	DESIRED ACCURACY	UNCERTAINTY	AVAILABILITY
DIC	±1 ìmol kg^{-1}	±1 ìmol kg^{-1}	since 1991
TA	±1 ìmol kg^{-1}	±1 ìmol kg^{-1}	since 1996
pH	±0.002	±0.003	since 2009
Mole fraction of CO$_2$ in dry air	0.5 ìmol mole^{-1}	$\pm$0.1 ìmol mole^{-1}	since 1995

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ANNEX 4: Metadata list for reporting of monitoring of chemical aspects of ocean acidification

This metadata list is based on reporting requirements identified for nutrients reporting in the GO-SHIP Manual (Hydes *et al.*, 2010a).

General information

Cruise information

- Vessel (name, country, vessel ID).
- Principal scientist for cruise.
- Date and port of departure.
- Date and port of arrival.
- Cruise ID (EXPOCODE).
- Name of experiment (e.g. P16 or M60/5).
- Leg.
- Geographical coverage (e.g. North Atlantic; 30°N to 50°N and 60°W to 10°W).
- Number of CTD stations.
- Number of surface (underway) samples.

Carbonate measurements

PI and analysts carrying out analyses

- Name of project PI reporting data.
- Name of analytical service PI.
- Name of senior analyst.
- Organization.
- Address.
- Telephone.
- E-mail.

Variables descriptions

- Variable names, e.g. xCO_2 or pCO_2 at e.g. 25°C or *in situ* temperature.
- Database parameter codes.
- Reporting units.

Dates of:

- Collection.
- Reception by analytical service.
- Measurement.

Sampling procedures and storage

- Sampling containers (e.g. 500 ml Schott Glass Duran clear glass); grease for the stopper.

- Processing of sampling during collection (e.g. filtering of alkalinity samples – method e.g. vacuum filter size, e.g. GF/F).

- Poisoning of samples (e.g. 100 microlitre saturated $HgCl_2$).

- Storage (e.g. in dark refrigerated 4°C).

Method description (separate details for each method DIC/TA/pCO_2/pH)

- Instrument: instrumentation used for the measurements, e.g. VINDTA 3C.

- Method for each measured parameter, and appropriate reference, e.g. Dickson *et al.* (2007): SOP 6.

- Note deviations in 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 are prepared: on the ship, or premade in the lab prior to cruise.

- Which medium was used for the reagents, e.g. MilliQ, NaCl solution.

Standardization

- How stock solutions were prepared (initial salts, medium) plus method (volumetric, mass).

- How stock solutions were diluted to working concentrations (medium) plus method (volumetric, mass).

- How stock solutions were standardized, i.e. coulometric standardization of acid titrant.

- Blank measurements (medium).

- Which pipettes were used, and calibration information of the pipettes.

Reference material

- Certified reference materials used (state batch numbers, producer, etc.).

- pCO_2 calibration gases and reference gases used for calibration of working standard gases.

- 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. pCO_2 – Pierrot *et al.* (2009).

- Calibration curves/ranges, e.g pCO_2 number of standard gases 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

Before reporting the data to, e.g. CDIAC, the data should be flagged, in the first instance by the analyst following the WOCE codes, and then by the project scientist following the SOCAT procedure: 2 (good), 3 (questionable), or 4 (bad).

Notes

- A significant part of the information required above is 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.

- "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.

- "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 gy); http://www.bipm.org/utils/common/documents/jcgm/JCGM_200_2008.pdf

ANNEX 5: Summary of recent, current, and future measurement activities in the Northeast Atlantic and Baltic Sea

Overview of work in OSPAR and HELCOM regions

Listed are measurements on larger scientific cruises and/or repeated sections, time-series stations, ships of opportunity (SOO), and moorings that the authors are currently aware of carrying out measurements of the carbonate system in the ICES maritime area. The list should be considered to be incomplete.

Many of these activities, if sustained on a longer term, could form the basis on which to build coordinated monitoring. Only some of the listed activities have long-term funding commitments (greater than five years) as part of national monitoring programmes. Monitoring ocean acidification in order to fulfil requirements of regional sea conventions and EU Directives would require long-term funding to be put in place.

Open Ocean – Arctic, Atlantic (OSPAR Regions I and V)

In the long term, the accumulation of CO_2 in ocean waters will determine what happens in shelf seas, as these are the main source waters for the shelf.

SOO (Ships of Opportunity). An effective basis for monitoring of surface waters exists in the SOO operations that are already being conducted for the study of air–sea CO_2 fluxes. These may, in future, be coordinated by ICOS. For the study of acidification, measurement of TA is being added to the work lines included in national OA measurement programmes.

At present, measurements at the surface are undertaken by:

1) UK (UEA): Portsmouth–Caribbean, with a time-series extending back to 1995/1996 and continuous from 2002; samples water, including waters on the northwestern European shelf, and the route crosses the Porcupine Abyssal Plain (PAP) mooring site, which provides data on deep mixing (partial CarboChange).

2) Norway – NO (UB): Copenhagen–Greenland route, sampling on this route began in 2002; provides data from OSPAR Regions I, II, and V (partial CarboChange).

3) Germany – D (IfM–GEOMAR): Europe/US east coast since 2002; currently Liverpool, UK to Halifax, Canada.

4) Norway – NO (NIVA): Tromsø–Spitsbergen, existing SOO line to which CO_2/TA measurements could be added to collect data in the Arctic; should be supported due to the potential sensitivity of Arctic waters to acidification.

Hydrography: Knowledge is needed of: (i) the variability of subsurface CO_2 accumulation and transport back to the surface as a result of variation in the depth of deep winter mixing; (ii) subsurface structures of water adjacent to the shelf that are source waters to the shelf; and (iii) the change in saturation state of aragonite and calcite. This requires cruises that are conducted on a regular basis, reoccupying the same stations at least once a year. Consideration needs to be given to sampling in deep waters in the location of potentially sensitive ecosystems, such as cold-water corals.

These types of hydrographic measurements are undertaken by:

1) Spain – ES (IEO): Winter and summer cruises in the Bay of Biscay. The Bay of Biscay is a system with a limited amount of advection in the deeper waters, making it a good location to study as changes tend to be due to local vertical processes rather than large-scale advection. (Spanish monitoring funded – CO_2 is not supported for regular work).

2) United Kingdom – UK (NERC): "Ellett Line" from Scottish west coast to Iceland (samples in OSPAR Regions III and I / V) surveys – annual surveys through the source waters for the North Sea (measurements of TA/DIC are

now supported for regular work by NERC; surface pCO_2 has been measured for 3 years by NOC).

3) Iceland – IS (MRI): Time-series measurements (quarterly) of carbon parameters in the Irminger and Iceland seas as a part of repeat hydrography network (OSPAR Region I).

4) Other relevant hydrographic cruises on the northern edge of the northwestern European shelf are conducted by Norwegian MRI and UK Marine Scotland. The Marine Institute and the National University of Ireland Galway (IE) have conducted surveys extending across Rockall Trough to west of Ireland.

Buoys/moorings: Buoys and moorings provide high-resolution data on both the air–sea transfer of CO_2 and deep-mixing-related transport.

At present, mooring measurements are undertaken by:

1) United Kingdom – UK (NOCS) Porcupine Abyssal Plain (PAP) observatory mooring (OSPAR Region V): pCO_2 measurements were made successfully at this site in 2005, and a newly designed mooring with measuring pCO_2 has been deployed since 2010. This site is important as the observations complement those made by the UEA and IfM–GEOMAR transatlantic SOOs.

2) UEA–SOO line (see above) is in an area of the North Atlantic where CO_2 uptake is known to be variable, but the cause of the variability has not yet been defined.

3) Norway – NO UB Ocean Weather Ship Station Mike site (OSPAR Region I): Time-series of information for CO_2 at this site is available up to 2009. A mooring has replaced the weather ship.

OSPAR Regions II, III, IV, and V

A key to understanding the impact of OA in open shelf seas is the identification of the transition between waters that are influenced by changes in the ocean source waters and those waters where local shelf sea processes are important, such as river inputs or interaction with seabed processes such as denitrification.

SOO: SOO-based observations provide the most cost-effective way of monitoring this transition and are being done in the North Sea using lines that are already instrumented for pCO_2 observations:

1) Norway – NO (UB) and the Netherlands – N (NIOZ): The SOO line Bergen–Amsterdam started taking pCO_2 measurements in 2006. Support has not been constant.

2) Germany – D (HZG) sensor systems for pCO2 and pH measurements in the North Sea (www.ferrybox.org).

3) France – F (CNRS, SBR): Roscoff–Plymouth – regular sample collection.

Hydrography: The Marine Institute/National University of Ireland Galway (IE) have undertaken surveys of shelf waters around Ireland, including an annual winter standard section on 53°N to the west of Ireland since 2008, and coastal transects since 2010. Detailed surveys of the greater North Sea have been undertaken by NIOZ in 2001/2002 (four seasons), and in the summers of 2005, 2008, and 2011. These provide considerable background knowledge of regional differences and the ability to esti-

mate fluxes to and from the North Sea. These are research exercises rather than the basis for a cost-effective monitoring programme. Since 2011, Cefas has collected discrete samples for analysis of TA/DIC on annual fishery stock assessment cruises in the North Sea, English Channel, Irish Sea, and Celtic Sea. In addition, underway pCO_2 systems have been installed by the UKOA (Ocean Acidification programme) on the Cefas RV "Endeavour" and the Marine Scotland RV "Scotia". For work largely in the southern North Sea, MUMM has fitted a FerryBox system, including pCO_2 and pH sensors, on the Belgian RV "Belgica".

Coastal and estuarine

Regions of freshwater influence (ROFI) are already areas of concern for marine monitoring because of high inputs of nutrients and enhanced levels of production and respiration. These waters need to be studied both from the point of view of their potential vulnerability to ocean acidification and because the pH is an important variable affecting the speciation of other components, such as ammonia and trace metals, making them more or less available to biota. In these areas, studies of acidification need to be fully integrated with existing monitoring that provides information on the processes driving changes in the carbonate system.

Monitoring should cover the range of coastal and estuarine areas, from relatively pristine regions with freshwater inputs that are low in both nutrients and organic carbon, such as those on the west coasts of Scotland, Norway, and Sweden, and the Baltic Sea, to the estuary of the Scheldt, which has high inputs of organic carbon, and the Thames and Severn, with high inputs of nutrients.

Collection and preservation of samples for the determination of carbonate species is a relatively simple task, so that potentially many existing coastal and estuarine monitoring programmes could be extended to include the collection of the required samples. The degree to which this can be done will depend on the capability and capacity of individual national groups to measure the samples. Additional funding commitments will need to be obtained from the government departments responsible for financing national monitoring programmes. Initially, this might be done by subcontracting the processing of samples to laboratories that already have a recognized capability in these measurements.

Existing work which provides examples of the approach needed include:

i)   United Kingdom – UK PML Stations E1 and L4, coastal sites, salinity >34. Existing monitoring on a monthly and weekly basis, respectively, in surface and subsurface waters. These sites represent relatively pristine waters. These also provide a historical context to changes in hydrography that can, in the case of the E1 site, be traced back over 100 years.

ii)   The Netherlands – NL RIKZ/Deltares, Dutch Coastal Grid; high flow.

iii) United Kingdom – UK NERC POL, Liverpool Bay; high load and production.

iv)   United Kingdom – UK Marine Scotland, Stonehaven, coastal site, salinity ~35. Existing monitoring on a weekly basis in surface and subsurface waters.

v)   Belgium – BE Scheldt Estuary; high nutrients and high organic input, low pH, high CO_2 water.

vi)   Other key areas are the rivers Gironde and Loire, which have high flows greater than that of the Rhine.

Baltic Sea (HELCOM)

There have been some ongoing activities in the Baltic Sea analysing parameters of the carbonate system (except direct pH measurements until now). These activities cover short-term experiments as well as measurements on SOO or platforms, which have been performed for periods of years, in some cases. Experiments have looked at methodological aspects. Most measurements have focused on seasonal and spatial variability and its relation to processes of the seasonal cycle. The results have been used to quantify or model some of these processes (e.g. plankton development, nitrogen fixation).

Work has been carried out on research cruises (e.g. Löffler *et al.*, 2012).

The Baltic Sea Research Institute (IOW) in Warnemünde have operated a SOO system measuring pCO_2 working with the Finnish Marine Institute (now SYKE) since the late 1990s (Thomas and Schneider, 1999; Rutgersson *et al.*, 2008). This route is from Helsinki to Travemünde. Since 2011 SHMI has operated a FerryBox pCO_2 system (General Oceanics) between Kemi and Gothenberg using the MV "Trans Carrier".

Additionally, several research projects are ongoing in the Baltic Sea aiming to improve the monitoring techniques and increase the understanding of the carbon system dynamics in this brackish marine environment.
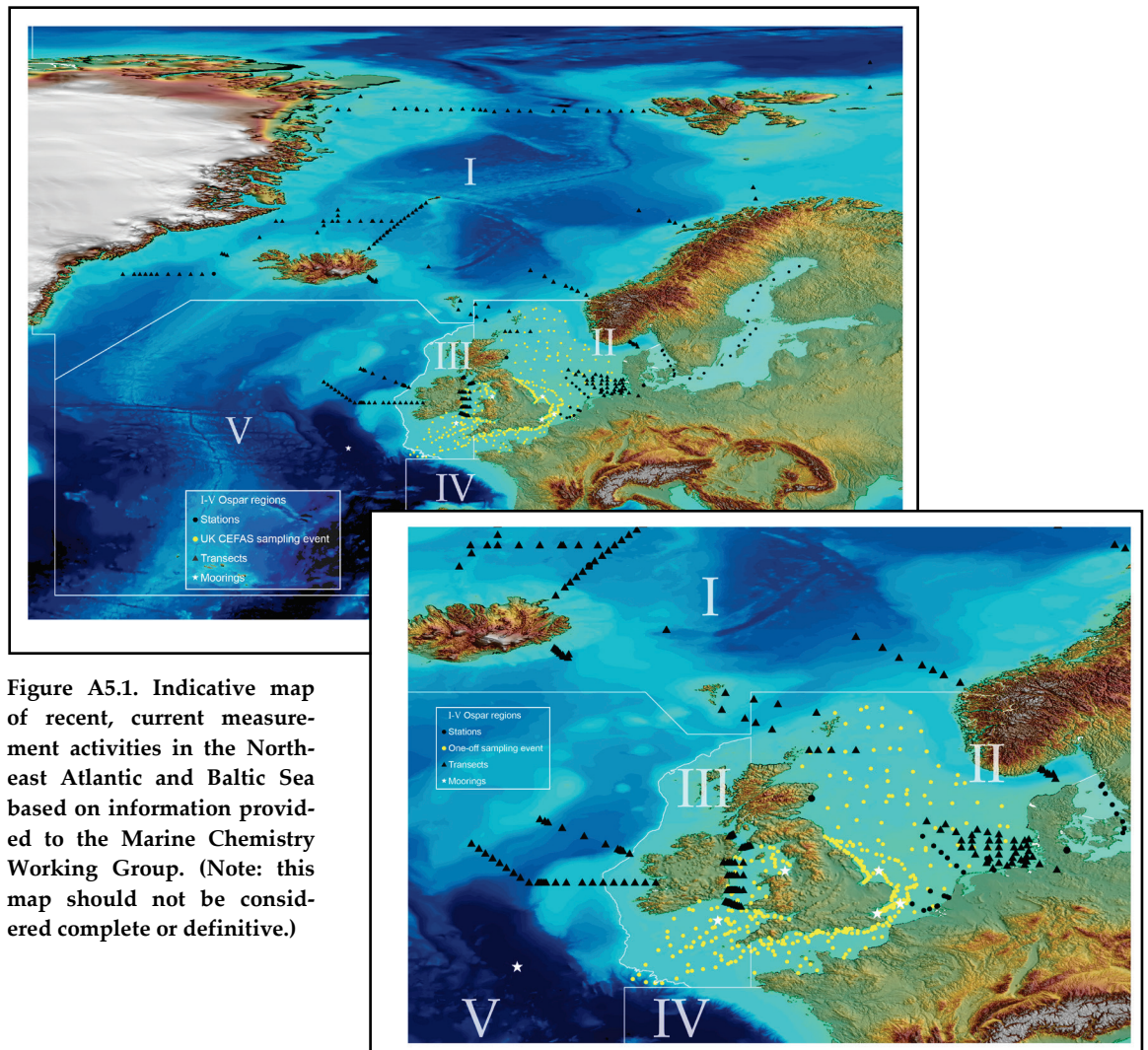

Figure A5.1. Indicative map of recent, current measurement activities in the Northeast Atlantic and Baltic Sea based on information provided to the Marine Chemistry Working Group. (Note: this map should not be considered complete or definitive.)

Table A5.1. Table of recent, current, and future measurement activities in the Northeast Atlantic and Baltic Sea (note: the table is indicative).

COUNTRY/INSTITUTE	PI	AREA	OSPAR/HELCOM REGION	PLATFORM/TYPE	PARAMETERS	PERIOD
Belgium / ULg	Borges	Southern Bight of North Sea	OSPAR II	RV "Belgica"	Underway pCO_2	2000–ongoing
Belgium / ULg	Borges	Ste Anna (Scheldt estuary)	OSPAR II	FS Fixed station, continuous	pCO_2	2002–ongoing
Belgium / ULg	Borges	Celtic Sea	OSPAR III	RV research cruises, OMEX-II, CCCC, PEACE	pCO_2, TA, pH	1997–1999, 2002, 2004, 2006–2009
Belgium / ULg	Wollast/Chou	Iberian upwelling system	OSPAR IV	RV research cruises (OMEX-II)	pCO_2, TA, pH	1997–1999
Belgium / ULg / NIOO		RV "Luctor" monitoring (Scheldt estuary)	OSPAR II	RV monthly cruises	pCO_2 TA	2008–ongoing
Estonia	Lipps	Helsinki–Tallinn		SOO	Underway pCO_2	2010
France		Plymouth–Roscoff (FERRYBOX Armorique)	OSPAR II	SOO	Underway pCO_2	from 2010
France		ASTAN (48°46'N 3°56'W)		FS Mooring	pCO_2?, pH	from 2009
France / IFREMER		MAREL Iroise (48°22'N 4°33'W)	OSPAR II	FS Mooring	pCO_2 , pH	from 2003
France / IFREMER		MAREL Carnot (50°44.71'N 1°34.18'W)	OSPAR II	FS Mooring	pH	from 2004
France / IFREMER		MAREL La Tremblade–Marennes Oléron	OSPAR II	FS Mooring	pH	
France / EDF		Cordemais (Loire Estuary)	OSPAR IV	FS Mooring	pH	from 2005
France / CNRS–INSU	Patrick Raimbault	MOOSE (DYFAMED, ANTARES, MOLA) – Mediterranean Sea	Barcelona Convention	Niskin bottles RV monthly or annually cruises	pH, DIC, carbon flow	from 1995 (DYFAMED) from 2003 (MOLA) from 2005 (ANTARES)
France	Benoit Sautour	SOMLIT – English Channel, Atlantic Ocean, and Mediterranean Sea	OSPAR II, IV Barcelona Convention	SO	pH	1984 – according to station

COUNTRY/INSTITUTE	PI	AREA	OSPAR/HELCOM REGION	PLATFORM/TYPE	PARAMETERS	PERIOD
France	Nathalie Simon	RESOMAR–PELAGOS – English Channel, Atlantic Ocean, and Mediterranean Sea	OSPAR II, IV Barcelona Convention	SO	pH	1987 – according to station
France / AAMP-PNMI	Patrick Pouline Pascale-Emmanuelle Lapernat	PNMI – Iroise Sea	OSPAR II	SO RV cruises 3/year	pH	from 2010
France		RNF (Seine estuary, Bouches de Bonifaccio)	OSPAR II Barcelona Convention	Seine : monthly measure Bonifaccio : RV cruises 4/year during summer	pH	
France / GIP Seine – Aval	Céline Dégremont Loïc Guézennec	SYNAPSES (Seine Estuary)	OSPAR II	FS Mooring	pH	from 2011
France / LOCEAN	Lefevre	France–French Guyana	?	SOO (MN Colibri) ~6/year	Underway pCO$_2$	from 2006
France / LOCEAN	Lefevre	France–Brazil	?	SOO (Monte Olivia) ~6/year	Underway pCO$_2$	from 2007
Germany		Irregular		RV "Polarstern"	Underway pCO$_2$	
Germany / AWI?		Nordic seas (Greenland Sea?)	OSPAR I	RV research cruises	?	?
Germany / IFM–GEOMAR		Boknis Eck (54.52°N 10.03°E)		FS Time-series station	?	?
Germany / IOW	Schneider, now Reider	Helsinki–Lübeck		SOO	Underway pCO$_2$	
Germany / IFM–GEOMAR Kiel	Koertzinger/Wallace	Liverpool–Halifax	OSPAR V	SOO (A. Companion)	two per five weeks Underway pCO$_2$	2005
Iceland / MRI	Olafsson/Olafsdottir	Iceland Sea and Irminger Sea	OSPAR I	FS Single time-series stations	DIC, discrete pCO$_2$, pH	from 1983
Iceland / MRI	Olafsson/Olafsdottir	Icelandic waters and the Iceland Sea	OSPAR I	RV "Bjarni Saemundsson"	Underway pCO$_2$	from 1995

COUNTRY/INSTITUTE	PI	AREA	OSPAR/HELCOM REGION	PLATFORM/TYPE	PARAMETERS	PERIOD
Ireland / NUI Galway & MI	Ward	Irish Shelf and offshelf	OSPAR III and V	RV "Celtic Explorer"	Underway pCO_2	2009–2011
Ireland / NUI Galway & MI	O'Dowd/Ward	Mace Head Coastal Atmospheric research station	OSPAR III	FS Buoy	pCO_2	2008–2009
Ireland / NUIG & MI	McGovern/Cave	Irish Shelf and offshelf	OSPAR III and V	RV research cruises	TA, DIC	from 2008
Ireland / NUIG & MI	McGovern/Cave	Rockall Trough Winter Transects	OSPAR V	RV "Celtic Explorer"	TA, DIC	from 2008
Netherlands / NIOZ	de Baar	Basinwide North Sea	OSPAR II	RV research cruises	DIC, pCO_2 (TA)	2001, 2005, 2008, 2011
Netherlands / NIOZ		Southern Bight of the North Sea/German Bight	OSPAR II	SOO? JetSet (53°N 4°46'E) Weekly time-series	Underway DIC, TA?	?
Netherlands	Houben	North Sea	OSPAR II	Research vessel	pH	ongoing
Norway/IMR	Chierici	Torungen–Hirtshals	North Sea	IMR research vessels	water column DIC, TA, nutrients	start 2010–2012, 2–4 times annually: 2013–2016: 1/year
Norway/IMR	Chierici	Gimsøy–NW	Norwegian Sea	IMR research vessels	water column DIC, TA, nutrients	start 2010–2012, 2–4 times annually: 2013–2016: 1/year
Norway/IMR	Chierici	Svinøy–NW	Norwegian Sea	IMR research vessels	water column DIC, TA, nutrients	start 2010–2012, 2–4 times annually: 2013–2016: 1/year
Norway/IMR	Chierici	Fugløya–Bjørnøya	Barents Sea (SW)	IMR research vessels	water column DIC, TA, nutrients	start 2010–2012, 2–4 times annually: 2013–2016: 1/year
Norway/IMR	Chierici	Bjørnøya–Sørkapp	Barents Sea (SW)	IMR research vessels	water column DIC, TA, nutrients	start 2013 to 2016: 1/year

COUNTRY/INSTITUTE	PI	AREA	OSPAR/HELCOM REGION	PLATFORM/TYPE	PARAMETERS	PERIOD
Norway/ IMR	Chierici	Vardø–N	Barents Sea (NE)	IMR research vessels	water column DIC, TA, nutrients	start 2010–2012, 2–4 times annually: 2013–2016: 1/year
Norway/ IMR and FRAM centre (OA Flagship)	Chierici/Fransson (NPI)	Fram Strait	Arctic Ocean/Greenland Sea	RV "Lance"	water column DIC, TA, nutrients	start 2011 ongoing
Norway/ IMR and FRAM centre (OA Flagship)	Chierici/Fransson (NPI)	N of Svalbard to Polar Basin, 81–82°N 30°E	Arctic Ocean	RV "Lance"	water column DIC, TA, nutrients	start 2012 ongoing. 1/year
Norway / UiB and Bjerknes	Johannessen	75°N transect	OSPAR I	RV research cruises	DIC, TA	2003, 2006, 2008?
Norway / UiB and Bjerknes	Skjelvan/Johannessen	OWS M	OSPAR I	FS WS Monthly profiles	DIC, TA	2001–2009
Norway / UiB and Bjerknes	Skjelvan/Johannessen	OWS M	OSPAR I	FS WS continuous	pCO_2	2005–2009
Norway / UiB and Bjerknes	Skjelvan/Johannessen	OWS M	OSPAR I	FS Buoy continuous	pCO_2	2011
Norway / UiB and Bjerknes	Johannessen/Olsen/ Lauvset	Nordic seas	OSPAR I	RV "G. O. Sars"	Underway pCO_2	ongoing
Norway / UiB and Bjerknes	Johannessen/Olsen/ Omar	Aarhus–Nuuk		SOO (Nuka Arctica)	Underway pCO_2	from 2005
Norway / UiB and Bjerknes	Johannessen/Omar	Bergen–Amsterdam	OSPAR II	SOO / weekly	Underway pCO_2	2005–2009
Norway / UiB and Bjerknes	Johannessen/Omar	North Sea	Sleipner	RV "G. O. Sars"	Underway pCO_2	June 2012
Norway / UiB and Bjerknes	Johannessen/Omar	North Sea	Sleipner	RV "G. O. Sars"	TA, DIC	June 2012

Country/Institute	PI	Area	OSPAR/Helcom Region	Platform/Type	Parameters	Period
Norway / NIVA	Sorensen	line up to Svalbard	Ferry-box	SOO	Underway pCO_2	2012
Spain / IIM	Rios/Perez	OVIDE, Iberian Peninsula–Greenland	OSPAR V	RV research cruise	Underway pCO_2, pH, TA	2002–2012
Spain / IIM	Rios/Perez	Spain–Antarctic	OSPAR V	SOO	Underway pCO_2.2	2000–2009
Spain / ULPGC	Davila	English Channel–Durban	OSPAR V	SOO various ships	Underway pCO_2	2005
Spain / ULPGC	Davila	ESTOC Station	Canary Islands	FS Time-series	pCO_2, TA, pH	from 1996
Spain / ICMAN	Huertas	Gulf of Cadiz	OSPAR IV	RV P3A2 Cruises	pH, TA	2003–2008
Spain / ICMAN/IIM/IEO	Huertas	Strait of Gibraltar (35.862°N 5.974°W)	OSPAR IV	FS Mooring	pCO_2, pH	from 2011
Spain / ICMAN/IIM/IEO	Huertas	GIFT (35.862°N 5.974°W; 35.957°N 5.742°W; 35.985°N 5.368°W)	OSPAR IV	FS Time-series stations	Water column pH, TA	from 2005
Spain / IEO / IIM	Rios	Cantabric Sea and west coast	OSPAR IV	RV "Vaclan" cruises	Underway pCO_2, pH, TA	2005, 2007, 2009
Spain / IEO–Gijon	Scharek	Cantabric Sea	OSPAR IV	FS Time-series (three stations)	pH, TA	2010–2011
Sweden / SMHI		Swedish waters		RV Monitoring cruises?	TA, pH	?
Sweden / SMHI	Karlson	Kemi–Gothenburg Baltic		SOO	Underway pCO_2	2010
Sweden / U Gothenberg		Arctic Ocean	OSPAR I	RV research cruises	DIC, TA, pH	2005, ?
UK / Cefas		Liverpool Bay	OSPAR III	Buoy, DEFRA tests	pCO_2	2010
UK / Cefas	Greenwood/Pearce	Irish Sea and Celtic Sea	OSPAR III	RV research cruises	DIC, TA, and underway pCO_2	2011
UK / MSS	Walsham	Stonehaven	Coastal site	Time-series	TA/DIC	from 2008
UK / MSS	Walsham	Faroe Shetland Channel, Atlantic inflow to North Sea	OSPAR I and II	RV research cruise, May and December	TA/DIC, hydrography	from 2012

COUNTRY/INSTITUTE	PI	AREA	OSPAR/HELCOM REGION	PLATFORM/TYPE	PARAMETERS	PERIOD
UK / MSS/NOC	Walsham		OSPAR I, II, III, and V	RV "Scotia"		
UK / NOC/UEA		26°N line	?	RV	?	?
UK / NOCS	Hydes	English Channel	OSPAR II	SOO (Pride of Bilbao)	DIC, TA	2005–2010
UK / NOCS	Lampitt	Porcupine Abyssal Plain (49°N 16.5°W)	?	RV Mooring	pCO_2	? –
UK / NOCS?	Hydes	Portsmouth–Spain	OSPAR II and IV	SOO (Pride of BIlbao), 2/week	Underway pCO_2	2005
UK / PML	Mountford/Kitidis	Holyhead–Dublin	OSPAR III	RV "Prince Madog"	Underway pCO_2	2006–2009
UK / PML	Mountford/Kitidis	Irish Sea Coastal Observatory	OSPAR III ?	RV (quasi-monthly)	Underway pCO_2 Transects (Prince Madog)	2007–2010
UK / UEA	Schuster	Portsmouth (UK) Windward Islands–	?	SOO (Santa Lucia/Santa Maria)	Underway pCO_2	Monthly from 2002
UK / MSS/NOC	Walsham	Stonehaven	OSPAR II	FS Weekly single time-series station	TA/DIC	from 2008
UK / PML	Mountford/Kitidis	English Channel (E1, L4)	OSPAR II	Weekly (L4) and monthly (E1)	TA/DIC	from 2008
UK / PML	Mountford/Kitidis	English Channel (E1, L4)	OSPAR II	Weekly (L4) and monthly (E1)	Underway pCO_2 Transects (Plymouth Quest)	
UK "Ellett Line"	Reid/Hartman	Greenland–UK	OSPAR I and III	Scientific cruise	Hydrography	2008, 2010, 2011
UK / Cefas	Greenwood/Pearce	Basinwide North Sea and English Channel	OSPAR II	RV research cruises, RV "Endeavour"	DIC, TA and underway pCO_2	from 2011
USA / France	Metzel	Charleston–Reykjavik	?	SOO (Reykjafoss)	Underway pCO_2	From 2005

This table should be considered indicative. It is based on information collated by ICES Marine Chemistry Working Group and the Joint OSPAR–ICES Study Group on Ocean Acidification and does not purport to be definitive or complete.

ANNEX 6: Links to related projects and sources of equipment

Related projects

Design of a long-term monitoring programme needs to take into account what can be learned from previous work and current and planned activities in the OSPAR area. It further needs to take into account relevant international research and observation programmes.

Relevant former, ongoing, and planned projects, networks, and organizations include:

Key international coordinating activities are the:

- IOCCP: The International Ocean Carbon Coordination Project is a communication and coordination service for the ocean carbon ty www.ioccp.org.

- CDIAC: The Carbon Dioxide Information Analysis Center is the primary climate-change data and information analysis centre of the US Department of Energy (DOE). CDIAC is located at DOE's Oak Ridge National Laboratory (ORNL) and includes the World Data Center for Atmospheric Trace Gases. http://cdiac.ornl.gov/

Other activities:

- BIOACID: Biological Impacts of Ocean Acidification (2009–); www.bioacid.de/

- BOOM: Biodiversity of Open Ocean Microcalcifiers (2006–2009); www.sb-roscoff.fr/BOOM/

- CARBOCHANGE: Changes in carbon uptake and emissions by oceans in a changing climate (2011–2015); http://carbochange.b.uib.no/

- CARBON–OPS: UK underway pCO_2 observations from research vessels (2007–2009); www.bodc.ac.uk/carbon-ops

- CARBOOCEAN: IP – Marine carbon sources and sinks assessment (2005–2009); www.carboocean.org

- CARINA: Carbon dioxide in the Atlantic Ocean data-synthesis ject; http://cdiac.ornl.gov/oceans/CARINA/about_carina.html

- CLIVAR: Climate variability and predictability; www.clivar.org

- COCOS: Coordination Action Carbon Observing System (2009–2011); http://www.cocos-carbon.org/

- EPOCA: European Project on Ocean Acidification (2008–2012); www.epoca-project.eu

- EUROSITES: is a FP7 Collaborative Project forming an integrated European network of nine deep-ocean (>1000 m) ries; http://www.eurosites.info/

- FERRYBOX: www.ferrybox.org

- GLODAP: Global Ocean Data Analysis ject; http://cdiac.ornl.gov/oceans/glodap/index.html

- GOOS: Global Ocean Observing System; http://www.ioc-goos.org/

- ICOS: Integrated Carbon Observation System; http://www.icos-infrastructure.eu

- IMBER: Integrated Marine Biogeochemistry and Ecosystem Research Project; www.imber.info/

- IPCC: Intergovernmental Panel on Climate Change; http://ipcc.ch/

- MEECE: Marine Ecosystem Evolution in a Changing ment; www.meece.eu/

- OCB: US Ocean Carbon and Biogeochemistry; www.us-ocb.org/

- PEACE: Role of Pelagic Calcification and Export of Carbonate Production in Climate Change (2007–2009); www.co2.ulg.ac.be/peace/

- PEECE: Pelagic Ecosystem CO_2 Enrichment Study (2001–2005); www.peece.ifm-geomar.de

- SCOR: Scientific Committee on Oceanic Research; http://www.scor-int.org/

- SOCAT: Surface Ocean CO_2 Atlas; www.socat.info/

- SMHI–UGOT: Ocean acidification project 2010-2012; www.smhi.se

- SOLAS: Surface Ocean Lower Atmosphere Study; www.solas-int.org

- SOPRAN: Surface Ocean Processes in the Anthropocene (2007–2012); www.sopran.pangaea.de/

Sources of equipment and ongoing developments

The following constitutes a probably incomplete survey of commercially available instrumentation. It is known that a number of laboratories are working on the development of underway sensors, particularly for pH. See so www.ioccp.org/Sensors.html.

pCO_2 on moorings

Measurements of pCO_2 on mooring have been made less widely than on SOOs, and the technology is less mature than for underway systems. Particular issues to be considered for mooring applications are long-term stability of sensors, biofouling, and power consumption. Measurements may be made with high temporal resolution from such platforms, but have low spatial resolution. ACT carried out evaluation studies in 2010 (Tamburi *et al.*, 2011).

- Pro Oceanus (http://www.pro-oceanus.com/co2pro.html), taking part in the Alliance for Coastal Technology evaluation of i*n situ* pCO_2 analysers (http://www.act-us.info); accuracy ±1 ppm CO_2, precision ±0.01 ppm CO_2.

- Battelle (NOAA) http://www.battelle.org/seaology/; accuracy 0.01 ppm CO_2, precision ~1 ppm CO_2. Contros (www.contros.eu); accuracy < 10 ppm CO_2.

- SAMI2 – CO_2 (http://www.sunburstsensors.com/), taking part in the Alliance for Coastal Technology evaluation of *in situ* pCO_2 analysers (http://www.act-us.info/evaluation/rft.php); accuracy ±3 ppm CO_2, precision < 1 ppm CO_2, long-term drift < 1 ppm CO_2 over 6 months.

- CARIOCA (http://www.dt.insu.cnrs.fr/carioca/carioca.php); accuracy ±3 ppm CO_2, precision ±1 ppm CO_2.

- Aanderaa has a pCO_2 optode device which is at the beta evaluation stage.

pCO_2 on ships

pCO_2 measurements have been made on vessels since the mid-1990s, and the technology is more mature than that for *in situ* measurement systems. A mixture of commercial and custom-made systems exist. Measurements made on regular transects, such as from ferries and shipping lines, allow a system to be characterized over time. Measurements made from research vessels may provide wider spatial resolution, but lower temporal resolution.

The systems that are available commercially are based on infrared measurements, while systems using cavity ring-down detectors are currently being tested (Friedrichs *et al.*, 2011).

- Pro OCEANUS (http://www.pro-oceanus.com); accuracy ±1 ppm CO_2, precision ±0.01 ppm CO_2.

- General Oceanics (http://www.generaloceanics.com/home.php?cat=69); accuracy ±1 ppm CO_2, precision 0.01 ppm CO_2.

- Dartcom–PML (http://www.bodc.ac.uk/carbonops/instrumentation/telemetry_and_pco2/); accuracy ±1 ppm CO_2, precision (LI–COR) 0.01 ppm, repeatability 0.2 ppm CO_2.

- Kimoto air marine CO_2 system (Japan) (http://www.kimoto-electric.co.jp/english/product/ocean/co2.html); precision ±0.3 ppm CO_2, minimum detectable 0.1 ppm CO_2.

- Contros (www.contros.eu); accuracy < 10 ppm CO_2. SAMI2 – CO_2 (http://www.sunburstsensors.com/); accuracy ±3 ppm CO_2, precision < ±1 ppm CO_2, long-term drift < 1 ppm CO_2 over 6 months.

- Apollo SciTech (http://www.apolloscitech.com/PCO2.htm); repeatability better than ±1 ppm CO_2.

- SubCTech (http://subctech.eu/products/); accuracy ±3 ppm CO_2, resolution < 1 ppm CO_2.

pH

- SAMI2 – pH (http://www.sunburstsensors.com/) designed for mooring and underway, measured on the total hydrogen ion scale precision ±0.001 pH, accuracy ±0.003 pH, long-term drift 0.001 pH over 6 months.

- Satlantic SeaFET (http://www.satlantic.com/seafet) in beta version (Martz *et al.*, 2011).

Author contact information

David J. Hydes
National Oceanography Centre Southampton
European Way
Southampton
SO14 3ZH, UK
david.hydes@noc.ac.uk

Evin McGovern
Marine Institute
Marine Environment and Food Safety Services
Rinville
Oranmore, Galway, Ireland
evin.mcgovern@marine.ie

Pamela Walsham
Marine Scotland Science
Marine Laboratory
375 Victoria Road, Aberdeen
AB11 9DB, UK
Pamela.Walsham@scotland.gsi.gov.uk

Alberto V. Borges
University of Liège
Interfacultary Center for Marine Research
(MARE)
Chemical Oceanography Unit
Institut de Physique (B5)
Allée du Août, 17
B-4000 Liège, Belgium
alberto.borges@ulg.ac.be

Carlos Borges
Instituto Hidrográfico
Divisão de Química e Poluição de Meio
Marinho
Rua das Trinas, 49
1249-093 Lisbon, Portugal
carlosborges@hidrografico.pt

Naomi Greenwood
Centre for Environment, Fisheries and Aquaculture Science (Cefas)
Lowestoft Laboratory
Pakefield Road, Lowestoft, Suffolk
NR33 0HT, UK
naomi.greenwood@cefas.co.uk

Susan E. Hartman
National Oceanography Centre Southampton
European Way
Southampton
SO14 3ZH, UK
s.hartman@noc.ac.uk

Caroline Kivimae
National Oceanography Centre Southampton
European Way
Southampton
SO14 3ZH, UK
anck@noc.ac.uk

Klaus Nagel
Leibniz–Institut für Ostseeforschung Warnemünde
Sektion Meereschemie
Seestr. 15
18119 Rostock–Warnemünde, Germany
klaus.nagel@io-warnemuende.de

Solveig Olafsdottir
Marine Research Institute
Skulagata 4
121 Reykjavik, Iceland
solveig@hafro.is

David Pearce
Centre for Environment, Fisheries and Aquaculture Science (Cefas),
Pakefield Road, Lowestoft
Suffolk
NR33 0HT, UK
david.pearce@cefas.co.uk

Carmen Rodriguez
Instituto Español de Oceanografía
Centro Oceanográfico de Santander
Apdo. 240
39080 Santander, Spain
carmen@st.ieo.es

Elisabeth Sahlsten
Swedish Agency for Marine and Water
Management
Gullbergs Strandgata 15
SE-404 39 Göteborg, Sweden
elisabeth.sahlsten@havochvatten.se

Lynda Webster
Marine Scotland Science
Marine Laboratory
375 Victoria Road
Aberdeen
AB11 9DB, UK
lynda.webster@scotland.gsi.gov.uk

Acronyms and abbreviations

13C	carbon 13 isotope
18O	oxygen 18 isotope
ACT	Alliance for Coastal Technologies
Ag / AgCl	silver / silver chloride
a_i	activity of species i
AMP	2-amino-2-methyl-1-propanol
$B(OH)_4^-$	tetrahydroxyborate
CARBOCHANGE	EU FP7 Changes in carbon uptake and emissions by oceans in a changing climate (2011–2015); http://carbochange.b.uib.no/
CARBOOCEAN	EU FP6 CARBOOCEAN: Integrated project – Marine carbon sources and sinks assessment (2005–2009); www.carboocean.org
CCC	Carbonate Chemistry Computation
CCD	charge-coupled device
CCGG	NOAA Carbon Cycle Greenhouse Group
CDIAC	Carbon Dioxide Information Analysis Center
CFCs	chlorofluorocarbons
CH_4	methane
CO_2	carbon dioxide
COCOS	Coordination Action Carbon Observing System
CO_3^{2-}	carbonate ion
CPs	Contracting Parties
CTD	conductivity–temperature–depth probe
DEFRA	UK Department of Environment Food and Rural Affairs
DIC	dissolved inorganic carbon
DOI	digital object identifier
EC	European Commission
EPOCA	European Project on Ocean Acidification (2008–2012); www.epoca-project.eu
ESSD	Earth System Science Data
ESTOC	European Station for Time Series in the Ocean
$f CO_2$	fugacity of carbon dioxide
F^-	fluoride ion

GT C year^{-1}	gigatonne carbon per year
H$^+$	hydrogen ion
H$_2$CO$_3$	carbonic acid
H$_3$O$^+$	hydronium ion
HCO$_3$$^-$	bicarbonate ion
HELCOM	Helsinki Commission
HF	hydrofluoric acid
HPTS	8-hydroxypyrene-1,3,6-trisulfonic acid
HSO$_4$	hydrogen sulphate
ICOS	Integrated Carbon Observation System
IEO	Instituto Español de Oceanográfico
IOCCP	International Ocean Carbon Coordination Programme
ISFET	Ion-Selective Field Effect Transitions
JAMP	Joint Assessment and Monitoring Programme
JAMSTEC	Japan Agency for Marine-Earth Science and Technology
K	Units Kelvin
KCl	potassium chloride
LSID	Life Science Identifier
MBARI	Monterey Bay Aquarium Research Institute
MCCIP	Marine Climate Change Impacts Partnership (UK)
MCWG	Marine Chemistry Working Group (ICES)
MSFD	EU's Marine Strategy Framework Directive
mV	millivolts
NA	North Atlantic
NBS	National Bureau of Standards (USA)
NERC	National Environment Research Council UK
NIOZ	Royal Netherlands Institute for Sea Research
nm	nanometre
NOAA	National Oceanic and Atmospheric Administration
NOCS	National Oceanography Centre, Southampton
NSF	National Science Foundation (USA)
OA	ocean acidification
OH$^-$	hydroxide ion

OSPAR	OSPAR Convention 1992 (formerly Oslo and Paris Conventions)
PAP	Porcupine Abyssal Plain
pCO_2	partial pressure of carbon dioxide
pH	log scale measure of the acidity of a liquid
pHCF	free hydrogen ion scale
PI	principal investigator
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control
RID	Riverine Input and Direct Discharges
RM	reference material
SO_4^{2-}	sulfate ion
SOCAT	Surface Ocean CO_2 Atlas
SOO	Ships of Opportunity
SOP	standard operating procedure
SWS	seawater scale (pH)
TA	total alkalinity, also denoted AT
URN	Uniform Resource Name
UUID	Universally Unique Identifiers
VINDTA	Versatile Instrument for the Determination of Titration Alkalinity
WMO	World Meteorological Organization
WOCE	World Ocean Circulation Experiment
γi	activity coefficient
Δ	change in…
μatm year^{-1}	microatmosphere per year
μ_i	chemical potential of species i
μi°	chemical potential of species i in standard state
μm	micrometre = 10^{-6} metre
μmol	micromole = 10^{-6} mole