Chemical aspects of ocean acidification monitoring in the ICES marine area
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# Contents

Acknowledgements .......................................................................................................................... 1

Executive summary .......................................................................................................................... 2

1 Background information and monitoring objectives .............................................................. 4
   1.1 Scope of the report ........................................................................................................... 4
   1.2 Ocean acidification ....................................................................................................... 5
   1.3 Carbonate system components ..................................................................................... 7
   1.4 Definition of pH and pH scales .................................................................................... 8

2 Variability of the carbonate system across the OSPAR area .............................................. 11

3 Monitoring framework ............................................................................................................. 16
   3.1 Objectives of chemical monitoring ............................................................................ 16
   3.2 Sampling strategies and target areas .......................................................................... 17
   3.3 Required information .................................................................................................. 18
   3.4 Minimum dataset ......................................................................................................... 18
   3.5 Sampling and sampling platforms .............................................................................. 20

4 Measurement methods and quality assurance ...................................................................... 22
   4.1 Procedures ...................................................................................................................... 22
   4.2 Calibration and quality control ..................................................................................... 24
       4.2.1 DIC and TA ........................................................................................................ 24
       4.2.2 pCO2 ................................................................................................................ 25
       4.2.3 pH ...................................................................................................................... 25

5 Data reporting and assessment ............................................................................................... 26
   5.1 Data reporting ............................................................................................................... 26
   5.2 Metadata requirements ................................................................................................. 26
   5.3 Specific metadata requirements for seawater carbonate chemistry and ancillary parameters ......................................................................................................................... 27
   5.4 Assessment ..................................................................................................................... 28

6 Findings and recommendations ............................................................................................... 30
   6.1 Parameters, protocols, and quality assurance ............................................................. 30
   6.2 Approach and coverage for monitoring ........................................................................ 31
   6.3 Reporting ......................................................................................................................... 31

7 References for main text and annexes (except Annex 3) ........................................................ 32

ANNEX 1: Direct measurement of pH ....................................................................................... 42

ANNEX 2: Possible sources of error related to calculations ..................................................... 47

ANNEX 3: Draft OSPAR Monitoring Guidelines for Chemical Aspects of Ocean Acidification .......................................................................................................................... 51
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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 CO₂ 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), pCO₂, 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 pCO₂ 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 (CO₂) 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 CO₂ (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\textsubscript{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\textsubscript{2} (carbon dioxide) and the resulting net oceanic CO\textsubscript{2} uptake (Figure 1.2).

Ocean acidification and potential climate change from the increase in concentration of the greenhouse gas CO\textsubscript{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\textsubscript{2} between the atmosphere and the ocean is governed by the difference in fugacity of CO\textsubscript{2} between the two phases and the transfer velocity. It is influenced by a number of conditions, particularly water temperature and windspeed. CO\textsubscript{2} reacts with water to form carbonic acid (H\textsubscript{2}CO\textsubscript{3}). H\textsubscript{2}CO\textsubscript{3} dissociates to carbonate (CO\textsubscript{3}\textsuperscript{2−}), bicarbonate (HCO\textsubscript{3}−) and hydrogen ions (H\textsuperscript{+}). CO\textsubscript{3}\textsuperscript{2−} reacts further with the H\textsuperscript{+} to form additional HCO\textsubscript{3}− ions. The total of dissolved inorganic carbon (DIC) in seawater is the sum of about ~90% HCO\textsubscript{3}−, ~9% CO\textsubscript{3}2−, and ~1% as dissolved CO\textsubscript{2} and H\textsubscript{2}CO\textsubscript{3}. As the concentration of CO\textsubscript{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\textsubscript{2} in the water as in the atmosphere; concentrations of HCO\textsubscript{3}− and CO\textsubscript{2} will increase while concentrations of CO\textsubscript{3}2− and pH will decrease (Zeebe and Wolf-Gladrow, 2001). This reduction in concentration of CO\textsubscript{3}2− will result in lowered saturation states of CaCO\textsubscript{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\textsubscript{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\textsubscript{2} in the atmosphere are small. Consequently, local differences in conditions in the ocean are important in determining the rate of uptake of CO\textsubscript{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\textsuperscript{−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.
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)** = \([HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+]\) plus other minor components.

**Total dissolved inorganic CO$_2$ (DIC)** = the sum of the concentrations of dissolved CO$_2$ (CO$_2$ + H$_2$CO$_3$) 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 solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid.

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

where $K_o$ (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).

\[
CO_2 + 2H_2O = H_3O^+ + HCO_3^- \hspace{1cm} 1
\]
\[
HCO_3^- + H_2O = H_3O^+ + CO_3^{2-} \hspace{1cm} 2
\]

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 four different definitions of the pH scale [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:

$$\mu_i - \mu_i^\circ = RT \ln (a_i) = RT \ln (c_i \gamma_i)$$

where $\mu_i$ 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 $\gamma_i$ 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:

$$\text{pH} = -\log_{10} (a_{H^+})$$

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):

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

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

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)]:

$$a_{H^+}(T) = [H^+] + [\text{HSO}_4^-] = [H^+] \left[ 1 + K_{\text{HSO}_4} [\text{SO}_4^{2-}]_{\text{tot}} \right]$$

where

$$K_{\text{HSO}_4} = \frac{[\text{HSO}_4^-] / [H^+][\text{SO}_4^{2-}]}{}$$
\[ pH(T) = -\log_{10}[a_{\text{H}^+}(T)] \quad (6) \]

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 \([pH\text{(SWS)}]\):

\[ a_{\text{H}^+}(\text{SWS}) = [\text{H}^+] + [\text{HSO}_4^-] + [\text{HF}] \]
\[ = [\text{H}^+] (1 + K_{\text{HSO}_4^-}[\text{SO}_4^{\text{tot}}] + K_{\text{HF}}[\text{F}^{\text{tot}}]) \quad (7) \]

where

\[ K_{\text{HF}} = [\text{HF}]/([\text{H}^+][\text{F}^-]) \]
\[ pH(\text{SWS}) = -\log_{10}[a_{\text{H}^+}(\text{SWS})] \quad (8) \]

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.

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**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 Caldera 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 anthropogenic 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).
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 pCO₂ data. In all OSPAR regions, the reported rate of increase in pCO₂ in seawater is equivalent to or higher than the increase in atmospheric CO₂ (Table 2.3). The fact that pCO₂ 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).

<table>
<thead>
<tr>
<th>OSPAR REGION</th>
<th>pCO2 (µATM)</th>
<th>TA (µMOL KG⁻¹)</th>
<th>pH</th>
<th>DIC (µMOL KG⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔpCO2</td>
<td>ΔTA</td>
<td>ΔpCO2</td>
<td>ΔTA</td>
</tr>
<tr>
<td>Amplitude of daily variations (maximum, i.e. most productive period)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>20 a</td>
<td>-0</td>
<td>0.020</td>
<td>~0</td>
</tr>
<tr>
<td>II</td>
<td>20 b</td>
<td>-0</td>
<td>0.020</td>
<td>~0</td>
</tr>
<tr>
<td>III</td>
<td>15 b</td>
<td>-0</td>
<td>0.015</td>
<td>~0</td>
</tr>
<tr>
<td>IV</td>
<td>15 b</td>
<td>-0</td>
<td>0.015</td>
<td>~0</td>
</tr>
<tr>
<td>V</td>
<td>20 xc</td>
<td>-0</td>
<td>0.020</td>
<td>~0</td>
</tr>
</tbody>
</table>

Amplitude of seasonal variations |
| I            | 45 d        | 20 b           | 0.047 | 0.003 | 23 | 17 |
| II           | 220 e       | 60 i           | 0.309 | 0.010 | 175 | 52 |
| III          | 70 b        | 50 h           | 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 i         | ?              | 0.005 | ? | 2  | ? |
| II           | 150 e       | ?              | 0.183 | ? | 96 | ? |
| III          | 50 k        | 20 h           | 0.052 | 0.003 | 25 | 17 |
| IV           | 50 k        | 10 k           | 0.052 | 0.002 | 25 | 9 |
| V            | 20 m        | ?              | 0.020 | ? | 10 | ? |

* 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 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).

<table>
<thead>
<tr>
<th>OSPAR REGION</th>
<th>pCO₂ (µATM 100 KM⁻¹)</th>
<th>TA (µMOL KG⁻¹ 100 KM⁻¹)</th>
<th>ΔpCO₂</th>
<th>ΔTA</th>
<th>ΔpCO₂</th>
<th>ΔTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2±</td>
<td>8±</td>
<td>0.002</td>
<td>0.001</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>II</td>
<td>20±b,c,d</td>
<td>20b</td>
<td>0.020</td>
<td>0.003</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>III</td>
<td>10b</td>
<td>5b</td>
<td>0.010</td>
<td>0.001</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>IV</td>
<td>10b to 50e</td>
<td>5e</td>
<td>0.010–0.052</td>
<td>0.001</td>
<td>5–26</td>
<td>4</td>
</tr>
<tr>
<td>V</td>
<td>2f</td>
<td>5f</td>
<td>0.002</td>
<td>0.001</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

* Olsen et al. (2008); b Frankignouille and Borges (2001b); c Thomas et al. (2004); d Omar et al. (2010); e Borges and Frankignouille (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 CO₂ (pCO₂) 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 pCO₂ assuming a constant total alkalinity.

<table>
<thead>
<tr>
<th>OSPAR REGION</th>
<th>pCO₂ (µATM YEAR⁻¹)</th>
<th>pH (PH UNITS YEAR⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1.5–3.0 a</td>
<td>−0.0015 to −0.0030</td>
</tr>
<tr>
<td>I</td>
<td>2.1 ± 0.2 d</td>
<td>−0.0024 ± 0.002</td>
</tr>
<tr>
<td>II</td>
<td>4.4 b</td>
<td>−0.0044</td>
</tr>
<tr>
<td>III</td>
<td>3.2 c</td>
<td>−0.0032</td>
</tr>
<tr>
<td>IV</td>
<td>3.2 c</td>
<td>−0.0032</td>
</tr>
<tr>
<td>V</td>
<td>1.9–4.9 e</td>
<td>−0.0019 to −0.0049</td>
</tr>
<tr>
<td>V</td>
<td>−0.002 e</td>
<td></td>
</tr>
</tbody>
</table>

* 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, pCO₂ 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 CO₂ from the atmosphere into the North Atlantic (e.g. the Surface Ocean CO₂ 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).
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).

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

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

Providing information to national and international policymakers on the impacts of increased global CO₂ concentrations and underpin the need for international agreements to reduce CO₂ 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 near-shore environments, increased production resulting from eutrophication has probably driven larger changes in acidity than CO₂ 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 (pCO₂), 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). 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 pCO₂, 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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ification 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**

**All of**

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)

**Two out of**

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) pCO₂: (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 (Juraneck 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.

**Hydrographic cruises:** 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 CO₂. 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) pCO₂: 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) pCO₂: ±1–2 µatm.
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 \( p\text{CO}_2 \)

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 \( \text{CO}_2, \text{CH}_4, \text{CO} \), and \( \text{CO}_2 \), 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 \( \text{CO}_2, \text{CH}_4, \text{CO} \), and the stable isotopes of \( \text{CO}_2: (^{13}\text{C} \text{ and } ^{18}\text{O}) \). These gases form the basis of calibration of the non-dispersive infrared (NDIR) analysers that are used as the detector in most underway \( p\text{CO}_2 \) systems. Recently, high-resolution, cavity-enhanced, direct-absorption spectroscopy \( \text{CO}_2 \) 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 \( \mu \text{atm} \text{CO}_2 \) 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 \( \text{pH} \)

There are currently two methods in routine use for measuring the \( \text{pH} \) 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 \( \text{pH} \)).

For work on the carbonate system, the “total scale” (see Section 1.4) is generally used for reporting \( \text{pH} \) data. It should be noted that the numerical values output by the different scales are significantly different. For example, at \( T = 25^\circ\text{C} \) and salinity = 35, \( \text{pH} \) (free scale) is ~0.11 higher than \( \text{pH} \) (total), while the difference between \( \text{pH} \) (total scale) and \( \text{pH} \) (seawater scale) is < 0.01. In every case, the \( \text{pH} \) 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 \( \text{pH} \) 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 \( \pm 0.1 \text{ pH} \) (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 \( \pm 0.0005 \text{ pH units per year} \) (Nemzer and Dickson, 2005). The uncertainties arising from the preparation of such buffers is typically less than 0.002 in \( \text{pH} \).
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. Coordinated 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. \(\mu\text{mol kg}^{-1}\)).

• **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 (\(\mu\text{mol kg}^{-1}\))**: 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 (\(\mu\text{mol kg}^{-1}\))**: type of titration and cell type (with reference), sample volume curve fitting method (with reference), RM information (correction magnitude, batch number, analysis log), overall precision, and accuracy.

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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 preci-
sion, and accuracy.

- **Carbon dioxide partial pressure (pCO₂ (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 (xCO₂, pCO₂, or fCO₂), gas, standard gas
  concentrations, frequency of standardization, overall precision, and accu-
  racy (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 accu-
  racy.

Three software packages, Seacarb (Lavigne and Gattuso, 2010), CO2SYS (Lewis and
Wallace, 1998), and SWCO₂ (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 individ-
ual 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 computa-
tions. Pesant *et al.* (2010) recommended that these “Carbonate Chemistry Computa-
tion” 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 exam-
ple, with pH, “pH was computed on the total scale using Seacarb (Lavigne and Gat-
tuso, 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 parame-
ters (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 pro-
cesses. 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 com-
prehensive range of physical, chemical, and biological processes at a variety of spatial
(point to global) and temporal (subseasonal to century) scales. Models have limita-
tions, as they are simplified representations of reality, for example, aggregating bio-
logical diversity to a limited number of functional types. Although they are generally
incapable of exact replication of specific observations and are dependent on function-
al 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 datasets.

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 pCO₂. 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 pCO₂ 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 pCO₂ 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 CO₂ Atlas (SOCAT – http://www.socat.info) gives access to global surface CO₂ data in a uniform format database.
7 References for main text and annexes (except Annex 3)


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 be 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 an 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 ship-board 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:
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.

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.

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

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.

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 CO2 system meas-
uring surface seawater pH, carbon dioxide fugacity ($f\text{CO}_2$), 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 $f\text{CO}_2$, 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 phototoxicity 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 ($RF_1,F_2 = F_1/F_2$) 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 pK$_a$ 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 pCO₂ concentration could be determined in experimental systems working at high levels of pCO₂ (>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 CO₂.

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), pCO₂, 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 titratable organic matter can be present in samples from coastal waters and mesocosms at levels equivalent to a few tens of µM 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 pCO₂ calculated from measurements of total alkalinity.

3) The three main different software packages (CO2SYS, CO₂SW, and Sea-carb) available for the calculation of CO₂ 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
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$_2$O 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$_2$O 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

(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).
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$_2$O interactions are already included in the results. In some cases the CO$_2$–H$_2$O 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$_2$O molecular interactions. The magnitude of the double correction is not known because of the difference in the proportion of H$_2$O 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$_2$O 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 CO₂ and the partitioning of CO₂ into seawater. CO₂ reacts with seawater to produce carbonate, bicarbonate, and hydrogen ions. Since the industrial revolution, the concentration of hydrogen ions in seawater has increased by 30%. Ecosystems in certain seas such as Arctic waters are potentially more vulnerable to these changes as they will tend to become 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 CO₂ during primary production (Borges and Gypens, 2010; Provoost et al., 2010; Cai et al., 2011). The degree of ocean acidification may be assessed through the measurement of carbonate species in solution and the calculation of the saturation states of the shell-forming carbonate mineral aragonite and calcite. At present, a recommendation cannot be made for a minimum reliable approach to monitoring (such as measurement of pH during late winter immediately prior to the spring bloom during eutrophication-related surveys). This 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 CO₂ inventories and air–sea fluxes. Planning of the two activities should be coordinated.

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

1) 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);

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;

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 (pCO₂), 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

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. CO₂ 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 \(\text{pCO}_2\) (measurements can be referenced against WMO-approved gas standards\(^7\)). For assessment of ocean acidification, in some areas where only measurements of \(\text{pCO}_2\) 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 \(\text{pCO}_2\) 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 \(\text{pCO}_2\) 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 \(\text{CO}_2\), \(\text{CH}_4\), and \(\text{CO}\).
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 ($\pm 0.05$), salinity ($\pm 0.005$), 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 CO₂ by coulometry; (iii) pCO₂ underway samples: equilibration of gas stream with the surface water and determination of the equilibrated mole fraction of CO₂ in the gas stream by 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 pCO₂ (see above). Recommendations and Matlab tools for pCO₂ QC procedures have been developed as part of the Surface Ocean CO₂ 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 CO₂ 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 CO₂ should be reported as the partial pressure pCO₂ 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).

<table>
<thead>
<tr>
<th>Method</th>
<th>State of art</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Total dissolved inorganic carbon µmol kg⁻¹</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A) Acidification / vacuum extraction / manometric determination</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>(B) Acidification / gas stripping / coulometric determination</td>
<td>2–3</td>
<td></td>
</tr>
<tr>
<td>(C) Acidification / gas stripping / infrared detection</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>(D) Closed-cell acidimetric titration</td>
<td>10+</td>
<td></td>
</tr>
<tr>
<td>(E) Auto-analyser colorimetric</td>
<td>5+</td>
<td></td>
</tr>
<tr>
<td><strong>Total alkalinity µmol kg⁻¹</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(F) Closed-cell acidimetric titration</td>
<td>2–3</td>
<td></td>
</tr>
<tr>
<td>(G) Open-cell acidimetric titration</td>
<td>1–2</td>
<td></td>
</tr>
<tr>
<td>(H) Other titration systems</td>
<td>2–10</td>
<td></td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(I) Electrometric determination with standard TRIS buffer</td>
<td>0.005</td>
<td>0.01–0.03</td>
</tr>
<tr>
<td>(J) Spectrophotometric determination using <em>m</em>-cresol purple</td>
<td>0.003</td>
<td></td>
</tr>
</tbody>
</table>
Table A3.2. Availability of reference materials for the quality control of carbon dioxide measurements in seawater (Dickson, 2010).

<table>
<thead>
<tr>
<th>Analytical Measurement n</th>
<th>Desired Accuracy</th>
<th>Uncertainty</th>
<th>Availability</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIC</td>
<td>±1 μmol kg⁻¹</td>
<td>±1 μmol kg⁻¹</td>
<td>since 1991</td>
</tr>
<tr>
<td>TA</td>
<td>±1 μmol kg⁻¹</td>
<td>±1 μmol kg⁻¹</td>
<td>since 1996</td>
</tr>
<tr>
<td>pH</td>
<td>±0.002</td>
<td>±0.003</td>
<td>since 2009</td>
</tr>
<tr>
<td>Mole fraction of CO₂ in dry air</td>
<td>0.5 μmol mole⁻¹</td>
<td>±0.1 μmol mole⁻¹</td>
<td>since 1995</td>
</tr>
</tbody>
</table>

11. References


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. xCO2 or pCO2 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 HgCl₂).
- Storage (e.g., in dark refrigerated 4°C).

Method description (separate details for each method DIC/TA/pCO₂/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.).
- pCO₂ 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.

**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 pCO₂ 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.

Buoy/moorings: Buoys and moorings provide high-resolution data on both the air–sea transfer of CO₂ 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): pCO₂ measurements were made successfully at this site in 2005, and a newly designed mooring with measuring pCO₂ 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 CO₂ 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 CO₂ 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 pCO₂ observations:

1) Norway – NO (UB) and the Netherlands – N (NIOZ): The SOO line Bergen–Amsterdam started taking pCO₂ measurements in 2006. Support has not been constant.


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 pCO2 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 pCO2 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 CO2 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 pCO₂ 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 pCO₂ 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).

<table>
<thead>
<tr>
<th>COUNTRY/INSTITUTE</th>
<th>PI</th>
<th>AREA</th>
<th>OSPAR/HELCOM REGION</th>
<th>PLATFORM/TYPE</th>
<th>PARAMETERS</th>
<th>PERIOD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belgium / ULg</td>
<td>Borges</td>
<td>Southern Bight of North Sea</td>
<td>OSPAR II</td>
<td>RV “Belgica”</td>
<td>Underway pCO₂</td>
<td>2000–ongoing</td>
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<tr>
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<td>Borges</td>
<td>Ste Anna (Scheldt estuary)</td>
<td>OSPAR II</td>
<td>FS Fixed station, continuous</td>
<td>pCO₂</td>
<td>2002–ongoing</td>
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<td>Belgium / ULg</td>
<td>Wollast/Chou</td>
<td>Iberian upwelling system</td>
<td>OSPAR IV</td>
<td>RV research cruises (OMEX-II)</td>
<td>pCO₂, TA, pH</td>
<td>1997–1999</td>
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<td>RV “Luctor” monitoring (Scheldt estuary)</td>
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<td>RV monthly cruises</td>
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<td>2008–ongoing</td>
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<tr>
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<td>Lipps</td>
<td>Helsinki–Tallinn</td>
<td>SOO</td>
<td>Underway pCO₂</td>
<td></td>
<td>2010</td>
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<tr>
<td>France</td>
<td>Plymouth–Roscoff (FERRYBOX Armorique)</td>
<td>OSPAR II</td>
<td>SOO</td>
<td>Underway pCO₂</td>
<td></td>
<td>from 2010</td>
</tr>
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<td>France</td>
<td>ASTAN (48°46'N 3°56'W)</td>
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<td>pCO₂, pH</td>
<td></td>
<td>from 2009</td>
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<tr>
<td>France / IFREMER</td>
<td>MAREL Iroise (48°22'N 4°33'W)</td>
<td>OSPAR II</td>
<td>FS Mooring</td>
<td>pCO₂, pH</td>
<td>from 2003</td>
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<td>MAREL Carnot (50°44.71'N 1°34.18'W)</td>
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<td>pH</td>
<td>from 2004</td>
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<td>MAREL La Tremblade–Marennes Oléron</td>
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<td>FS Mooring</td>
<td>pH</td>
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<td>France / EDF</td>
<td>Cordemais (Loire Estuary)</td>
<td>OSPAR IV</td>
<td>FS Mooring</td>
<td>pH</td>
<td>from 2005</td>
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<td>France / CNRS–INSU</td>
<td>Patrick Raimbault</td>
<td>MOOSE (DYFAMED, ANTARES, MOLA) – Mediterranean Sea</td>
<td>Barcelona Convention</td>
<td>Niskin bottles RV monthly or annually cruises</td>
<td>pH, DIC, carbon flow</td>
<td>from 1995 (DYFAMED) from 2003 (MOLA) from 2005 (ANTARES)</td>
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<td>Benoit Sautour</td>
<td>SOMLIT – English Channel, Atlantic Ocean and Mediterranean Sea</td>
<td>OSPAR II, IV Barcelona Convention</td>
<td>SO</td>
<td>pH</td>
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<td>Patrick Pouline, Pascale-Emmanuelle Lapernet</td>
<td>PNMI – Iroise Sea</td>
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<td>SO RV cruises 3/year</td>
<td>pH</td>
<td>from 2010</td>
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<td>France</td>
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<td>RNF (Seine estuary, Bouches de Bonifacio)</td>
<td>OSPAR II Barcelona Convention</td>
<td>Seine : monthly measure Bonifacio : RV cruises 4/year during summer</td>
<td>pH</td>
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</tr>
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<td>France / GIP Seine – Aval</td>
<td>Céline Dégremont, Loïc Guézennec</td>
<td>SYNAPSES (Seine Estuary)</td>
<td>OSPAR II</td>
<td>FS Mooring</td>
<td>pH</td>
<td>from 2011</td>
</tr>
<tr>
<td>France / LOCEAN</td>
<td>Lefevre</td>
<td>France–Brazil</td>
<td>?</td>
<td>SOO (Monte Olivia) ~6/year</td>
<td>Underway pCO₂</td>
<td>from 2007</td>
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<td>Germany</td>
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<td>Irregular</td>
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<td>RV “Polarstern”</td>
<td>Underway pCO₂</td>
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<td>Germany / AWP?</td>
<td></td>
<td>Nordic seas (Greenland Sea?)</td>
<td>OSPAR I</td>
<td>RV research cruises</td>
<td>?</td>
<td>?</td>
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<tr>
<td>Germany / IFM–GEOMAR</td>
<td>Schneider, now Reider</td>
<td>Boknis Eck (54.52°N 10.03°E)</td>
<td>FS Time-series station</td>
<td>?</td>
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<tr>
<td>Germany / IOW</td>
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<td>Helsinki–Lübeck</td>
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<td>Germany / IFM–GEOMAR Kiel</td>
<td>Koertzinger/Wallace</td>
<td>Liverpool–Halifax</td>
<td>OSPAR V</td>
<td>SOO (A. Companion) two per five weeks Underway pCO₂</td>
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<td>Iceland / MRI</td>
<td>Olafsson/Olafsdottir</td>
<td>Iceland Sea and Irminger Sea</td>
<td>OSPAR I</td>
<td>FS Single time-series stations</td>
<td>DIC, discrete pCO₂, pH</td>
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<td>Icelandic waters and the Iceland Sea</td>
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<td>RV “Bjarni Saemundsson”</td>
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<td>Irish Shelf and offshelf</td>
<td>OSPAR III and V</td>
<td>RV “Celtic Explorer”</td>
<td>Underway pCO₂</td>
<td>2009–2011</td>
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<td>Mace Head Coastal Atmospheric research station</td>
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<td>FS Buoy</td>
<td>pCO₂</td>
<td>2008–2009</td>
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<td>McGovern/Cave</td>
<td>Irish Shelf and offshelf</td>
<td>OSPAR III and V</td>
<td>RV research cruises</td>
<td>TA, DIC</td>
<td>from 2008</td>
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<tr>
<td>Ireland / NUIG &amp; MI</td>
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<td>Rockall Trough Winter Transects</td>
<td>OSPAR V</td>
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<td>TA, DIC</td>
<td>from 2008</td>
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<td>Netherlands / NIOZ</td>
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<td>Southern Bight of the North Sea/German Bight</td>
<td>OSPAR II</td>
<td>SOO? JetSet (53°N 4°46'E) Weekly time-series</td>
<td>Underway DIC, TA?</td>
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<td>Netherlands</td>
<td>Houben</td>
<td>North Sea</td>
<td>OSPAR II</td>
<td>Research vessel</td>
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<td>Norway/ IMR</td>
<td>Chierici</td>
<td>Bjørnøya–Sørkapp</td>
<td>Barents Sea (SW)</td>
<td>IMR research vessels</td>
<td>water column DIC, TA, nutrients</td>
<td>start 2013 to 2016: 1/year</td>
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<td>Country/Institute</td>
<td>PI</td>
<td>Area</td>
<td>OSPAR/HELCOM Region</td>
<td>Platform/Type</td>
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<tr>
<td>Norway/IMR and FRAM centre (OA Flagship)</td>
<td>Chierici/Fransson (NPI)</td>
<td>Fram Strait</td>
<td>Arctic Ocean/Greenland Sea</td>
<td>RV “Lance”</td>
<td>water column DIC, TA, nutrients</td>
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<td>N of Svalbard to Polar Basin, 81–82°N 30°E</td>
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<td>water column DIC, TA, nutrients</td>
<td>start 2012 ongoing, 1/year</td>
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<td>75°N transect</td>
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<td>RV research cruises</td>
<td>DIC, TA</td>
<td>2003, 2006, 2008?</td>
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<td>Norway / UiB and Bjerknes</td>
<td>Skjelvan/Johannessen</td>
<td>OWS M</td>
<td>OSPAR I</td>
<td>FS Buoy continuous</td>
<td>pCO₂</td>
<td>2011</td>
</tr>
<tr>
<td>Norway / UiB and Bjerknes</td>
<td>Johannessen/Olsen/Lauvset</td>
<td>Nordic seas</td>
<td>OSPAR I</td>
<td>RV “G. O. Sars”</td>
<td>Underway pCO₂</td>
<td>ongoing</td>
</tr>
<tr>
<td>Norway / UiB and Bjerknes</td>
<td>Johannessen/Olsen/Omar</td>
<td>Aarhus–Nuuk</td>
<td>SOO (Nuka Arctica)</td>
<td>Underway pCO₂</td>
<td>from 2005</td>
<td></td>
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<tr>
<td>Norway / UiB and Bjerknes</td>
<td>Johannessen/Omar</td>
<td>North Sea</td>
<td>Sleipner</td>
<td>RV “G. O. Sars”</td>
<td>Underway pCO₂</td>
<td>June 2012</td>
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<td>Norway / UiB and Bjerknes</td>
<td>Johannessen/Omar</td>
<td>North Sea</td>
<td>Sleipner</td>
<td>RV “G. O. Sars”</td>
<td>TA, DIC</td>
<td>June 2012</td>
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<td>PI</td>
<td>Area</td>
<td>OSPAR/HELCOM Region</td>
<td>Platform/Type</td>
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<tr>
<td>Norway / NIVA</td>
<td>Sorensen</td>
<td>line up to Svalbard</td>
<td>Ferry-box</td>
<td>SOO</td>
<td>Underway pCO₂</td>
<td>2012</td>
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<tr>
<td>Spain / ULPGC</td>
<td>Davila</td>
<td>ESTOC Station Canary Islands</td>
<td>FS Time-series</td>
<td>pCO₂, TA, pH</td>
<td></td>
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<td>Spain / ICMAN</td>
<td>Huertas</td>
<td>Gulf of Cadiz</td>
<td>OSPAR IV</td>
<td>FS Mooring</td>
<td>pCO₂, pH</td>
<td>2003–2008</td>
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<td>Spain / ICMAN/IIM/IEO</td>
<td>Huertas</td>
<td>Strait of Gibraltar <em>(35.862°N 5.974°W)</em></td>
<td>OSPAR IV</td>
<td>FS Time-series stations</td>
<td>Water column pH, TA</td>
<td>from 2005</td>
</tr>
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<td>RV Monitoring cruises?</td>
<td>TA, pH</td>
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<td>Sweden / SMHI</td>
<td>Karlson</td>
<td>Kemi–Gothenburg Baltic</td>
<td>SOO</td>
<td>Underway pCO₂</td>
<td></td>
<td>2010</td>
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<td>Sweden / U Gothenberg</td>
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<td>Arctic Ocean</td>
<td>OSPAR I</td>
<td>RV research cruises</td>
<td>DIC, TA, pH</td>
<td>2005, ?</td>
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<td>UK / Cefas</td>
<td></td>
<td>Liverpool Bay</td>
<td>OSPAR III</td>
<td>Buoy, DEFRA tests</td>
<td>pCO₂</td>
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<td>UK / Cefas</td>
<td></td>
<td>Greenwood/Pearce</td>
<td>OSPAR III</td>
<td>RV research cruises</td>
<td>DIC, TA, and underwater pCO₂</td>
<td>2011</td>
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<td>UK / MSS</td>
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<td>Faroe Shetland Channel, Atlantic inflow to North Sea</td>
<td>OSPAR I and II</td>
<td>RV research cruise, May and December</td>
<td>TA/DIC, hydrography</td>
<td>from 2012</td>
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<td></td>
<td>Stonehaven</td>
<td>Coastal site</td>
<td>Time-series</td>
<td>TA/DIC, hydrography</td>
<td>from 2008</td>
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<td>COUNTRY/INSTITUTE</td>
<td>PI</td>
<td>AREA</td>
<td>OSPAR/HELCOM REGION</td>
<td>PLATFORM/TYPE</td>
<td>PARAMETERS</td>
<td>PERIOD</td>
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<td>UK / MSS/NOC</td>
<td>Walsham</td>
<td></td>
<td>OSPAR I, II, III, and V</td>
<td>RV “Scotia”</td>
<td></td>
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<tr>
<td>UK / NOC/UEA</td>
<td>Hydes</td>
<td>26°N line</td>
<td>?</td>
<td>RV</td>
<td>?</td>
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<td>UK / NOCS</td>
<td>Lampitt</td>
<td>Porcupine Abyssal Plain (49°N 16.5°W)</td>
<td>?</td>
<td>RV Mooring</td>
<td>pCO₂</td>
<td>?–</td>
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<tr>
<td>UK / NOCS?</td>
<td>Hydes</td>
<td>Portsmouth-Spain</td>
<td>OSPAR II and IV</td>
<td>SOO (Pride of Bilbao), 2/week</td>
<td>Underway pCO₂</td>
<td>2005</td>
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<td>UK / UEA</td>
<td>Schuster</td>
<td>Portsmouth (UK) Windward Islands–</td>
<td>?</td>
<td>SOO (Santa Lucia/Santa Maria)</td>
<td>Underway pCO₂</td>
<td>Monthly from 2002</td>
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<td>Walsham</td>
<td>Stonehaven</td>
<td>OSPAR II</td>
<td>FS Weekly single time-series station</td>
<td>TA/DIC</td>
<td>from 2008</td>
</tr>
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<td>UK / PML</td>
<td>Mountford/Kitidis</td>
<td>English Channel (E1, L4)</td>
<td>OSPAR II</td>
<td>Weekly (L4) and monthly (E1)</td>
<td>TA/DIC</td>
<td>from 2008</td>
</tr>
<tr>
<td>UK / PML</td>
<td>Mountford/Kitidis</td>
<td>English Channel (E1, L4)</td>
<td>OSPAR II</td>
<td>Weekly (L4) and monthly (E1)</td>
<td>Underway pCO₂</td>
<td>Transects (Plymouth Quest)</td>
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<tr>
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<td>Greenwood/Pearce</td>
<td>Basinwide North Sea and English Channel</td>
<td>OSPAR II</td>
<td>RV research cruises, RV “Endeavour”</td>
<td>DIC, TA and under way pCO₂</td>
<td>from 2011</td>
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<tr>
<td>USA / France</td>
<td>Metzel</td>
<td>Charleston–Reykjavik</td>
<td>?</td>
<td>SOO (Reykjafoss)</td>
<td>Underway pCO₂</td>
<td>From 2005</td>
</tr>
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</table>

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/
- CARBON–OPS: UK underway pCO₂ observations from research vessels (2007–2009); www.bodc.ac.uk/carbon-ops
- CLIVAR: Climate variability and predictability; www.clivar.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
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 in 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.sunburst sensors.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.
• CARIOMA (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$_2$.

• SubC Tech (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.

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Acronyms and abbreviations

13C  carbon 13 isotope
18O  oxygen 18 isotope
ACT  Alliance for Coastal Technologies
Ag / AgCl  silver / silver chloride
ai  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/
CCC  Carbonate Chemistry Computation
CCD  charge-coupled device
CCGG  NOAA Carbon Cycle Greenhouse Group
CDIAC  Carbon Dioxide Information Analysis Center
CFCs  chlorofluorocarbons
CH₄  methane
CO₂  carbon dioxide
COCOS  Coordination Action Carbon Observing System
CO₃²⁻  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
fCO₂  fugacity of carbon dioxide
F⁻  fluoride ion
<table>
<thead>
<tr>
<th>Symbol</th>
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<td>GT C year(^{-1})</td>
<td>gigatonne carbon per year</td>
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<tr>
<td>H(^+)</td>
<td>hydrogen ion</td>
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<tr>
<td>H(_2)CO(_3)</td>
<td>carbonic acid</td>
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<tr>
<td>H(_3)O(^+)</td>
<td>hydronium ion</td>
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<tr>
<td>HCO(_3)(^-)</td>
<td>bicarbonate ion</td>
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<td>HELCOM</td>
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<td>hydrofluoric acid</td>
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<td>HPTS</td>
<td>8-hydroxypyrene-1,3,6-trisulfonic acid</td>
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<tr>
<td>HSO(_4)</td>
<td>hydrogen sulphate</td>
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<tr>
<td>ICOS</td>
<td>Integrated Carbon Observation System</td>
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<tr>
<td>IEO</td>
<td>Instituto Español de Oceanográfico</td>
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<tr>
<td>IOCCP</td>
<td>International Ocean Carbon Coordination Programme</td>
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<tr>
<td>ISFET</td>
<td>Ion-Selective Field Effect Transitions</td>
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<td>JAMP</td>
<td>Joint Assessment and Monitoring Programme</td>
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<td>JAMSTEC</td>
<td>Japan Agency for Marine-Earth Science and Technology</td>
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<td>Units Kelvin</td>
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<td>KCl</td>
<td>potassium chloride</td>
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<td>Life Science Identifier</td>
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<td>Monterey Bay Aquarium Research Institute</td>
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<td>MCCIP</td>
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<td>MCWG</td>
<td>Marine Chemistry Working Group (ICES)</td>
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<td>MSFD</td>
<td>EU’s Marine Strategy Framework Directive</td>
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<td>mV</td>
<td>millivolts</td>
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<td>NBS</td>
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<td>NERC</td>
<td>National Environment Research Council UK</td>
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<td>NIOZ</td>
<td>Royal Netherlands Institute for Sea Research</td>
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<td>nm</td>
<td>nanometre</td>
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<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
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<td>NOCS</td>
<td>National Oceanography Centre, Southampton</td>
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<td>National Science Foundation (USA)</td>
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<td>OA</td>
<td>ocean acidification</td>
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<td>OH(^-)</td>
<td>hydroxide ion</td>
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<td>Description</td>
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<td>OSPAR</td>
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<td>PAP</td>
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<td>pCO₂</td>
<td>partial pressure of carbon dioxide</td>
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<td>pH</td>
<td>log scale measure of the acidity of a liquid</td>
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<td>pHCF</td>
<td>free hydrogen ion scale</td>
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<td>PI</td>
<td>principal investigator</td>
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<td>PTFE</td>
<td>polytetrafluoroethylene</td>
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<td>QA</td>
<td>quality assurance</td>
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<tr>
<td>QC</td>
<td>quality control</td>
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<td>RID</td>
<td>Riverine Input and Direct Discharges</td>
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<tr>
<td>SO₄²⁻</td>
<td>sulfate ion</td>
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<td>SOCAT</td>
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<td>SOO</td>
<td>Ships of Opportunity</td>
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<td>SOP</td>
<td>standard operating procedure</td>
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<td>SWS</td>
<td>seawater scale (pH)</td>
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<tr>
<td>TA</td>
<td>total alkalinity, also denoted AT</td>
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<tr>
<td>URN</td>
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<td>UUID</td>
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<td>VINDTA</td>
<td>Versatile Instrument for the Determination of Titration Alkalinity</td>
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<td>WOCE</td>
<td>World Ocean Circulation Experiment</td>
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<td>γᵢ</td>
<td>activity coefficient</td>
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<td>Δ</td>
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<tr>
<td>µatm year⁻¹</td>
<td>microatmosphere per year</td>
</tr>
<tr>
<td>µᵢ</td>
<td>chemical potential of species i</td>
</tr>
<tr>
<td>µᵢ⁺</td>
<td>chemical potential of species i in standard state</td>
</tr>
<tr>
<td>µₘ</td>
<td>micrometre = 10⁻⁶ metre</td>
</tr>
<tr>
<td>µmol</td>
<td>micromole = 10⁻⁶ mole</td>
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Chemical aspects of ocean acidification monitoring in the ICES marine area