United Nations
Educational, Scientific and
Cultural Organization

Intergovernmental
Oceanographic
Commission

January 2019

The original version of this Methodology is available as IOC/EC-LI/2 Annex 6

INDICATOR METHODOLOGY FOR 14.3.1

Indicator Description 14.3.1 – Average marine acidity (pH) measured at agreed suite of representative sampling stations.

Target

14.3: Minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels.

Tier level

Tier II - Indicator is conceptually clear, has an internationally established methodology and standards are available, but data are not regularly produced by countries.

Definition

This indicator is based on observations that constrain the carbon system, which are required to capture the variability in ocean acidity at locations providing ocean services. The carbon system in this context refers mainly to the four measurable parameters: pH (the concentration of hydrogen ions on a logarithmic scale), DIC (total dissolved inorganic carbon), $p\mathrm{CO}_2$ (carbon dioxide partial pressure), and TA (total alkalinity). Ocean acidification is a reduction in the pH of the ocean over an extended period of typically decades or longer, which is caused primarily by uptake of carbon dioxide from the atmosphere1. Ocean services are the benefits the ocean provides to people, which may be recreational, economic, environmental (by providing coastal protection) or cultural. Average2 as used herein is the equally weighted annual mean.

A agreed suite of representative sampling stations are sites that: 1) have a measurement frequency adequate to describe variability and trends in carbonate chemistry to deliver critical information on the exposure of and impacts on marine systems to ocean acidification, 2) provide data of sufficient quality and with comprehensive metadata information to enable integration with data from other sites in the country.

Unit

pH on total scale

and/or $p\mathrm{CO}_2$ [µatm or ppt], DIC [$\mu\mathrm{mol\ kg}^{-1}$], TA [$\mu\mathrm{mol\ kg}^{-1}$]

---

[1] The International Panel on Climate Change (IPCC) Workshop on Impacts of Ocean Acidification on Marine Biology and Ecosystems (2011, p. 37) defines Ocean Acidification (OA) as “a reduction in the pH of the ocean over an extended period, typically decades or longer, which is caused primarily by uptake of carbon dioxide from the atmosphere, but can also be caused by other chemical additions or subtractions from the ocean.”

[2] Although this indicator requests “average acidity” values from nations, the complete data set (which comprises the average) will provide valuable insight into the variability of the measurements

Rationale for inclusion

The ocean absorbs up to 30% of the annual emissions of anthropogenic CO_2 to the atmosphere, helping to alleviate the impacts of climate change on the planet. However, this comes at a steep ecological cost, as the absorbed CO_2 reacts with seawater and results in shifts in the dissolved carbonate chemistry including increased acidity levels in the marine environment (decreased seawater pH). The observed changes have been shown to cause a range of responses at the organism level that can affect biodiversity, ecosystem structure and food security. For example, a decrease in dissolved carbonate reduces the solubility of carbonate minerals including aragonite and calcite, the two main forms of calcium carbonate used by marine species to form shells and skeletal material (e.g. reef building corals and shelled molluscs). Aragonite is the more soluble form and its availability for shell building by organisms such as corals and oysters, called the aragonite saturation state [Ω (aragonite)], is used together with pH as an indicator in tracking the progression of ocean acidification. In addition, of equal importance to some key marine organisms is the dissolved CO_2 and bicarbonate concentration. It is, therefore, of the upmost urgency that a full categorization of the changing carbonate system is delivered.

Regular observations of marine acidity at open-ocean locations over the past 20-30 years have revealed a clear trend of decreasing pH and that present-day conditions are often outside preindustrial bounds. Observational trends in coastal areas have been reported to be more difficult to determine. In some regions, the changes are amplified by natural processes like upwelling (whereby cold, often CO_2 and nutrient rich, water from the deep rises toward the sea surface). In addition, other factors, including freshwater run-off, ice-melting, nutrients, biological activity, temperature change and large ocean oscillations influencing carbon dioxide levels, particularly in coastal waters need to be taken into account when interpreting drivers of ocean acidification and the related impacts.

Ocean acidification has potentially direct consequences for marine life and cascades through to the services provided by the open ocean and coastal areas including food and livelihood, tourism, coastal protection, cultural identity, transportation and recreation. The impacts on ocean services from ocean acidification may be lessened through appropriate monitoring and improved understanding of variability and rates of change, helping to inform mitigation and/or adaptation strategies.

Although this indicator requests “average acidity” values from nations, the data which comprises the average ought to provide insight into the variability of the measurements, which is more relevant for the impact on marine life. In other words, species do not respond to “average” conditions, but to real time conditions. At a minimum, the total range (minimum and maximum values) should be reported in addition to the average.

Coastal countries often have long-term monitoring of water quality, including information on nutrient concentrations, temperature, salinity and occasionally carbonate chemistry. These water quality monitoring sites provide historical context about biogeochemical variability of the system and should be considered ideal location for ocean acidification monitoring. Additional sites may also need to be established to characterize variability.

The data variables associated with the monitoring of ocean acidification (variables include pH, carbon dioxide partial pressure [pCO_2], total dissolved inorganic carbon [DIC], and total alkalinity [TA]) have the potential to serve global, national, regional, and local data needs, such as tracking the exposure of marine ecosystems and aquaculture sites to corrosive[3] conditions, and identifying

---

[3] Aragonite saturation values below 1.0 in seawater are often referred to as corrosive conditions, dissolution of pure aragonite and unprotected aragonite shells will begin to occur (Feely, R. A., Byrne, R. H., Acker, J. G., Betzer, P. R., Chen, C. T. A., Gendron, J. F., & Lamb, M. F. (1988). Winter-summer variations of calcite and aragonite saturation in the northeast Pacific. Marine Chemistry, 25(3), 227-241.).

opportunities to reduce ecosystem and economic vulnerability to ocean acidification. For example, local monitoring of pH and aragonite saturation state on the Pacific coast of the United States has enabled shellfish farmers to adapt to damaging conditions present during upwelling events, which reduce pH and threaten brood stock.

Measurement methods and calculation

Computation Method

As mentioned in the definition paragraph, this indicator calls for the collection of multiple observations (individual data points) so as to capture the variability in ocean acidity.

Individual data points for pH (hydrogen ion concentrations on a logarithmic scale) that are measured either directly or calculated based on data of two other parameters - TA, DIC, pCO_2 - will be provided by countries and/or data providers designated by countries. Average pH is the annual equally weighted mean of multiple data points at representative sampling stations (see *Definition*). The exact number of samplings and therefore data points varies depending on the natural variation of ocean acidity at the site(s); the minimum should be the number of measurements needed to characterize the seasonal cycle for the site (Box 1). Higher frequency measurements (e.g. daily) using calibrated autonomous sensors may be useable in some locations to characterise shorter term variability that can be as significant in influencing ecosystem impacts. In addition to the data value, standard deviation and the total range (minimum and maximum values) of replicates should be reported, along with the underlying data used to provide traceability and transparency (metadata information).

In order to include calculations about the rate of change and to compare natural variability and anthropogenic alterations, available historical data should be released.[4] (IOC guidelines on data sharing).

National data sets should be reported annually (see *Data collection*, *Data sources* paragraphs). The first assessment in 2018 will include first-level quality controlled data, since and including 2010 (all of the years or a subset).

Disaggregation

Countries provide complete data sets with respective site-specific data and metadata files.

Regional aggregates

Every country will provide annually updated national data sets. Aggregation across nations will require that data of similar quality and metadata with site-specific information and information on parameters be reported. Given the variability in ocean acidification measurements across coastal habitat types, aggregated averages (equally annual mean) across habitat types will be difficult to decipher and are thus discouraged.

Regional aggregates according to the IAEG SDG Regional groupings as used in 2017 Report and Statistical Annex, will refer to change of ocean acidification to the previous year (equal +/- 5%; increase in ocean acidification > 5% (pH decrease), decrease in ocean acidification <5% (pH increase)).

---

[4] IOC resolution IOC-XXII-6: IOC Oceanographic Data Exchange Policy.

Treatment of missing values

- At country level

  Some missing values may be modelled or calculated if established methodologies exist (see *Recommendations for calculation of the carbonate system*).

- At regional and global levels

  Regional aggregates are permissible if more than 50% of coastal nations have reported values.

Sources of discrepancies

As this indicator only takes into account data submitted by Member States, there are no discrepancies between estimates and submitted data sets.

What to report

The 14.3.1 data and metadata files give detailed information about the requested data and metadata to report. Data and metadata files contain compulsory variables to be reported and additional variables to be included if available.

Data providers/Member States are encouraged to submit primary quality controlled data sets of two variables characterizing the carbonate system: pH, TA, DIC or $p\text{CO}_2$, plus precise location, temperature, salinity and hydrostatic pressure (depth) (see *Quality control*). Depending on data quality, different categories will be assigned to the submitted data sets. In addition, corresponding macro nutrient concentrations are requested, if nitrate, phosphate and silicate data are available (see *Data quality*).

Further, data providers will be invited to submit all data, independent of where the data were collected within the water column; however, they are encouraged to provide surface data (≤ 10 m), to be visualized in the ocean acidification Map 2 (see *Data visualization*).

Sampling strategy

A sampling strategy will need to be developed or adapted for each sampling site. It is envisaged that new observation sites will be created at locations providing ocean services or marine products that are potentially vulnerable to ocean acidification and on which the countries and their communities rely. It is strongly advised that, in order to understand the context of measurements and to leverage existing infrastructures, sites where long-term water quality monitoring has been conducted should be considered for additional ocean acidification monitoring. These sites can provide the historical context with respect to water quality, ecosystem productivity, change in highly vulnerable habitats e.g. corals, and/or provide relative baselines for biodiversity. The utilisation of existing monitoring sites may also facilitate the development of algorithms/proxies that can be used to extend the time series back even at newly established sites with similar conditions. These sites are not always optimal for ocean acidification monitoring and additional sites should be added to characterise variability if needed.

The development of sampling strategies will need to consider the following items: 1. Question and expected outcome, 2. Constraints and opportunities, 3. Data needs, 4. Methodology and Instrumentation (Figure 1).

Each of these items requires an individual assessment (guidelines presented below) in order to obtain an appropriate sampling strategy, tailored to local and national demands and possibilities.

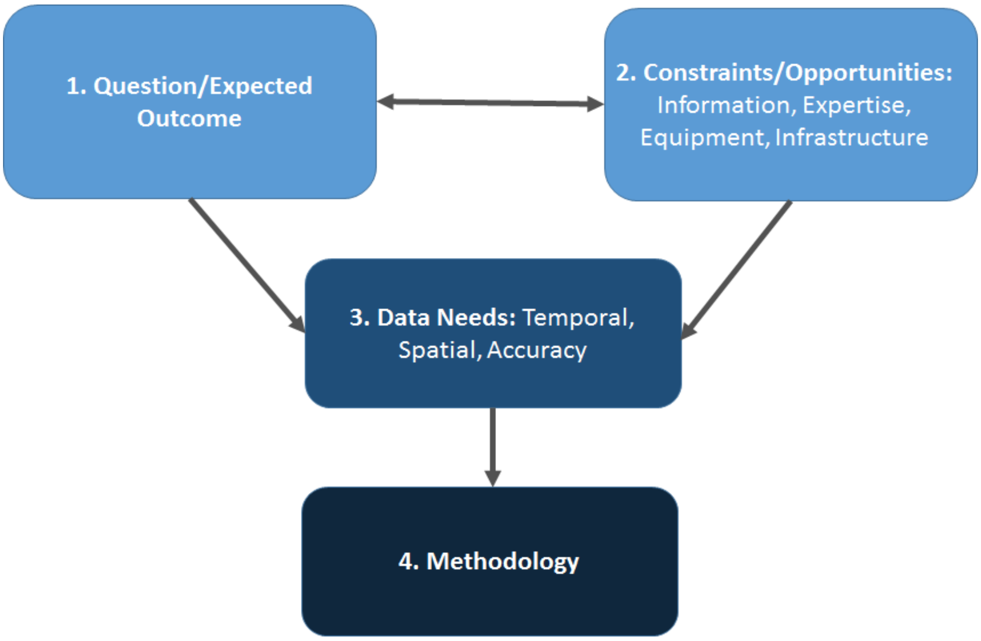

Figure 1. *Sampling strategy flow chart for ocean acidification observations.*

1. Question/expected outcome

Depending on the local and national research strategy and observations/monitoring already undertaken, the rationale behind establishing a new sampling strategy for ocean acidification observation will differ. For each new sampling site, established in the framework of SDG 14.3.1 reporting requirements, it is likely that at the same time specific scientific questions will outline the observations, such as the evaluation of ocean acidification impacts on key marine species and habitats, and the development of predictive capabilities.

2. Constraints/opportunities

When developing a new ocean acidification observing strategy, a balance of: a) research questions and b) with local and national constraints and opportunities, in particular existing scientific/technical infrastructure, financial resources to establish and maintain the observations, human capacities and accessibility of site are important. The inclusion of ocean acidification measurements to already established observation sites increases the probability of sustained observations and gives the possibilities to broaden the scope of the investigation. However, not all these sites will be optimal for monitoring locations e.g. upwelling sites where ecosystem services may be more exposed to ocean acidification and other stressors like deoxygenation and shifts in temperature.

3. Data needs

In order to determine the number, times and places for sampling, the natural variability in ocean chemistry (in particular seasonal variability) and the driving forces behind it (e.g. tides, seasons, runoff etc.) need to be considered in designing a sampling strategy. Box 1 shows examples of how sampling frequency for waters with different variability will influence the mean and range of results and related data. If historical data on the variability of ocean acidification are not available, general knowledge of the oceanographic variability (e.g. observations using temperature and salinity) might help in the design of the sampling strategy. Sampling at frequencies appropriate to capturing seasonal salinity and temperature variability is a useful first step. For each newly established ocean acidification observation site it is recommended to include surface samples (up to 10 m depth).

Finally, the accuracy of measurements is determined by the combination of research question and local/national constraints (see Measurement quality).

***Box 1**. Simulations to determine the temporal resolution of sampling the carbonate system to cover the natural variability in order to define the minimum number of samplings per year needed to obtain average or minimum values for e.g. pH with an accuracy of 0.05 pH. The results of a simplified power analysis for two 'sampling sites' with different natural variability serve as a guide to determine the frequency of measurements or instrumentation for the ocean acidification sampling strategy*[5,6,7].

When monitoring the carbonate chemistry, it is important to consider the spatio-temporal resolution. Data points for pH and other parameters of the carbonate system can be highly variable in space and time.[8] Different questions will require capturing different aspects of this variability. For example, predicting organism sensitivity and identifying relevant future scenarios for biological experimentation require capturing the yearly pH niche experienced by the organism, including extremes, such as the minimum value experienced.[9]

The frequency of observation will depend on the parameter to be measured (e.g. average pH or minimum pH), the required accuracy and the characteristic of the temporal variability at the sampling site. For example, the coastal zone is often characterized by higher temporal variability in the carbonate chemistry compared to the open ocean, thus more data points are required to accurately capture the average pH. The number of observations needed to capture extreme pH values will also depend on their frequency and intensity.

In order to define the required sampling frequency simulations applying simplified power analysis can be used.[10] Figure 2 illustrates the yearly variability in pH at two different locations with contrasting levels of variability: (i) La Push (USA; Figure 2A), with pH ranging between 7.88 and 8.58 and, (ii) Kangaroo island (Australia; Figure 2B), with pH ranging between 8.03 and 8.11. Due to the low variability and absence of extreme events at Kangaroo Island, the average and minimum pH with an accuracy of 0.05 pH units can be captured with only 10 observations per year (Figure 2D & 2F). For LaPush, more than 100 yearly observation are needed to capture the average pH with an accuracy of 0.05 pH units (Figure 2C) and more than 400 for the minimum pH (Figure 2E).

This comparison illustrates the importance of considering variability for the development of a meaningful monitoring strategy. The level of variability at a given site can be evaluated by a preliminary sampling and/or existing datasets from similar sites (e.g. upwelling zones).

---

[5] Karl, D.M. (2010) Oceanic ecosystem time-series programs: Ten lessons learned. Oceanography 23(3):104–125.

[6] Hofmann, G.E., Barry, J.P., Edmunds, P.J., Gates, R.D., Hutchins, D.A., Klinger, T. and Sewell, M.A., (2010) The effect of ocean acidification on calcifying organisms in marine ecosystems: an organism-to-ecosystem perspective. Annual Review of Ecology, Evolution, and Systematics, 41:127-147.

[7] Alin, S.R., R.E. Brainard, N.N. Price, J.A. Newton, A. Cohen, W.T. Peterson, E.H. DeCarlo, E.H. Shadwick, S. Noakes, and N. Bednaršek (2015) Characterizing the natural system: Toward sustained, integrated coastal ocean acidification observing networks to facilitate resource management and decision support. Oceanography 28(2):92–107.

[8] Hofmann GE, Smith JE, Johnson KS, Send U, Levin LA, Micheli F, et al. (2011) High-Frequency Dynamics of Ocean pH: A Multi-Ecosystem Comparison. PLoS ONE 6(12): e28983.

[9] Vargas C, Lagos N, Lardies M, Duarte C, Manríquez P, Aguilera V, Broiman B, Widdicombe S & Dupont S (2017) Species-specific responses to ocean acidification should account for local adaptation and adaptive plasticity. Nature Ecology and Evolution. 1:84.

[10] Dupont S. (in prep.) Simulations to determine the temporal resolution of sampling the carbonate system to cover the natural variability.

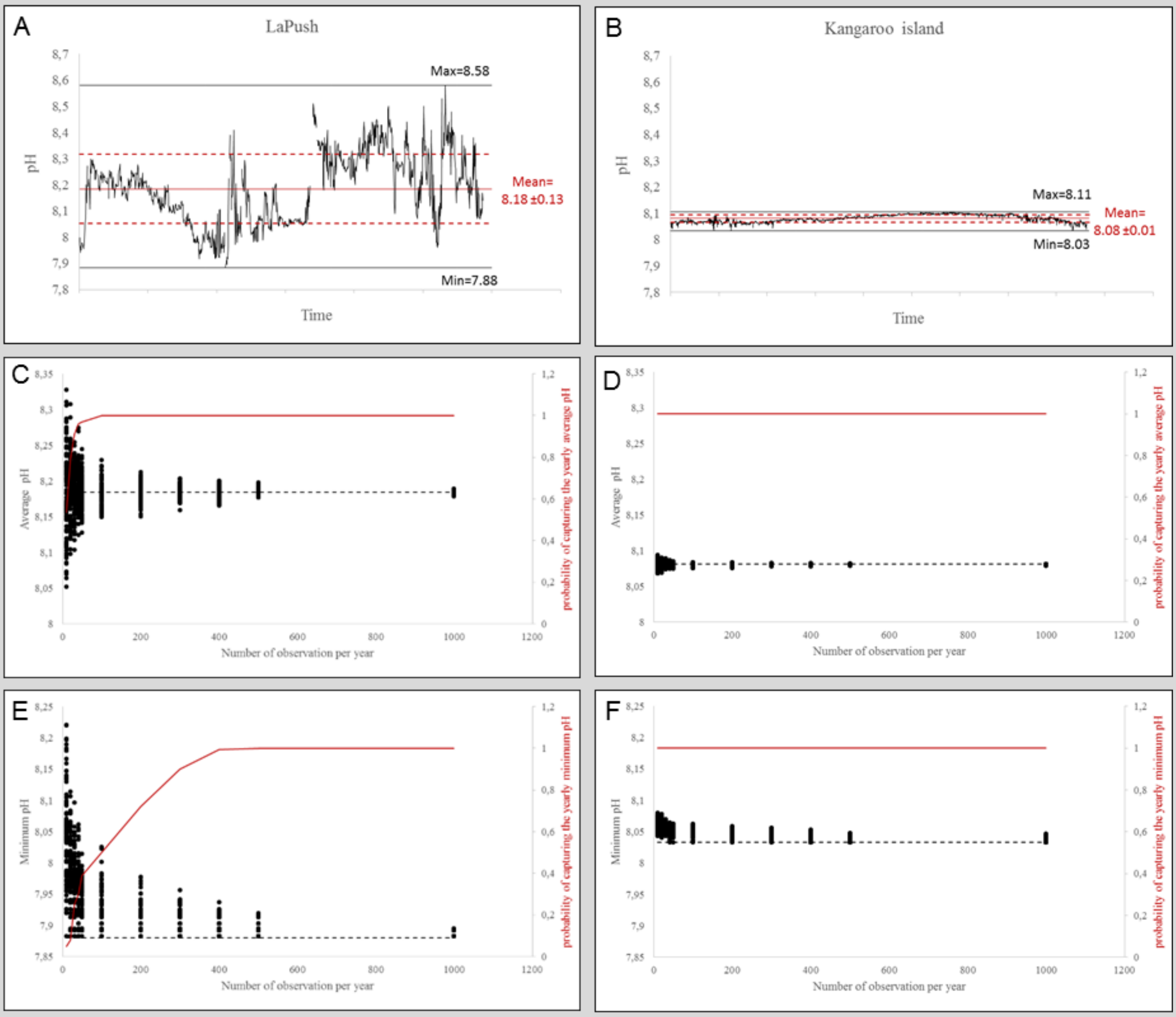

Figure 2. *Comparison of the yearly pH variability at two sampling sites (A. LaPush; B. Kangaroo island) and the relation between the calculated average pH (C, D) and minimum pH (D,F) for different frequencies of observation per year (10 to 1000). The probability (calculated from 100 randomized subsample for each frequency of observation) of capturing the average or minimum pH with an accuracy of 0.05 pH unit is presented in red.*

4. Methodology/Instrumentation

Methodologies and instruments to observe ocean acidification at a particular site are informed based on decisions made using the above three sections. The choice of methodology and instrumentation has to take into consideration the marine ecosystem structure, biological activity and behaviour, biofouling experiences, and any strong physical and chemical modulators (e.g. upwelling, tides, freshwater run-off). Some preliminary non-comprehensive assessment of sensor technologies for coastal observations have been made (http://www.act-us.info/) and new guidelines for coastal ocean acidification observation have been published[11]. Local constraints (e.g. limited financial resources) and the availability of existing equipment may orient decisions on sampling strategy, including choices of methodology and instrumentation.

---

[11] Pimenta, A.R. and Grear, J.S. (2018) EPA Guidelines for Measuring Changes in Seawater pH and Associated Carbonate Chemistry in Coastal Environments of the Eastern United States. Office of Research and Development, National Health and Environmental Effects Research Laboratory. EPA/600/R-17/483

Methods and guidance available to countries for the compilation of the data at the national level

Overview statements on best practices

There are four measurable variables in the ocean carbon system. Two of the four must be measured or estimated in order to “constrain” the carbon system relative to ocean acidification: pH, carbon dioxide partial pressure (pCO_2), total alkalinity (TA), and total dissolved inorganic carbon (DIC). In addition, temperature and salinity data are required.

As detailed in the Requirements and Governance Plan of the Global Ocean Acidification Observing Network (GOA-ON) (Newton et al., 2015)[12], common practices include the following approaches:

- Collection of seawater samples for laboratory analyses of DIC and TA is a standard practice if ship or fixed platform access to the water allows. Parameters of interest, such as pH and aragonite saturation, can be derived via commonly available software (e.g., CO2SYS). Some calculations require nutrients and other variables (see *Recommendations for calculation of the carbonate system*).
- As of 2018, sensors are only commercially available for measurements of pH and pCO_2 in the ocean. Currently, sensors capable of measuring either of these parameters with the high precision required to detect the ocean acidification signal are costly and require high maintenance. New developments are underway to produce less expensive and high accuracy sensors.
- Use of empirical proxies, such as more easily and accurately measured variables (salinity, temperature, oxygen), to estimate pH and aragonite saturation has been tested for use in oceanic waters, but has yet to be established for estuarine waters where other factors may interfere.

The Global Ocean Observing System (GOOS) considers these parameters Essential Ocean Variables (EOVs) and provides detailed specifications here.

Table 1 illustrates an example of combined relative uncertainties in calculated parameters based on different measurement pairs (redrawn from McLaughlin et al. 2015), stressing the strong covariation of pCO_2 and pH, as well as DIC and TA, assuming state-of-the art measurement accuracy:[13]

Table 1. *Combined uncertainties in calculated ocean carbon cycle parameters based on different measurement (Mc.Laughlin et al. 2015).*

Pairing	pH	DIC	TA	pCO_2
pH + DIC	0.3%	0.5%	1%	6%
pH + pCO_2	0.3%	7%	7%	3%
DIC + TA	0.3%	0.5%	0.5%	12%
DIC + pCO_2	0.3%	0.5%	1%	3%

---

[12] Newton J. A., Feeley, R. A., Jewett, E. B., Williamson, P. and Mathis, J. (2015) Global Ocean Acidification Observing Network: Requirements and Governance Plan (2nd edition)

[13] McLaughlin, K., S.B. Weisberg, A.G. Dickson, G.E. Hofmann, J.A. Newton, D. Aseltine-Neilson, A. Barton, S. Cudd, R.A. Feely, I.W. Jefferds, E.B. Jewett, T. King, C.J. Langdon, S. McAfee, D. Pleschner-Steele, and B. Steele. 2015. Core principles of the California Current Acidification Network: Linking chemistry, physics, and ecological effects. Oceanography 28(2):160–169.

Overview description of data collection methods

All contributors of data to SDG 14.3.1 are encouraged to read and follow the standard operating procedures provided in Dickson et al. 2007. This document covers ocean carbon chemistry, sample-handling techniques, quality assurance procedures, the use of Certified Reference Materials (CRMs) and Standard Operating Procedures (SOPs) for discrete sampling of pH, pCO_2, TA, and DIC. Data contributors are also encouraged to read the Guide to Best Practices in Ocean Acidification Research and Data Reporting, which focuses on best practices for laboratory experiments, but also includes background on carbon chemistry (Riebesell et al. 2010).[14] For coastal environments, which can be subject to large variability and a range of influences such as nutrient and freshwater inputs, guidelines for the measurement of pH and carbonate chemistry can be found here[15].

Recent developments discussed among the scientific Ocean Acidification Community, advising and recommending operating procedures for new emerging technologies are recorded on the Ocean Acidification Information Exchange online platform. These methodologies are not referenced in Table 2 yet, but are expected to be included in the near future.

All data submitted to SDG 14.3.1 must include an estimate of measurement uncertainty in the metadata. Autonomous sensors for pH and pCO_2 require calibration and maintenance to validate sensor performance and identify drift or sensor malfunction. Where possible, the analysis of discrete bottle samples analysed for pH, DIC or TA collected next to the sensors can be used to calculate pH and pCO_2.

All ocean acidity datasets submitted to SDG 14.3.1 must also include associated temperature (*in situ* [and temperature of measurement if different than *in situ*]), salinity, and pressure (water depth). If submitting pH values, all pH values must be on the total scale (see Dickson et al. 2007).[16]

Measurement quality

For the purposes of SDG 14.3.1, three categories of measurement quality were established (adapted from Newton et al. 2015)[17]:

Category 1: Climate quality

The climate quality objective is typically used to determine trends in the open ocean, shelf and coastal waters, providing data on seasonal through interannual variability on regional scales. The climate quality objective requires that a change in the dissolved carbonate ion concentration to be estimated at a particular site with a relative standard uncertainty of 1%. The carbonate ion concentration is calculated from two of the four carbonate system parameters and implies an uncertainty of approximately 0.003 in pH; of 2 $\mu mol\ kg^{-1}$ in measurements of TA and DIC; and a relative uncertainty of about 0.5% in the pCO_2. Such precision is only currently achievable by a limited number of laboratories and is not typically achievable for all parameters by even the best autonomous sensors.

---

[14] Riebesell U., Fabry V. J., Hansson L. & Gattuso J.-P. (Eds.) (2011) Guide to best practices for ocean acidification research and data reporting. Luxembourg, Publications Office of the European Union, 258pp. (EUR 24872 EN).

[15] Pimenta, A.R. and Grear, J.S. (2018) EPA Guidelines for Measuring Changes in Seawater pH and Associated Carbonate Chemistry in Coastal Environments of the Eastern United States. Office of Research and Development, National Health and Environmental Effects Research Laboratory. EPA/600/R-17/483

[16] Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) (2007) *Guide to best practices for ocean CO_2 measurements*. PICES Special Publication 3, 191 pp.

[17] Newton J. A., Feeley, R. A., Jewett, E. B., Williamson, P. and Mathis, J. (2015) Global Ocean Acidification Observing Network: Requirements and Governance Plan (2nd edition)

Category 2: Weather quality

The weather quality objective is suitable for many coastal and nearshore environments, particularly those with restricted circulation or where CO_2 system parameters are forced by processes like upwelling, pollution or freshwater inputs that can cause large variability. The weather objective requires the carbonate ion concentration (used to calculate saturation state) to have a relative standard uncertainty of 10%. This implies an uncertainty of approximately 0.02 in pH; of 10 μmol kg^{-1} in measurements of TA and DIC; and a relative uncertainty of about 2.5% in $p\mathrm{CO}_2$. Such precision should be achievable in competent laboratories, and is also achievable with the best autonomous sensors.

Category 3: Measurements of undefined quality

For SDG 14.3.1, pH measurements using glass electrodes will be considered Category 3 due to the challenges of using glass pH electrodes in seawater.[18] It is intended that the methodology provided here gives useful information for countries building capacity towards Category 1 and 2 measurements. For example, carefully calibrated glass pH electrodes may help in the identification of coastal ocean acidification hot spots and help prioritize future monitoring plans. In annual SDG 14.3.1 summary products, Category 3 measurement sites will be presented as data collection sites only, no data values will be visualized.

All those contributing data to SDG 14.3.1 are encouraged to adopt measurement quality Category 1 or 2. A variety of capacity development activities to support Member States' capacity in this regard are conducted by different organizations (more information can be found here: e.g. www.iaea.org/ocean-acidification; http://ioccp.org; http://www.ioc-cd.org/index.php; http://www.whoi.edu/courses/OCB-OA/).

For more information, see the GOA-ON Requirements and Governance Plan (Newton et al., 2015)[19].

---

[18] Dickson, A.G., Sabine, C.L. and Christian, J.R. (Eds.) (2007) Guide to best practices for ocean CO_2 measurements. SOP6a. PICES Special Publication 3, 191 pp.

[19] Newton J. A., Feeley, R. A., Jewett, E. B., Williamson, P. and Mathis, J. (2015) Global Ocean Acidification Observing Network: Requirements and Governance Plan (2nd edition)

Standard Operating Procedures (SOP)

Table 2 provides links to existing SOPs for discrete, underway (ships of opportunity), and autonomous sensors.

Table 2. *List of standard operating procedures to measure different parameters of the carbonate system (procedures marked with * are able to attain climate quality).*

	Discrete	**Underway**	**Fixed autonomous sensors**
pH	Spectrophotometric * Potentiometric	Spectrophotometric ISFET	Spectrophotometric ISFET
DIC	IR detection Coulometry *	-	-
TA	Potentiometric titration (open and closed cell; open recommended) *	-	-
$p\mathrm{CO}_2$	-	Equilibration, headspace * Membrane-based	Equilibration * Membrane-based
Temperature	Sensor measurements	Sensor measurements	Sensor measurements
Salinity	Sensor measurements	Sensor measurements	Sensor measurements

Recommendations for calculation of the carbonate system

At least two out of four measurable parameters in the ocean carbon system (pH, $p\mathrm{CO}_2$, TA, DIC) are needed to “constrain” the carbonate system. Computer programmes are commonly used to calculate other carbonate chemistry parameters from the measured parameters and many of these software packages are publicly accessible. In addition to the two carbonate system parameters the software packages require temperature (*in situ* at time of sampling and temperature at time of measurement, if different), salinity and pressure (depth).Nutrient concentrations provide additional information. The calculations of the carbonate system should follow the recommendations made by Orr et al. (2015)[20]. Based on the submitted data sets it is intended to obtain equally weighted monthly means, though annual equally weighted means will be considered for the SDG 14.3.1 reporting.

Empirical relationships to calculate alkalinity from salinity and other variables are published[21,22] although these may not be suitable in coastal waters. Careful calibration against direct measurements at each site are needed.

---

[20] Orr, J. C.; Epitalon, J.-M.; Gattuso, J.-P. (2015) Comparison of ten packages that compute ocean carbonate chemistry. Biogeosciences, 12(5):1483-1510

[21] Carter, B R, N L Williams, A R Gray, and R A Feely. (2016) Locally interpolated alkalinity regression for global alkalinity estimation. Limnology and Oceanography: Methods,14: 268–277

[22] Carter, B R, R A Feely, N L Williams, A G Dickson, M B Fong, and Y Takeshita. (2018) Updated methods for global locally interpolated estimation of alkalinity, pH, and nitrate.Limnology and Oceanography: Methods 16: 119-131.

Uncertainty of measurement

Uncertainty of measurement comprises, in general, many components. Some of these components may be evaluated from the statistical distribution of the results of series of measurements and can be characterised by standard deviations. The other components, which also can be characterised by standard deviations, are evaluated from assumed probability distributions based on experience or other information.[23]

A key goal for any observing network is to ensure that the measurements made are of appropriate quality for their intended purpose, and are comparable across sites. It is thus essential to ascertain and report through the metadata the uncertainty of measurements. The definition of the term uncertainty (of measurement) is:[24] “A parameter associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurement.”

Thus, measurement uncertainty is not a synonym for measurement repeatability or even reproducibility.[25] Its evaluation requires a significant investment of effort.[26]

The provided guidelines, best practices and SOPs provide information on how to calculate the uncertainty (*see Methods and guidance available to countries for the compilation of the data at the national level)*. Furthermore, the 14.3.1 SDG methodology metadata template contains information on data quality and the related required information, in particular guidance on how to report the used instruments and measurement guidelines. All data and metadata submitted under SDG 14.3.1 must be accompanied by the associated uncertainty information.

A complete uncertainty budget has a double role: on one side it allows the comparability of the data, on the other hand it enables to identify the main sources of errors and therefore improve the data quality (see Q*uality control).*

Data Sources

Description

The general IOC data collection process is described in Document IOC-XXIX/2Annex 14.
The novelty of assessing ocean acidification at the global level, as in indicator 14.3.1, requires the IOC secretariat to collect the data via different pathways. Future data collections are expected to be a mixture of:

- direct requests to National Statistical Offices (NSOs), as new national reporting mechanisms are now installed allowing them to provide the required information,
- annual requests to the IOC national focal points,
- collaboration with National Oceanographic Data Centres, international data centres and
- directly with data providers via the GOA-ON data portal (Figure 3).

---

[23] S L R Ellison and A Williams (Eds). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, (2012) ISBN 978-0-948926-30-3. Available from www.eurachem.org.

[24] Guide To The Expression Of Uncertainty In Measurement. ISO, Geneva (1993). (ISBN 92-67-10188-9) (Reprinted 1995: Reissued as ISO Guide 98-3 (2008), also available from http://www.bipm.org as JCGM 100:2008)

[25] P de Bièvre, Measurement uncertainty is not a synonym of measurement repeatability or measurement reproducibility . . . Accred. Qual. Assur. 13:61–62 (2008).

[26] S L R Ellison and A Williams (Eds). Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, (2012) ISBN 978-0-948926-30-3. Available from www.eurachem.org.

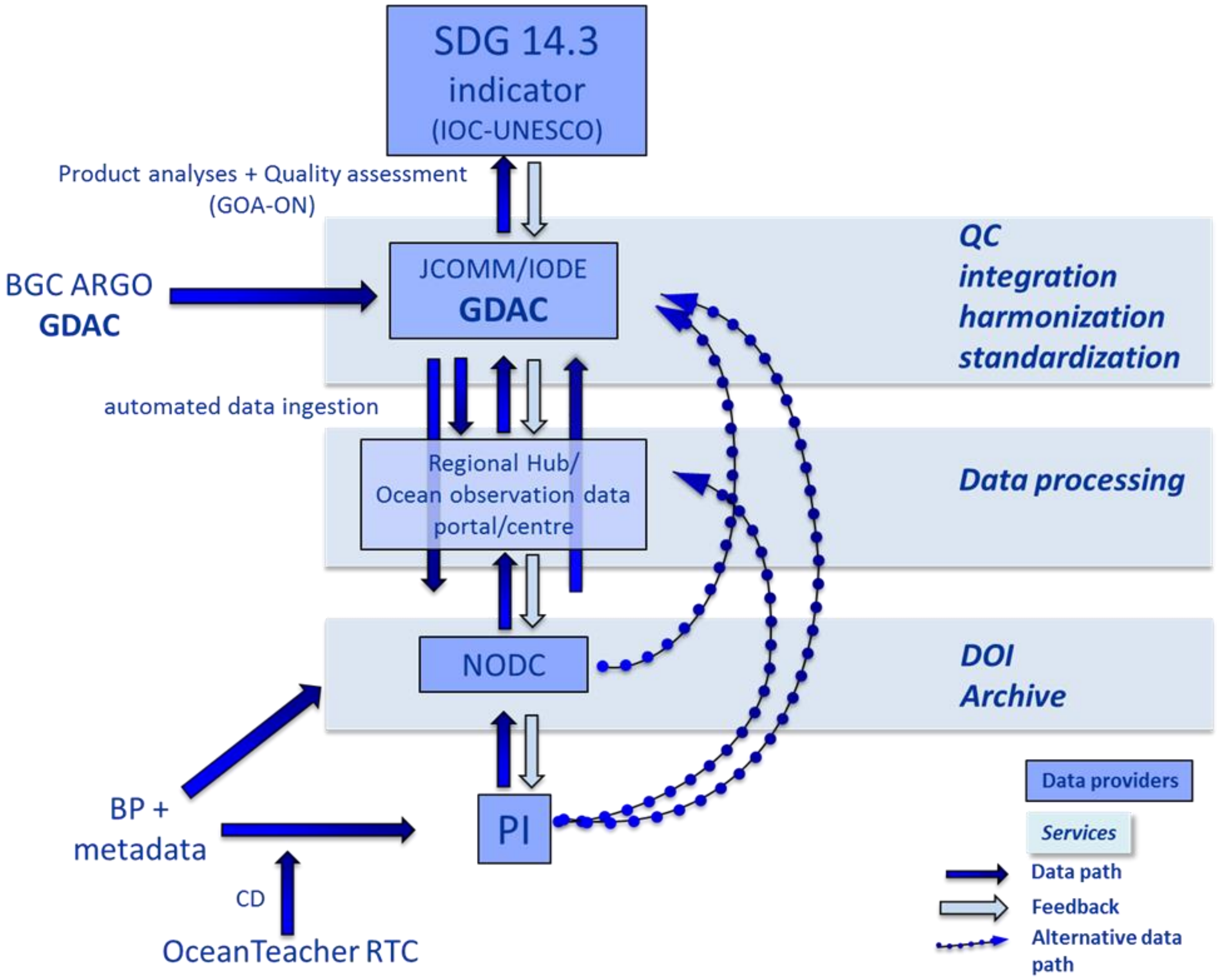

Figure 3. *Scheme to illustrate the proposed data collection and publication process related to national contributions of data related to 14.3.1 (SDG: Sustainable Development Goal; IOC-UNESCO: Intergovernmental Oceanographic Commission of UNESCO; GOA-ON: Global Ocean Acidification – Observing Network; JCOMM: WMO-IOC Joint Technical Commission for Oceanography and Marine Meteorology; WMO: World Meteorological Association; IODE: International Oceanographic Data and Information Exchange of IOC UNESCO; GDAC: Global Data Assembly Center; BGC ARGO: Biogeochemical Argo floats; QC: Quality Control; NODC: National Oceanographic Data Centre; DOI: Digital Object Identifier; BP: Best Practice; CD: Capacity Development; PI: Principal Investigator; RTC: Regional Training Centre).*

Global scientific efforts (GO-SHIP, SOCAT, GCOS) which host and feature data from various ocean observing efforts and/or focus on collecting measurements in international waters will also be queried for annual or more likely multi-year data sets representing status and change of ocean acidification variables in the open ocean.

As mentioned the data collection process will take place in close collaboration with the IOC Project Office for IODE Oostende, Belgium and relevant data providers/national archives, the GOA-ON data portal, and entities such as the marine chemistry part of the European Marine Observation and Data Network (EMODnet).

The GOA-ON data portal features open access data, in addition to a global monitoring asset inventory. The portal is designed to offer two levels of access: 1) visualization and 2) download capabilities. Combining different open-access data sets may provide incentives to create new observing systems in under-sampled areas and to increase the application of open access data policies worldwide, according to the IOC Criteria and Guidelines for the Transfer of Marine Technology[27].The detailed SDG 14.3.1metadata and data forms (part of the final methodology to ensure inter-comparability between measurements) will be included on the GOA-ON website. The information requested will include a detailed habitat description, which will be required to assess the natural and anthropogenic causes of variability within the data sets.

Collection process:

(I) Counterparts:

The official counterparts are the IOC focal points. They, as well as National Oceanographic Data Centres (NODCs), will initially be contacted by IOC to request relevant data from the appropriate national oceanographic data centres and/or relevant scientists, agencies or programmes. An annual data submission request will be sent out directly to the member states asking for the respective data and metadata. It is envisaged that an online submission interface, to be developed in collaboration with existing ocean carbon data centres and biogeochemical data platforms will facilitate the submission process in the future.

(II) Validation and consultation process:

The counterparts are invited to provide references (metadata) for the information provided. The quality control mechanisms are described in more detail later in this document *(see Quality Control)*.

Data visualization

Data provided by National Oceanographic Data Centres/National Statistical Offices or other relevant data portals/centres (Figure 3) can be visualized via the GOA-ON data portal. The submitted information will be used to produce the visualization products.
Two maps will be included in the visualized product, one showing the locations and quality of measurements taken, and the other showing the climatological mean (taken on the linear scale, i.e., total hydrogen ion concentration) and variance of high quality annual equally weighted pH values from each data collection site.

- Map 1 with points indicating data contributors – colour coded to show the 3 data quality categories
- Map 2 with points indicating high quality data of annual equally weighted mean pH (surface) and variability.

It is expected, that the visualization will evolve as more data become available with time.

---

[27] Intergovernmental Oceanographic Commission. *IOC Criteria and Guidelines on the Transfer of Marine Technology (CGTMT)/ Critères et principes directeurs de la COI concernant le Transfert de Techniques Marines (CPTTM)*. Paris, UNESCO, 2005. 68pp. (IOC Information document, 1203)

Quality control

Data quality control is a critical component of the data analysis, submission and process. Scientists and technicians who collected the submitted data will be responsible for the primary quality control of the data and accompanying detailed metadata. The metadata submitted with the data must also describe the quality control standard operating procedures (SOPs) followed for each parameter.

<u>Primary quality control</u>

- Quality control that is attached to the methodology (CRMs, tris buffer calibration, SOPs are provided),
- Quality control and quality assurance of the actual data (SOPs are provided) and usage of community agreed quality flags,
- Identifying and flagging of outliers,
- Making determinations regarding validity of those outlying points,
- Estimating uncertainty of the measurement,
- Identifying all the sources of uncertainty in the measurements,
- Rolling up the individual uncertainties into overall uncertainty (error propagation).

<u>Secondary quality control</u>

- Harmonization of the data and ensuring metadata completeness,
- External quality control/audit – Expert QC Group applying the weather and climate levels as defined by GOA-ON (following the example of SOCAT),
- Feedback to data holders.

<u>Following the quality control assessment described above, three categories of measurement quality will be attributed by the Expert QC Group (Figure 3):</u>

- Established oceanographic climate quality (Category 1)
- Weather quality data including that from sensors and capacity building simplified pH and alkalinity measurements, with appropriate uncertainty assessment (Category 2)
- Measurements of undefined quality (Category 3) (will not be displayed in the visualization of annual weighted means and variance of pH)

Glossary

Anthropogenic refers to what is caused or influenced by humans.

Aragonite saturation state is a measure of the thermodynamic tendency for the mineral calcium carbonate to form or to dissolve. Aragonite is the more soluble form of calcium carbonate and its saturation state $[\Omega]$, is used as an indicator in tracking the progression of ocean acidification. An aragonite saturation state greater than 1.0 indicates supersaturation, while values less than 1.0 indicate undersaturation with instability favouring dissolution.

BGC ARGO are the Biogeochemical Argo floats.

Biological activity describes all activity by living organisms in the ocean, including microbes, plants and animals, such as growth, biomass production, photosynthesis, respiration, calcification, dissolution of $CaCO_3$, nutrient uptake and release.

BP is Best Practice.

Calcium carbonate minerals ($CaCO_3$) are the building blocks for the skeletons and shells of many marine organisms, such as molluscs and corals. The two most abundant forms of calcium carbonate in the ocean are aragonite and calcite.

Calcite is a carbonate mineral and the more stable form of calcium carbonate ($CaCO_3$).

Carbonate chemistry encompasses the variables of carbon.

Carbonic acid is an acid that forms when carbon dioxide (CO_2) dissolves in water.

CD is Capacity Development.

Climate change describes progressive changes in weather characteristics like temperature, precipitation, or wind. Changes can be continuous increases or decreases, or they may be changes in variability.

Coastal areas are land areas adjacent to the ocean, extending to the continental shelf break or a water depth of 200m.

DIC (referred to as CT in some linked documents) is the abbreviation for total dissolved inorganic carbon and refers to the sum of the concentrations of inorganic carbon species in a solution. The inorganic carbon species include carbon dioxide, carbonic acid, bicarbonate anion, and carbonate.

DOI is Digital Object Identifier.

EMODnet is the European Marine Observation and Data Network.

Freshwater run-off is the input of freshwater into the ocean; this mostly refers to freshwater from rivers.

GDAC is the Global Data Assembly Center.

GCOS is the Global Climate Observing System.

GOA-ON is the Global Ocean Acidification Observing Network.

GO-SHIP is the Global Ocean Ship-based Hydrographic Investigations Program.

IAEA is the International Atomic Energy Agency.

IOC – UNESCO is the Intergovernmental Oceanographic Commission of the United Nations Educational, Scientific and Cultural Organization.

IODE stands for the International Oceanographic Data and Information Exchange of IOC UNESCO.

JCOMM is the WMO-IOC Joint Technical Commission for Oceanography and Marine Meteorology.

NODCs are National Oceanographic Data Centers.

NSO are the National Statistical Offices.

Nutrients in this instance refers to phosphate, nitrate and silicate. These nutrients affect alkalinity.

Ocean acidification is the ongoing reduction in the pH of the ocean, which is caused primarily by uptake of carbon dioxide from the atmosphere.

Ocean acidity is the current state of ocean acidification.

Ocean oscillations are large periodic variations over the oceans. These oscillations affect sea surface temperature, currents and wind patterns, thereby influencing climate patterns, often on a global scale. While these oscillations occur periodically, the exact timing of these events is mostly unpredictable. The El Niño Southern Oscillation is one of the most well-known ocean oscillation patterns.

Ocean services are the benefits the ocean provides to people, which may be recreational, economic, environmental (for example by providing coastal protection) or cultural. Ocean services also include food (fishery, aquaculture) and transportation.

Open ocean refers to the oceanic waters above the seabed which are not immediately bordered by landmasses.

pH is the negative log of the hydrogen ion concentration in solution.

$p\mathrm{CO}_2$ is the partial pressure of carbon dioxide (CO_2) in seawater.

PI is the Principal Investigator.

Preindustrial refers to the period of time before the Industrial Revolution, which began in the mid- to late 1700s. The carbon dioxide concentration in the atmosphere has continuously increased since the Industrial Revolution.

QC stands for Quality Control.

RTC is a Regional Training Center.

SDG stands for Sustainable Development Goal.

SOCAT is the Surface Ocean CO_2 Atlas.

TA (referred to as AT in some linked documents) is the total alkalinity.

Upwelling is an oceanographic current pattern that involves wind-driven motion resulting in cold, often CO_2 and nutrient rich water from the deep being brought toward the sea surface.

WMO is the World Meteorological Association.

Agencies & contacts

IOC-UNESCO	Julian Barbière Kirsten Isensee